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# Thin Film Processes Artifacts on Surface Phenomena and Technological Facets

Edited by Jagannathan Thirumalai





# THIN FILM PROCESSES -ARTIFACTS ON SURFACE PHENOMENA AND TECHNOLOGICAL FACETS

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# Meet the editor



Dr. Jagannathan Thirumalai received his PhD from Alagappa University, Karaikudi in 2010. He was also awarded the Post-doctoral Fellowship from Pohang University of Science and Technology (POSTECH), Republic of Korea, in 2013. He worked as Assistant Professor of Physics, B.S. Abdur Rahman University, Chennai, India (2011 to 2016). Currently, he is working as Assistant

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# Preface

The book Thin Film Processes - Artifacts on Surface Phenomena and Technological Facets aims to provide in-depth knowledge of classic topics on thin-film materials and it contains contributions of the researchers involved in different fields of research. The development of sophisticated thin-film technologies effectively depends on the manipulation of modernized physico-chemical materials. The framework of knowledge of thin-film materials provides a platform to innovate, which has the tendency to progress the life requirements rather than scientific pursuit. In modern times, thin-film technology is a developing and progressing scientific discipline at the front line of physical, chemical and biological sciences with remarkable international opportunities and relationships. Thin-film technology has diverse applications in daily life, starting from conventional lighting devices, and extending to solar cells and other electrical and electronic devices that pertain to thin- film materials. The chapters in the book have been written by established researchers in the area and cover the advanced areas of research and developments in the field of materials science.

This book consists of ten chapters that have been categorized into three sections. Section 1 consists of four chapters on the thin-film deposition methods with synthesis aspects: Introductory Chapter: The Prominence of Thin Film Science in Technological Scale; Synthesis of Thin Films of Sulfides of Cadmium Lead and Copper by Chemical Bath Deposition; Modified Spin Coating Method for Coating and Fabricating Ferroelectric Thin Films as Sensors and Solar Cells and Emission, Defects, and Structure of ZnO Nanocrystal Films Obtained by Electrochemical Method. Section 2 contains of three chapters: Lab-on-a-Tube Surface Micromachining Technology; Efficient Optimization of the Optoelectronic Performance in Chemically Deposited Thin Films and Thin Films as a Tool for Nanoscale Studies of Cement Systems and Building Materials. Section 3 comprises of three chapters: Layer-by-Layer Thin Films and Coatings Containing Metal Nanoparticles in Catalysis; RRAM Memories with ALD High-K Dielectrics: Electrical Characterization and Analytical Modeling and Advanced Multifunctional Corrosion Protective Coating Systems for Light-Weight Aircraft Alloys-Actual Trends and Challenges

Finally, I could never forget that my leap in the field of thin-film science was guided by Dr. R. Jagannathan and Professor R. Chandramohan. Our friendly collaboration has been going on for years and it's been very productive. I would like to thank all the authors in the book for their valuable contributions. A few words at the last, I would like to express my sincere gratitute to Ms. Andrea Koric, publishing process manager, for the effective support in the construction of this book.

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Thin Film Deposition Methods: A Synthesis Perspective

# Introductory Chapter: The Prominence of Thin Film Science in Technological Scale

Jagannathan Thirumalai

Additional information is available at the end of the chapter

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# 1. A succinct testimony of thin film science

Since antediluvian times, the term 'thin film coating technology' is more captivating towards mankind. More than 2000 eons ago, goldsmiths and silversmiths developed a variety of methods, including using mercury as an adhesive, to apply over thin films of metals to sculptures and other objects. The ancient mercury-based processes like fire gilding and silvering techniques were used for the surface coating of less precious substrates having thin layers made up of gold or silver. They developed the technology of thin-film coating that is unrivalled by today's process for manufacturing DVDs, electronic devices, solar cells and other relevant products and used it on statues, amulets, jewels and more common objects.

In reference to the technological aspect, these workmen over 2000 years ago manage to produce valuable metal coatings as thin and adherent as possible, which not only saved luxurious metals but also enriched resistance to wear that would cause from sustained usage and circulation. In ancient days, the craftsmen were methodically organized these metals to construct functional as well as decorative artistic objects, without having any fundamental knowledge about the physico-chemical processes. The mercury-based techniques were also deceitfully used in ancient times to create objects such as coins and jewels that looked like they would be made of gold or silver but actually had a less precious core. Ingo et al. [1, 2] set forth to apply the modern analytical methods to reveal the ancients' artistic secrets. By means of surface analytical methods, for example, selected area X-ray photoelectron spectroscopy and scanning electron microscopy combined with energy dispersive X-ray spectroscopy on Dark Ages objects such as St. Ambrogio's altar from 825 AD, they said that their discoveries endorse 'the high level of proficiency achieved by the craftsmen and artists of these primordial periods who created objects of an imaginative qualities that would not be ameliorated in ancient times and have not yet been technologically advanced in modern ones'.

A widespread responsiveness has found on thin film studies in many advanced new areas of research in the combination of chemical, physical and mechanical sciences, which are based on prodigies with unique features of the thickness, structure, geometry of the film, etc. [3]. Whereas bearing in mind, a thin film matter contains two surfaces that are as close to each other



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. that they could have a conclusive impact on the internal physical properties and methods of the substance, which would differ, therefore, in a reflective way from that of a bulk material. A new phenomenon is arisen due to the diminution in distance flanked by the surfaces and its mutual interaction. At this juncture, the one-dimensional structure of the material is abridged to an order of numerous atomic layers, which generate an intermediary scheme sandwiched between macro-molecular systems, thus it offers us a technique of studying the microphysical nature of different phenomena. Thin films are precisely suitable for applications in the field of microelectronics, opto-electronics, integrated optics, etc. Nonetheless, the physical properties of the films such as electrical resistivity do not considerably vary from the characteristics of the bulk material. The thickness is from a few tenths of nanometre to a few micrometres.

Albeit the erudition of thin film prodigies dates well back over an epoch, it is actually only over the last four decades, which they have been effectively used to a substantial extent in practical situations. The usages of thin and thick films are almost authoritative to the complete prerequisite of micro miniaturization. The growth of the computer technology would lead to an obligation for very high density systems of storage and it is this which has enthused utmost of the research on the opto-electronics, magnetic and optical properties of the thin films. Sundry thin film devices had been industrialized which might found themselves looking for the applications or perhaps more prominently market.

A wide range of thin film materials, its fabrication techniques, deposition processing, spectroscopic and the optical characterization would probe which are adopted to create many novel devices. Thin film deposition is usually divided into two broad categories [3, 4].

- Physical deposition process
- Chemical deposition process

Widespread thin film techniques are summarized in the flowchart of **Figure 1** [5, 53]. The films are often capable of producing films around 1  $\mu$ m or less and the thick films are naturally in the range of 1–20  $\mu$ m, the range of resistivities are 10  $\Omega$ /square to 10 M $\Omega$ /square, there are significant possibilities for building multi-layer structures. Though there are definite techniques that are only accomplished of producing thick films and these might include screen printing, electrophoretic deposition, flame spraying, glazing and painting.

Physical and chemical depositions are the two techniques that are used to create a very thin layer of material into a substrate. They are used greatly in the production of semiconductors where the very thin layers of p-type and n-type materials would create the necessary junctions. *Physical deposition* refers to a widespread range of technologies in that a material is released from the source and which would deposited on a substrate using mechanical, electromechanical or the thermodynamic processes. The two most general techniques of physical vapour deposition (PVD) are evaporation and sputtering. *Chemical deposition* is stated as when a volatile fluid precursor does a chemical change on a surface leaving a chemically deposited coating. When one tries to categorize deposition of films by chemical methods, one would find that they can be categorized into two classes. The first class is related to the chemical formation of the film from medium and typical methods included are chemical reduction plating, electroplating and vapour phase deposition. A second class is the formation of the respective film from

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Figure 1. Flowchart illustrates the physical and chemical deposition process wide spread thin film techniques.

the precursor elements, e.g. iodization, gaseous iodization, sputtering ion beam implantation, thermal growth, CVD, MOCVD and vacuum evaporation that is used to produce the highest purity, reliable-performance solid materials in the semiconductor industry nowadays.

Relationship between the structure and property of thin films is the characteristics of such devices and forms the basis of thin film technologies. For example, in PVD (physical vapour deposition), a pure source material is gasified through evaporation, the application of the high power electricity, laser ablation and other few techniques. The gasified material would then condense on the substrate material to form the desired layer. However, by CVD (chemical vapour deposition), the chemical reactions might depend on thermal effects, as in vapour phase deposition and also the thermal growth. However, in all of these cases (**Figure 1**), a definite chemical reaction is a requirement to obtain as the form of final film [5, 53].

### 2. Technological advancements in the science of thin films

Thin film technology could be applied to various substrate materials, for example ceramics metals or polymers. The very common substrate materials are silicon, steel and glass. By appropriately cherry-picking the deposition materials and the technology, properties of the substrate material could be upgraded, enriched and tailor-made to meet the exceptional desires of a specific application. Furthermore, currently, thin film technologies are accessible that could be applicable to either flat substrates or objects with multifaceted geometrical silhouettes. Highlighting on device miniaturization and the technological parameters of alternate processes (such as thick film) are contributing to the expansion of the thin film industry and to the development of lower cost thin film equipment and processes. When the thin film is deposited, in many applications, it is obligatory to contour the film to a pre-established pattern. This is usually accomplished by lithography and etching. The construction device process is accomplished by ultimate and packaging steps (such as assembly), which differ based on the type of device. Everyone owns a numerous astounding moments to have a high regard for the remarkable engage in regeneration of novel thin film devices, the consequence and the good organization of the assistance offered through thin film devices to extend our prospect, in addition to reward for its fascinated defects to make ourselves with recent technological illusions.

The well-equipped novel thin film techniques have broad accessibility by means of ease procedure, sensitivity, selectivity, speed, accuracy and precision [6, 9, 34]. The novel applications of thin film devices have tendered innovative advancements in technology over few decades and these technological aspects were rapidly employed for cutting-edge research mostly in all the field of science and technology. **Table 1** presents the some major innovative advancement in technology associated with the applications of thin films in a broad spectrum.

Thin-film device fabrication technology has great advantages. Due to their characteristic features that they could be placed at virtually any wavelength in the broad region of transparency of their respective materials simply by varying the thicknesses of their layers, and, once a design had been established, the time for the production is exceptionally of short duration. In addition, a large field of application of thin film systems is that they act as laser mirrors, anti-reflex coatings and other optically active surface modifications. In the optical industry, they have been coated on substrates which would ensure the stable mechanical and other specific properties. Thin films could similarly be present in opto-electronic, magnetic and electronic apparatuses which could only be factory-made due to the specific physical properties of thin films which might vary considerably in reference to the bulk material. A significant example for this case is hard disk read heads due to the giant magnetoresistance effect (GMR). These are having the special properties with a combination of insulating and magnetic thin flms.

The technological achievements in modern thin film synthesis over the past decade subsequently lead to the utilization of outstanding properties and development of a wide range of applications in various engineering fields. As a result, the current activity in the thin-film device fabrication technology has been correlated and to expand our prospects based on the new ideas in the field of nanotechnology, LEDs and displays, photovoltaics/solar cells, environmental, biological science and so on. The current experimental standards for the assessment of environmental risk are the ones, which rely on the growth inhibition triggered by the chemical substance and would not include qualitative evaluation such as the process of enunciating

Field	Application with examples					
Engineering/ Processing	Tribology:					
	• Protective coatings to reduce wear [6, 7]					
	Corrosion and erosion [8]					
	• Low friction coatings [9]					
	Self-supporting coatings:					
	Refractory metals for rocket nozzles [10]					
	Crucibles [11]					
	• Pipes [12]					
	Others:					
	Hard coatings for cutting tools [13]					
	Surface passivation [14]					
	Protection against high temperature corrosion [15]					
	• Decorative coatings [16]					
	Catalyzing coatings [17]					
Optics	Antireflex coatings ("multicoated optics") [18]					
	Highly reflecting coatings (laser mirrors) [19]					
	Interference filters [20]					
	Beam splitter and thin film polarizers [21]					
	Integrated optics [22]					
Optoelectronics	Photodetectors [23]					
	Image transmission [24]					
	Optical memories [25]					
	• LCD/TFT [26]					
Electronics	Passive thin film elements [27] (resistors, condensers, interconnects)					
	• Active thin film elements [28] (transistors, diodes)					
	Integrated circuits [29] (VLSI, very large-scale integrated circuit)					
	CCD (charge coupled device) [30]					
Electricity (without	Insulating/conducting films [31] e.g. for resistors, capacitors					
(without semiconductors)	Piezoelectric devices [32]					
Cryotechnics	Superconducting thin films, switches, memories [33]					
	SQUIDS (superconducting quantum interference devices) [34]					
Mechanics	• "Hard" layers (e.g. on drill bits) [35]					
	Adhesion providers [36]					
	Friction reduction [37]					

Field	Application with examples				
Magnetics	Hard" discs [38]				
	• Video/audio tape [38]				
Sensorics	Data acquisition in aggressive environments and media [39]				
	• Telemetry [40]				
	Biological sensorics [41]				
Chemistry	Diffusion barriers [42]				
	Protection against corrosion/oxidation [43]				
	Sensors for liquid/gaseous chemical [44]				
Biomedicine	Biocompatible implant coating [45]				
	Neurological sensors [46]				
New materials	Metastable phases: metallic glasses [47, 48]				
	• Spheroidization of high melting point materials (diameter 1–500 $\mu$ m) [49]				
	• High purity semiconductors (GaAs) [50]				
(Alternative) energies	Solar collectors and solar cells [51]				
	• Thermal management of architectural performance of ETFE foils (metal-coated foils) [52]				

Table 1. Innovative advancement with technological applications in thin films [53].

toxicity. Thus, it is figured out that this only evaluation is inadequate for building improvement, which leads to ecological preservation and to deep circumvention against human health.

# 3. Conclusion

Persistent to the above discussion, thin film is not only well thought-out a forerunner across the globe with highly novel scientific developments; however, facts also establish that it has been and would prolong to be imperious towards path-breaking research against novel applications for the societal benefits. Amongst the major noteworthy developments in different fields of nanotechnology, LEDs and displays, photovoltaics/solar cells, environmental, and medical diagnostics are the most important worldwide challenges so far. Progress must continue in the novel thin film techniques, which is used in the field of spectral imaging, time-correlated single-photon counting, kinetic chemical reaction rates, non-invasive optical biopsy and visual implants. Thus, research on unique thin film technological achievements might pave way for coating thin films in an atomic scale that may perhaps turn out to be the future signs of green energy in the upcoming scenario.

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# **Conflict of interest**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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## References

- [1] G. M. Ingo, G. Guida, E. Angelini, G. D. Carlo, A. Mezzi, and G. Padeletti. Ancient Mercury-Based Plating Methods: Combined Use of Surface Analytical Techniques for the Study of Manufacturing Process and Degradation Phenomena, Acc. Chem. Res. 2013;46(11): 2365–2375. DOI: 10.1021/ar300232e.
- [2] B. G. Brunetti, A. Sgamellotti, A. J. Clark. Advanced Techniques in Art Conservation. Acc. Chem. Res. 2010; **43**: 693–694. DOI: 1021/ar100072f.
- [3] Anthony R. West Solid State Chemistry and its Applications, 2nd Edition, John Wiley & Sons, Singapore, January 2014, 584, ISBN: 978-1-119-94294-8.
- [4] K. L. Chopra. Thin Film Phenomena, 1st Edition, McGraw Hill, New York, 1969, 736 p, ISBN-10: 0070107998.
- [5] K. Seshan. Handbook of Thin-Film Deposition Processes and Techniques (Principles, Methods, Equipment and Applications). 2nd Edition, William Andrew Publishing, New York, 2002, 656 p. DOI: 10.1002/anie.198908221.
- [6] S. Zhang, editor. Nanostructured Thin Films and Coatings: Mechanical Properties. Volume 1 Edition, CRC Press, Boca Raton, Florida, USA, 2010. 550, ISBN: 9781420094022.
- [7] Y. Su, V. G. Kravets, S. L. Wong, J. Waters, A. K. Geim, R. R. Nair. Impermeable Barrier Films and Protective Coatings Based on Reduced Graphene Oxide. Nature Commun. 2014; 5(1–5): 4843. DOI: 10.1038/ncomms5843.
- [8] W. Aperador, J. Caballero-Gómez, A. Delgado. Erosion Corrosion Evaluation of CrN/ AlN Multilayer Coatings, by Varying the Velocity and Impact Angle of the Particle. Int. J. Electrochem. Sci. 2013;8(5): 6709–6721.
- [9] K. D. Bakoglidis, S. Schmidt, M. Garbrecht, I. G. Ivanov, J. Jensen, G. Greczynski, L. Hultman. Low-Temperature Growth of Low Friction Wear-Resistant Amorphous Carbon Nitride Thin Films by Mid-Frequency, High Power Impulse, and Direct Current Magnetron Sputtering. J. Vac. Sci. Technol. A. 2015; 33(5): 05E112. DOI: 10.1116/1.4923275.

- [10] P. Thakre, V. Yang. Chemical Erosion of Graphite and Refractory Metal Nozzles and Its Mitigation in Solid-propellant Rocket Motors. J. Propulsion Power. 2009;25(1): 40–50. DOI: 10.2514/1.37922.
- [11] E. J. Tuthill, G. Strickland, G. G. Weth. Platinum for High Temperature Crucibles Used in Processing Radioactive Wastes. Ind. Eng. Chem. Process Des. Dev. 1969;8(1): 36–43. DOI: 10.1021/i260029a007.
- [12] L. R. Higgins, R. Keith Mobley, D. Wikoff. Maintenance Engineering Handbook. 7th Edition, McGraw-Hill Companies, Inc., New York, 2008, pp. 1–1244. DOI: 10.1036/0071546464.
- [13] L. A. IvashchenkoG. V. RusakovV. I. IvashchenkoO. K. Porada. Hard Coatings on Cutting Tools. Powder Metall. Metal Ceram. 2004;43(11): 606–610. DOI: 10.1007/ s11106-005-0028-z.
- [14] Y. Cao, A. Stavrinadis, T. Lasanta, D. So, G. Konstantatos. The Role of Surface Passivation for Efficient and Photostable PbS Quantum Dot Solar Cells. Nature Energy. 2016;1: 16035. DOI: 10.1038/nenergy.2016.35.
- [15] E. A. YatsenkoA. P. ZubekhinA. A. Nepomnyashchev. Protection of Copper Against High-Temperature Corrosion. Glass Ceram. 1999; 56(9): 295–297. DOI: 10.1007/BF02681380.
- [16] B. R. Marple, R. S. Lima. Engineering Nanostructured Thermal Spray Coatings: Process– Property–Performance Relationships of Ceramic Based Materials. Adv. Appl. Ceram.– Struct. Funct. Bioceram. 2007;106(5): 265–275. DOI: 10.1179/174367607X202591.
- [17] S. Sepeur. Nanotechnology: Technical Basics and Applications. 1st Edition, Vincentz Network GmbH & Co KG, Germany, 2008, 168 p. DOI: 9783866309067.
- [18] U. Schulz. Review of Modern Techniques to Generate Antireflective Properties on Thermoplastic Polymers. Appl. Opt. 2006;45(7): 1608–1618. DOI: 10.1364/AO.45.001608.
- [19] O. Duyar, H. Zafer Durusoy. Design and Preparation of Antireflection and Reflection Optical Coatings. Turk J Phys. 2004;28(1): 139–144. DOI: 10.1.1.492.1404.
- [20] H. Angus Macleod. Thin-Film Optical Filters. 4th Edition, CRC Press, Boca Raton, FL, 2010, 791 p. ISBN: 978-1-4200-7302-7.
- [21] L. Li, J. A. Dobrowolski. High-Performance Thin-Film Polarizing Beam Splitter Operating at Angles Greater Than the Critical Angle. Appl. Opt. 2000;39(16): 2754–2771. DOI: 10.1364/AO.39.002754.
- [22] R. G. Hunsperger. Integrated Optics Theory and Technology. 1st Edition, Springer, New York, 2009, 513 p. DOI: 10.1007/b98730.
- [23] K. F. Mak, J. Shan. Photonics and Optoelectronics of 2D Semiconductor Transition Metal Dichalcogenides. Nature Photonics. 2016;10(4): 216–226. DOI: 10.1038/nphoton.2015.282.
- [24] A. A. Friesem, U. Levy. Parallel Image Transmission by a Single Optical Fiber. Opt. Lett. 1978;2(5): 133–135. DOI: 10.1364/OL.2.000133.

- [25] C. Ríos, M. Stegmaier, P. Hosseini, D. Wang, T. Scherer, C. D. Wright, H. Bhaskaran, W. H. P. Pernice. Integrated All-Photonic Non-Volatile Multi-Level Memory. Nature Photonics, 2015;9(11): 725–732. DOI: 10.1038/nphoton.2015.182.
- [26] C-L. Kuo, C-K. Wei, M. Suzuki, W-T. Lin, W-Y. Li, Li-Yi Chen. Large-Area TFT-LCD Using MVA-LCD Mode for TV Applications. SID Symposium Digest of Technical Papers. 2003; 34(1): 1200–1203. DOI: 10.1889/1.1832502.
- [27] R. F. Graf. Modern Dictionary of Electronics. 7th Edition, Newnes, Oxford, 1999, 869 p. ISBN: 0080511988.
- [28] H. Khlyap. Physics and Technology of Semiconductor Thin Film-Based Active Elements and Devices. 1st Edition, Bentham Science Publishers, USA, 2009, 127 p. DOI: ISBN: 1608050211.
- [29] S-J. Han, A. Valdes Garcia, S. Oida, K.A. Jenkins, W. Haensch. Graphene Radio Frequency Receiver Integrated Circuit. Nature Commun. 2014;5(1): 3086. DOI: 10.1038/ncomms4086.
- [30] P. Felber. Charge-Coupled Devices [dissertation]. Illinois Institute of Technology, Illinois, NA, 2002. 18 p. Available from: http://www.ece.iit.edu/~pfelber/ccd/project.pdf.
- [31] P. G. Slade. Electrical Contacts: Principles and Applications, Second Edition. 2nd Edition, CRC Press, Ronda, 2013, 1311 p. DOI: ISBN: 1439881316.
- [32] B. Lu, Y. Chen, D. Ou, H. Chen, L. Diao, W. Zhang, J. Zheng, W. Ma, L. Sun, X. Feng. Ultra-flexible Piezoelectric Devices Integrated with Heart to Harvest the Biomechanical Energy. Sci Rep. 2015;5(1): 16065. DOI: 10.1038/srep16065.
- [33] N. Spyropoulos-Antonakakis, E. Sarantopoulou, G. Drazic, Z. Kollia, D. Christofilos, G. Kourouklis, D. Palles, A. C. Cefalas. Charge Transport Mechanisms and Memory Effects in Amorphous TaNx Thin Films. Nanoscale Res Lett. 2013;8(1): 432. DOI: 10.1186/1556-276X-8-432.
- [34] J. Gallop, L. Hao. Nanoscale Superconducting Quantum Interference Devices Add Another Dimension. ACS Nano. 2016;**10**(9): 8128–8132. DOI: 10.1021/acsnano.6b04844.
- [35] W. Shi, G. H. Fredrickson, E. J. Kramer, C. Ntaras, A. Avgeropoulos, Q. Demassieux, C. Creton. Mechanics of an Asymmetric Hard–Soft Lamellar Nanomaterial. ACS Nano. 2016;10(2): 2054–2062. DOI: 10.1021/acsnano.5b06215.
- [36] B. Persson, G. Carbone, V. N. Samoilov, I. M. Sivebæk, U. Tartaglino, A. I. Volokitin, C. Yang. Contact Mechanics, Friction and Adhesion with Application to Quasicrystals. In: Avouris, P., Bhushan, B., Bimberg, D., von Klitzing, K., Ning, C.-Z., Wiesendanger, R., editors. Nanoscience and Technology. 1st Edition, Springer, Berlin, Germany, 2015, pp. 249–287. DOI: 10.1007/978-3-319-10560-4\_13.
- [37] V. Popov, M. Heß. Method of Dimensionality Reduction in Contact Mechanics and Friction. 1st Edition, Springer-Verlag Berlin Heidelberg, Berlin, Germany, 2015, XVII, 265 p. DOI: 10.1007/978-3-642-53876-6.

- [38] K. C. Laudon, J.P. Laudon. Essentials of Management Information Systems: Organization and Technology, 1st Edition, Prentice Hall Inc., Englewood Cliffs, NJ, 1995, 640 p. DOI: ISBN: 978-0023680830.
- [39] M. C. Hemmsen, S. I. Nikolov, M. M. Pedersen, M. J. Pihl, M. S. Enevoldsen, J. M. Hansen, J.A. Jensen. Implementation of a Versatile Research Data Acquisition System Using a Commercially Available Medical Ultrasound Scanner. IEEE Trans. Ultrason. Ferroelectr. Freq. Control. 2012;59(7): 1487–1499. DOI: 10.1109/TUFFC.2012.2349.
- [40] Manner Sensortelemetrie GmbH. Sens2B Sensors [Internet]. 2016 [Updated: 2016]. Available from: http://www.sens2b-sensors.com/companies/item/manner-sensortelemetrie-gmbh [Accessed: 27-11-2016].
- [41] G. Harsanyi. Sensors in Biomedical Applications: Fundamentals, Technology and Applications. 1st Edition, CRC Press, Boca Raton, Florida, 2000.368 p.ISBN:9781420012910.
- [42] U. Grønbjerg Vej-Hansen, J. Rossmeisl, I. E. L. Stephens, J. Schiøtz. Correlation Between Diffusion Barriers and Alloying Energy in Binary Alloys. Phys. Chem. Chem. Phys. 2016;18(4z): 3302–3307. DOI: 10.1039/C5CP04694G.
- [43] Y. Qian, Y. Li, S. Jungwirth, N. Seely, Y. Fang, X. Shi. The Application of Anti-Corrosion Coating for Preserving the Value of Equipment Asset in Chloride-Laden Environments: A Review. Int. J. Electrochem. Sci., 2015;10 (1): 10756–10780.
- [44] Z. Ma, B. Su, S. Gong, Y. Wang, L. Wei Yap, G. P. Simon, W. Cheng. Liquid-Wetting-Solid Strategy to Fabricate Stretchable Sensors for Human-Motion Detection. ACS Sens. 2016;1 (3): 303–311. DOI:10.1021/acssensors.5b00195.
- [45] M. Saini, Y. Singh, P. Arora, V. Arora, K.Jain. Implant Biomaterials: A Comprehensive Review. World J Clin Cases. Jan; 2015;16(3(1)): 52–57. DOI: 10.12998/wjcc.v3.i1.52.
- [46] E. Brillas, C. A. Martínez Huitle. Synthetic Diamond Films: Preparation, Electrochemistry, Characterization and Applications: The Wiley Series on Electrocatalysis and Electrochemistry. 8th Edition, John Wiley & Sons, New Jersey, USA, 2011, 590 p. ISBN:9781118062357.
- [47] U. Herold, U. Köster and A.G. Dirks. The Amorphous to Crystalline Transition in Fe-B Metallic Glasses and Vapor-Deposited Thin Films. J. Magn Magn. Mat. 1980;19(1–3): 152–156. DOI: 10.1016/0304-8853(80)90580-6.
- [48] J. P. Chu, J.S.C. Jang, J.C. Huang, H.S. Chou, Y. Yang, J.C. Ye, Y.C. Wang, J.W. Lee, F.X. Liu, P.K. Liaw, Y.C. Chen, C.M. Lee, C.L. Li, Cut Rullyani. Thin Film Metallic Glasses: Unique Properties and Potential Applications. Thin Solid Films. 2012;**520**(1): 5097–5122. DOI: 10.1016/j.tsf.2012.03.092.
- [49] D. P. Langley, M. Lagrange, G. Giusti, C. Jiménez, Y. Bréchet, N. D. Nguyen and D. Bellet. Metallic Nanowire Networks: Effects of Thermal Annealing on Electrical Resistance. Nanoscale. 2014;6(1): 13535–13543. DOI: 10.1039/C4NR04151H.

- [50] S. Sathasivam, R.R. Arnepalli, D. S. Bhachu, Y. Lu, J. Buckeridge, D. O. Scanlon, B. Kumar, K. K. Singh, R. J. Visser, C. S. Blackman, and C. J. Carmalt. Single Step Solution Processed GaAs Thin Films from GaMe3 and tBuAsH2 under Ambient Pressure. J. Phys. Chem. C. 2016;120(13): 7013–7019. DOI: 10.1021/acs.jpcc.6b00850.
- [51] S. Sharma, K. Kumar Jain, A. Sharma. Solar Cells: In Research and Applications—A Review. Mat. Sci. Appl. 2015;6(1): 1145–1155. DOI: 10.4236/msa.2015.612113.
- [52] J. Hu, W. Chen, B. Zhaoa, D. Yang. Buildings with ETFE Foils: A Review on Material Properties, Architectural Performance and Structural Behaviour. Constr. Build. Mater. 2017;131(1): 411–422. DOI: 10.1016/j.conbuildmat.2016.11.062.
- [53] Available from: http://static.ifp.tuwien.ac.at/homepages/Personen/duenne\_schichten/ pdf/t\_p\_ds\_chapter1.pdf.

# Synthesis of Thin Films of Sulfides of Cadmium, Lead and Copper by Chemical Bath Deposition

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Additional information is available at the end of the chapter

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### Abstract

The goal of this chapter is to present three kind of thin films for the materials, done by Chemical Bath Deposition technique, the materials are CdS, PbS and CuS. The characterization has been diversified, but consisting mainly X-ray Diffraction (XRD) giving hexagonal, cubic and amorphous structures of CdS, PbS and CuS respectively. The Raman dispersion let to found the characteristics peaks of vibration, one for the CdS located on  $300.7 \text{ cm}^{-1}$ , three for PbS and two more for the CuS. We use X-rays Photoelectron Spectroscopy to formalize the chemical composition analysis, from this analysis we could to proof the high purity of the chemical bath deposition method in the materials preparation. We used UV-Vis Spectroscopy to determine simple optical responses, getting the biggest transmittances of 72% for CdS, 45% for PbS, and 80% for CuS, and direct energy band gaps of 2.47 eV for CdS, 1.78 eV for CuS as ground and with thermic annealing 2.45 eV which is believed result of amorphous to crystalline morphology changes, the indirect bandgap 0.94 eV is measured too. The AFM given information about the surface morphology and roughness, Scanning Electron Microscopy (SEM) micrography shows the polycrystallinity nature of the CuS including the smooth.

Keywords: thin films, semiconductors, solar cells, chalcogenides, CBD

### 1. Introduction

Lead sulfide (PbS) and cadmium sulfide (CdS) are two semiconductors studied since time ago, their combined research has around one century and the direct band gap for PbS is around 0.37 eV at 300 K [1–10]. The PbS is mainly used as an infrared detector in various fields has been used mainly as an infra-red detector in another diverse field [11–15]. On the other hand, the CdS material shows a direct band gap between 2.42 and 2.53 eV [16–25]. The CdS material was used as a pigment as well as for solar cells optical window; cadmium sulfide is a semiconductor



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. II–VI type which is mainly useful in optoelectronic devices and some researchers reported that it has low conductivity of 10.8 ( $\Omega$  cm)<sup>-1</sup>.

Lead sulfide has a cubic crystallographic structure, while cadmium sulfide can be cubic or hexagonal, basically. Here we also discuss some features of copper sulfide (CuS) semiconductor film. These materials are mostly found in amorphous nature with poor crystallinity tending to nanocrystals. Some reports showed the possibility of converting CuS films into the chalcocite phase by mean copper atomic implanting; in reference [26] the authors reported an indirect band gap of 1.28 eV for CuS. CuS is used in various applications such as ion sensitive electrodes and photothermal conversion solar controllers [27, 28].

## 2. Synthesis of the thin films

CdS thin films were deposited on microscope glass substrates, immersed into a 100 ml beaker containing a solution mixture of 31 ml of deionized water, 4 ml of 0.1 M cadmium nitrate tetrahydrate (Cd(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O), 5ml of 0.5 M glycine (NH<sub>2</sub>CH<sub>2</sub>COOH), 2 ml of pH 11 buffer, 5 ml of 1 M thiourea ((NH<sub>2</sub>)<sub>2</sub>CS) and finally in the mixture solution of 60 ml of deionized water was added in order to increase the reaction volume. The mix of solutions was placed in a thermal reservoir maintained at 70°C for 10 min and a homogeneous CdS film with a direct band gap of 2.47 eV was obtained.

PbS thin films were obtained by sequentially adding 5 ml of lead acetate (0.5 M) and 5 ml of sodium hydroxide (2 M), 6 ml of thiourea (1 M) and 2 ml of triethanolamine (1 M) in mixture solution and finally in the solution, 82 ml of ionized water is added. After stirring the mixture solution, in order to homogenize the mixture, the reaction mixture was placed in a thermal source at 70 °C for 5 min.

CuS thin films were deposited in glass substrates obtained from a solution by adding 2 ml of dilute copper nitrate (0.1 M) into 31 ml of deionized water and then adding sequentially 2 ml of barium hydroxide (0.01 M), 2 ml of triethanolamine (1 M), 4 ml of thiourea (1 M) and finally 19 ml of deionized water. The determined reaction time was 20 min. Using the process, we are able to obtained CuS thin films of around 150 nm thickness, amorphous, weakly adhered and a direct energy band gap of 1.26 eV [9].

Rigaku Ultima III diffractometer with micro-Raman X'Plora BXT40 at 2400T resolution was used to collect the X-ray patterns. The chemical analysis was carried out using an XPS Perkin-Elmer Phi-5000 model. Transmission spectra were obtained using an Ocean Optics USB4000-UV-VIS spectrometer in the 280–850 nm wavelength range. The surface morphology of the samples was studied by atomic force microscopy (AFM), using a JSPM-4210 scanning probe microscope (JEOL Ltd.), SEM Zeiss SUPRA 40.

This section describes the chemical formulations used to obtain the selected thin films materials such as CdS, PbS and CuS. As can be observed, the used chemical compounds (precursors) are so easy to manipulate and the procedure just consists of adding the ordered aqueous solutions sequentially, heating and waiting for the deposition time.

The following are the chemical formulations to obtain cadmium sulfide (CdS) thin films:

- **1.** 31 ml of H<sub>2</sub>O (deionized water)
- 2. 4 ml of Cd(NO<sub>3</sub>)<sub>2</sub> 4H<sub>2</sub>O, 0.1 M
- 3. 5 ml of glycine, (NH<sub>2</sub>CH<sub>2</sub>COOH), 0.1 M
- 4. 2 ml of buffer pH 11,  $[NH_4OH/NH_4Cl]$
- 5. 5 ml of thiourea, NH<sub>2</sub>CSNH<sub>2</sub>, 1 M
- 6. 13 ml of H<sub>2</sub>O (water until complete 60 ml)
- **7.** 10 min at 70°C

The following are the chemical formulations to obtain lead sulfide (PbS) thin films:

- 1. 5 ml of lead acetate, Pb (CH<sub>2</sub>COO)<sub>2</sub>, 0.5 M
- 2. 5 ml of sodium hydroxide (NaOH), 2 M
- 3. 6 ml of thiourea 1 M
- 4. 2 ml of triethanolamine (OHCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N, 1 M
- 5. 82 ml of H<sub>2</sub>O (water until complete 100 ml)
- 6. 5 min at 70°C and 5 min at 75°C

The following are the chemical formulations to obtain copper sulfide (CuS) thin films:

- 1. 31 ml of H<sub>2</sub>O (deionized water)
- 2. 2 ml of Cu(NO<sub>3</sub>), 0.1 M
- 3. 2 ml of Ba(OH)<sub>2</sub>, 0.01 M
- 4. 2 ml of triethanolamine (OHCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>N, 1 M
- 5. 4 ml of thiourea 1 M
- 6. 19 ml of deionized H<sub>2</sub>O (water until complete 60 ml)
- **7.** 20 min at 55°C
- 8. The obtained amorphous film was then thermal annealed at 180°C for 20 min

# 3. Results

The first characterizations to present are X-ray diffraction patterns for the thin films of materials (CdS, PbS and CuS) as ground and CuS thermal annealed (see **Figure 1**). **Figure 1** shows the precise labels for each film. CdS PDF # 02-0563, PbS PDF # 65-9496 and CuS amorphous.

The Raman dispersion characterizations were carried out using a laser with a wavelength of 532 nm. **Figure 2** shows a typical Raman signal for CdS [29], the Raman spectrum is noisy, but an adjustment was carried out in order to smooth.



Figure 1. XRD patterns for the synthesized CdS, PbS and CuS films, including a CuS film with thermal annealing.



Figure 2. Raman spectrum for CdS thin film prepared by chemical bath deposition at 70°C for 10 min.

For the PbS thin film, the Raman spectrum shows three more intense signals, located in 201.6, 319.9 and 449.07 cm<sup>-1</sup> (see **Figure 3**). Also a laser of 532 nm wavelength was used to obtain the Raman spectrum.



Figure 3. Raman spectrum for PbS thin film prepared by chemical bath deposition at 75°C for 5 min.



Figure 4. Raman spectrum for CuS thin film prepared by chemical bath deposition at 55°C for 20 min.

XPS						
Label	CdS		PbS		CuS	
	Energy level	eV	Energy level	eV	Energy level	eV
a	Cd MNN (Auger)	882.32	O KLL (Auger)	749.31	Cu 2p1	954.6
b	O KLL (Auger)	745.42	Pb 4p3	647.66	Cu 2p3	933.15
c	Cd 3p1	655.44	O 1s	536.17	O KLL (Auger)	743.58
d	Cd 3p3	620.19	Pb 4d3	438.41	O 1s	532.28
e	O 1s	534.11	Pb 4d5	416.89	-	416.89
f	Cd 3d3	414.83	C 1s	287.77	Cu LMM (Auger)	336.53
g	Cd 3d5	407.05	S 2p3	164.6	C 1s	285.71
h	C 1s	285.71	Pb 4f5	146.97	Cl 2s	264.19
i	S 2s	227.1	Pb 4f7	139.19	S 2p	225.045
j	S 2p	164.6	Pb 5d5	23.58	Si 2s	199.63
k	Cd 4d5	13.96	-		Cu 3s	162.54
1	-		-		Si 2p	123.39
m	-		-		Cu 3p3	76.46

Table 1. Main chemical composition for three thin films elaborated by chemical bath deposition and their binding energies.



Figure 5. XPS spectra for our three compounds, PbS, CdS and CuS thin films. These plots confirm the chemical composition the obtained materials.

Raman spectrum for as ground CuS thin film (see **Figure 4**) shows two well-defined signals or dispersions at 263.5 and 471 cm<sup>-1</sup>.

The next characterization is carried out by X-ray photoelectron spectroscopy; at this stage, it is possible to determine the chemical composition for the grown materials: CdS thin film, PbS



Figure 6. Optical absorption responses for the indicated thin films of CdS, PbS and CuS as ground and CuS thermal annealed.



Figure 7. The linear adjustment for the projected CdS thin film with a direct band gap of 2.47 eV.



Figure 8. Absorption coefficient and light penetration deep for the CdS, this graph can be used as a design tool to determine the thickness for the CdS layer for solar cells.



Figure 9. Band gap compute showing the region where is present the absorption edge for CuS as ground.

thin film and as ground CuS thin film and annealed CuS thin film (as with thermal annealing as without thermal annealing). The energetic levels located in each one of the thin films are shown in **Table 1** and **Figure 5**. **Table 1** also presents the name of each chemical compound and its location.



Figure 10. Band gap compute showing the region where is present the absorption edge for the CuS with thermic annealing.



Figure 11. Indirect band gap compute for CuS as ground.

**Table 1** shows 11 peaks identified for the CdS, 10 for PbS and 13 for the CuS. All these peaks confirm the high purity of the material preparation.

On the other hand, **Figure 6** depicts the absorption responses for one CdS, one PbS and two CuS thin films. The CuS thin films correspond one to as ground film and other with thermal annealing. Reaction conditions are as follows: for CdS: reaction temperature 70°C and reaction time, 10 min; for PbS: reaction temperature 75°C and reaction time 5 min; and for as ground CuS: reaction temperature 55°C and reaction time 20 min, while a replicate of CuS has been thermal annealed to 180°C for 20 min.



Figure 12. Images (a) and (b) show the surface profile corresponding to CdS thin film elaborated, (c) and (d) images show the corresponding PbS and (e) and (f) images show for CuS films [18].
**Figure 7** shows the graphical calculation procedure which determines the optical direct band gap and this procedure is typically denominated by Tauc procedure. The intercept had a value of -3.67123 (a.u.), while the slope was 1.48674 (a.u./eV)

A very interesting and useful analysis is the corresponding to comparison between the absorption coefficient (cm<sup>-1</sup>) and the light penetration deep (nm), see **Figure 8**. The relationships among them are basically multiplicative inverses; for example, we choose the wavelength value of 595 nm and from there, the values for the absorption coefficient ( $\alpha$ ) and light penetration deep (Lpd) are  $4 \times 10^4$  cm<sup>-1</sup> and  $2.5 \times 10^2$  nm, respectively. This curve is important because is a good tool to solar cell designs. In this curve is possible chose the thickness to satisfy a quantity of absorption and penetration length deep.

As shown in **Figure 9–Figure 11**, the direct band gap value is computed for the CuS thin films obtained by chemical bath deposition, in the curve seen in **Figure 9**, the direct band gap is 1.78 eV for the CuS as ground, in **Figure 10**, the band gap is 2.74 eV for CuS which is subjected at thermal annealing. The indirect band gap of 0.94 eV for CuS is shown in **Figure 11**.

**Figure 12** depicts the surface morphology of three sulfides CdS, PbS and CuS realized by AFM on square areas of  $2.0 \times 2.0 \ \mu\text{m}^2$  and  $498 \times 498 \ \mu\text{m}^2$ . (a) Image shows a top view for the CdS thin film, (b) image shows a perspective view corresponding to CdS material; (c) and (d) images show the PbS thin films and finally, the top and perspective views of the CuS thin film are shown in the images labeled (e) and (f). The cluster size of PbS is bigger than that of CdS, which are at the same scale, while the cluster size for CuS only was appreciable for a higher magnification; anyway, the higher profile heights were found for CuS films around six times bigger than CdS.

**Figure 13** depicts an SEM micrograph of PbS and the reference scale is 200 nm and the superficial particles have a size of approximately 70 nm and are presented with less frequency. The morphology of the rest of the thin film is of particles more little and tight.



Figure 13. SEM micrograph of PbS thin film showing the superficial morphology for special conditions of 75°C for 5 min.

#### 4. Photoresponse

The CdS was a unique material that shows the interesting behavior with time. The response should be instantaneously in a conductor however due to charge effects this is retarded in CdS and it is a dielectric material therefore the response is similar to a capacitor, when the energy is increased above of the band gap this exponential behavior is increased. **Figure 14** shows the behavior of the photoresponse at three different wavelengths, showing a greater need for stabilization time at a wavelength close to the bandwidth.



**Figure 14.** Response time for the CdS thin film synthetized by DBQ at 70°C for 10 min and studied at  $\lambda$  = 350.97, 498.9 and 510.02, respectively.

The graph of resistance vs. temperature for the CuS thin films with thermal annealing determines the semiconductor behavior from the slope of the curve of **Figure 15**. This curve is nearly linear and then it is possible fitting by a line. The minimal resistance is present at 112°C being 1047180  $\Omega$ . In this case, we can see that this curve is composed of three straight lines approximately all of these of semiconductor behavior but with different slopes (see **Figure 16**) [29].



Figure 15. Linear fitting from the resistance vs. temperature of the CuS thin film with thermal annealing.

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Figure 16. Nonlinear fitting from the resistance vs. temperature of the PbS thin film.

**Figure 17** shows the structure of a solar cell, where on a glass substrate covered by an ITO film is deposited CdS by the aforementioned procedure the PbS is then deposited following the formula of the section (Synthesis of the thin films) and finally are Deposited silver contacts to measure the complete structure, the contacts are periodically separated by 1 cm as shown in this figure.

The *I*–*V* curve in **Figure 18** shows an on voltage that increase with the increase of the measure area because each measure is realized considering first E1 respect to ITO, after that E1 + E2 = E2 respect to ITO and so on. The measure result is shown in the curve *I*–*V*, which indicates that when the slope increases the resistance decreases, increasing therefore with current.



Figure 17. Three-dimensional solar cell structure showing details of front and rear contact arrangement.



Figure 18. *I–V* response for the example structure.

## 5. Conclusions

The main conclusion establishes that the chemical bath deposition technique is a simple and low-cost process and that it is used to obtain thin films of CdS, PbS and CuS with very good homogeneity, pure enough and low cost, which can be used in wide range of applications.

CdS thin films obtained using glycine as a complexing agent presented hexagonal polycrystalline structure. The method used for PbS thin films in this work also produced a polycrystalline film but with cubic geometry. The CuS thin film was an amorphous material and weakly adhered to the substrate.

Their optical responses in the UV-vis range are according with some reported values. Some electrical and thermal tests were used on the obtained materials, In order to future applications.

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# References

- O.R. Akhmedov, M.G. Guseinaliyev, N.A. Abdullaev, N.M. Abdullaev, S.S. Babaev, N.A. Kasumov, Optical properties of PbS thin films, Semiconductors, 2016, Volume 50, Issue 1, pp. 50–53.
- [2] S. Seghaier, N. Kamoun, R. Brini, A.B. Amar, "Structural and optical properties of PbS thin films deposited by chemical bath deposition", Materials Chemistry and Physics, 2006, Volume 97, pp. 71–80.
- [3] J.A. García-Valenzuela, M.R. Baez-Gaxiola, M. Sotelo-Lerma, "Chemical bath deposition of PbS thin films on float glass substrates using a Pb(CH3COO)2-NaOH-(NH2)2CS-N (CH2CH2OH)3-CH3CH2OH definite aqueous system and their structural, optical and electrical/photoelectrical characterization", Thin Solid Films, 2013, Volume 534, pp. 126– 131
- [4] J.J. Valenzuela-Jauregui, R. Ramırez-Bon, A. Mendoza-Galvan, M. Sotelo-Lerma, "Optical properties of PbS thin films chemically deposited at different temperatures", Thin Solid Films, 2003, Volume 441, pp. 104–110.
- [5] J.I. Pankove, Optical Processes in Semiconductors, Dover Publications Inc., New York, 1971.
- [6] H. Kanazawa, S. Adachi, Optical properties of PbS, Journal Applied Physics, 1998, Volume 83, p. 5997.
- [7] C.O. Mosiori, Orori, W. N. Njoroge, , O. John, Optical and Electrical Properties of Pbs Thin Films Grown by Chemically Bath Deposition [CBD] at Different Lead Concentrations, International Journal of Advanced Research in Physical Science (IJARPS), May 2014, Volume 1, Issue 1, pp. 25–32.
- [8] S.V. Bhatt, M.P. Deshpande, B.H. Soni, N. Garg, S.H. Chaki, Chemical bath deposition of lead sulphide (PbS) thin film and their characterization, Solid State Phenomena, 2014, Volume, 209, pp. 111–115.
- [9] F. Gödea, F. Yavuza, I.A. Karıperb, Preparation and characterization of nanocrystalline pbs thin films produced by chemical bath deposition, Acta Physica Polonica A, 2015, Volume 128, Issue 2-B, pp. B215–B218.

- [10] C.E. Pérez-garcía, R. Ramírez-bon, Y.V. Vorobiev, PbS thin films growth with CBD and PCBD techniques: A comparative study, Chalcogenide Letters, November 2015, Volume 12, Issue 11, pp. 579–588.
- [11] S.M. Lee, D.H. Yeon, S.S. Chon, Y.S. Cho, Effect of double substitutions of Cd and Cu on optical band gap and electrical properties of non-colloidal PbS thin films, Journal of Alloys and Compounds, 2016, Volume 685, pp. 129–134.
- [12] E.M. El-Menyawy, G.M. Mahmoud, R.S. Ibrahim, Structural, optical and electrical properties of PbS and PbSe quantum dot thin films, Journal of Materials Science-Materials in Electronics, 2016, Volume 27, Issue 10, pp. 10070–10077.
- [13] I. E. Moreno-Cortez, A. Alvarado-Castaneda, D. F. Garcia-Gutierrez, Core-shell PEDOT: PSS-PVP nanofibers containing PbS nanoparticles through coaxial electrospinning, Synthetic Metals, 2016, Volume: 220, pp. 255–262.
- [14] W. Yao, W. Qisheng, Y. Lei, Epitaxial 2D PbS nanoplates arrays with highly efficient infrared response, Advanced Materials, 2016, Volume: 28 Issue 36, pp. 8051–8057.
- [15] W. Heng, Z. Guang-Mei, Z. Ji-Tao, PbS quantum dots: size, ligand dependent energy level structures and their effects on the performance of heterojunction solar cells, Journal of Inorganic Materials, 2016, Volume 31, Issue 9, pp. 915–922.
- [16] M. Gilic, J. Trajic, N. Romcevic, M. Romcevic, D. V. Timotijevic, G. Stanisic, I. S. Yahia, Optical properties of CdS thin films, Optical Materials, 2013, Volume 35, Issue 5, pp. 1112–1117.
- [17] K. Ravichandran, N. Nisha Banu, V. Senthamil Selvi, B. Muralidharan, T. Arun, Rectification of sulphur deficiency defect in CdS based films by introducing a novel modification in the SILAR cyclic process, Journal of Alloys and Compounds, 2016, Volume 687, pp. 402–412.
- [18] N. Susha, R. J. Mathew, S. S.Nair, Tuning of optical and magnetic properties of nanostructured CdS thin films via nickel doping, Journal of Materials Science, 2016, Volume 51, Issue 23, pp. 10526–10533.
- [19] M. Guo, L. Wang, Y. Xia, W. Huang, Z. Li, Enhanced photoelectrochemical properties of nano-CdS sensitized micro-nanoporous TiO<sub>2</sub> thin films from gas/liquid interface assembly, Journal of Alloys and Compounds, 2016, Volume 684, pp. 616–623.
- [20] L.V. Garcia, S.L. Loredo, S. Shaji, J.A. Aguilar Martinez, D.A. Avellaneda, T.K. Das Roya, B. Krishnana, Structure and properties of CdS thin films prepared by pulsed laser assisted chemical bath deposition, Materials Research Bulletin, 2016, Volume 83, pp. 459–467.
- [21] B. Liu, R. Luo, B. Lia, J. Zhang, W. Li, L. Wu, L. Feng, J. Wu, Effects of deposition temperature and CdCl<sub>2</sub> annealing on the CdS thin films prepared by pulsed laser deposition, Journal of Alloys and Compounds, 2016, Volume 654, pp. 333–339.

- [22] X. Yang, B. Liu, B. Li, J. Zhang, W. Li, L. Wu, L. Feng, Preparation and characterization of pulsed laser deposited a novel CdS/CdSe composite window layer for CdTe thin film solar cell, Applied Surface Science, 2016, Volume 367, pp. 480–484.
- [23] J. Maricheva, S. Bereznev, R. Naidu, N. Maticiuc, V. Mikli, J. Kois, Improved electrodeposition of CdS layers in presence of activating H<sub>2</sub>SeO<sub>3</sub> microadditive, Materials Science in Semiconductor Processing, 2016, Volume 54, pp. 14–19.
- [24] O.K. Echendu, U.S. Mbamara, K.B. Okeoma, C. Iroegbu, C.A. Madu, I.C. Ndukwel., M. Dharmadasa, Effects of deposition time and post-deposition annealing on the physical and chemical properties of electrodeposited CdS thin films for solar cell application, Journal of Materials Science: Materials in Electronics, 2016, Volume 27, Issue 10, pp. 10180–10191.
- [25] R.A. Harris, J.J. Terblans, Modeling the band gap of CdS quantum well structures, Physica E: Low-dimensional Systems and Nanostructures, 2016, Volume 84, pp. 415–422.
- [26] S.J. Castillo, A. Apolinar-Iribe, A. de León, C. Ruvalcava-Cornejo, Optical and structural analysis of ammonia-free cooper sulphide thin films using chemical deposition method, Journal of Optoelectronics and Advanced Materials, 2011, Volume 13, Issue 10, pp. 1258– 1261.
- [27] R. De Marco, R. Mattrall, J. Liesegang, G. Nyberg, I. Hamilton, Analytical Chemistry, 1992, Volume 64, p. 594.
- [28] I. Grozdanov, C.K. Barlingay, S.K. Dey, Materials Letters, 1995, Volume 23, p. 181.
- [29] L. Saviot, B. Champagnon, E. Duval, A.I. Ekimov, Resonant low-frequency Raman scattering in CdS-doped glasses, Journal of Crystal Growth, 1998, Volumes 184–185, pp. 370– 373.

# Modified Spin Coating Method for Coating and Fabricating Ferroelectric Thin Films as Sensors and Solar Cells

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Additional information is available at the end of the chapter

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#### Abstract

Spin coating process with a modified spin coater is performed well, especially the second generation of modified spin coater, which has a maximum value of 18,000 rpm, is able for manufacturing/coating photonic crystal-based ferroelectric thin films that require a high angular velocity (rpm). Ferroelectric thin films that use both 3000 and 6000 rpm have given good results in energy gap, electrical conductivity, etc. In addition, the modified spin coater has also produced several applications such as sensors in the device of blood sugar level noninvasively, sensors in the automatic drying system, sensors in the robotic system, and photovoltaic cells in the system of solar cells/panels which are being developed at present. These applications used ferroelectric material such as barium strontium titanate (BST), lithium niobate (LiNbO<sub>3</sub>), cuprous oxide (CuO), and lithium tantalate (LiTaO<sub>3</sub>).

Keywords: modified spin coating, ferroelectric thin films, sensors, solar cells

## 1. Introduction

Thin film technology is one of the pillars of the current smart material technology due to its material and cost efficiencies. Industrial applications of thin films include electronic semiconductors (especially solar cells), optical coatings, and sensors due to their dielectric constant, dielectric loss, pyroelectric coefficient, and dielectric tunability properties. Ferroelectric thin films such as barium strontium titanate, lithium tantalate, and lithium niobate can be manufactured by using CSD method and then performed by the spin coating process [1]. CSD method is one of the methods to create/develop thin films [2–12], which has advantages including the ability to control the film stoichiometry with good quality, easy procedure,



require relatively low cost, and generate a good crystalline phase [13–15]. In addition, thin films can also be fabricated by other methods such as metal organic chemical vapor deposition (MOCVD) [16–18], chemical vapor deposition [19], sol-gel [20–23], atomic layer deposition (ALD) [24], metal organic decomposition (MOD) [25], pulsed laser ablation deposition (PLAD) [26, 27], and RF sputtering [2, 21, 28].

Spin coating is a method for coating and fabricating uniform thin films by rotating substrate and solution of thin films with a certain angular velocity. Purwanto and Prajitno [29] stated that spin coating is a method to deposit a thin film by spreading the solution onto a substrate by utilizing the centripetal force, the substrate is rotated at a constant velocity and then thin film precipitate is obtained on the substrate. Spin coating process has several advantages: namely, it is a simple method that can be done at room temperature, and low cost, yet effective enough for manufacturing thin films [30]. Coating technique with spin coating method is the best technique used to produce thin films with uniform thickness ranging from 0.3 to 5.0  $\mu$ m on the substrate surfaces that are relatively small [31, 32]. The film thickness is determined by the flow rate and plating time [33]. A simple process of spin coating can be seen in **Figure 1**.



Figure 1. Simple process of spin coating [20, 21].

# 2. First generation of modified spin coater

Proper design of the modified spin coating can reduce cost in the international market because its components can be purchased in Indonesia and adequate for our laboratory-scale research. A schematic design of portable spin coating type 2004 can be seen in **Figure 2**. This device can be carried easily because it is very light and small as well as better than the traditional one in operational and production costs as well as in efficiency. For generating or rotating the disk in a spin coating, the step-down transformer of 1 A is required with the output voltages based on the digital system. The output voltages of 7, 9, and 12 V are connected to the potentiometer, diode, and capacitor which resulting in the spin coating rotation of 3480, 4380, and 5840 rpms, respectively. The accuration test of the rotational velocity can be conducted by using a stroboscope.

The work mechanism of the device is as follows: the solution of thin films is dripped on a substrate which has been placed on the spin coating device. Then, the attached solution on a substrate is rotated at the desired rpm velocity. The voltage source used in the device is 220 V AC with current of 1 A, which is obtained through the step-down transformer. The output voltage of 7, 9 or 12 V can be selected via potentiometer setting. A diode serves to rectify the AC current into DC and then the electrical charges stored in a capacitor. The rotations are about 3480, 4380, and 5840 rpms.

The modified spin coating device (**Figure 2**), which its patent has been registered in Indonesia with a number of P00201201122 in 2013, has a structural design that consists of four components.



Figure 2. Design of portable spin coating-type 2004.

#### 2.1. Current source

A current source of 220 V AC is connected to the switch and fuse safety systems.

#### 2.2. Step-down transformer and potentiometer

A step-down transformer of 1A with input voltages of 7, 9 and 12 V. These are a set based on the resistance that changes in the potentiometer.

#### 2.3. Diode and capacitor

A rectifier diode of standard currents is used to deliver a DC current of 50 V into a capacitor of 2200  $\mu$ F and 50 V. The capacitor serves to store the charges and acts as a charge source for powering the disk spinner.

#### 2.4. Disk of spin coating

The aluminum spinner device with a radius of 4 cm and thickness of 0.2 cm is used to rotate the substrate that has been dripped by solution of thin films. To generate rotation, a rotator machine is used to achieve the desired rpm velocity. **Figure 3** shows the exterior of the modified spin coating device. A disk spinner installed on a plastic container of PVC with a radius of 6 cm and thickness of 0.3 cm and a steel cantilever with a thickness of 2 cm and an area of 4 cm × 4 cm to stabilize the disk spinner. The electrical circuits are arranged in a container of 6.2 cm × 19 cm.



Figure 3. Exterior of the modified spin coating device.

# 3. Second generation of the modified spin coater

Currently, the development of the spin coating device has started in which the angular velocity of the device is increased up to 18,000 rpm. This is done because the manufacture of ferroelectric-based photonic crystals thin films requires a high-angular velocity. There are five stages in the development of a high-velocity spin coating device, namely designing, manufacturing, testing, analyzing, and developing the device. Modified Spin Coating Method for Coating and Fabricating Ferroelectric Thin Films as Sensors and Solar Cells 37 http://dx.doi.org/10.5772/66815



Figure 4. Block diagram.



Figure 5. Program flowchart.

#### 3.1. Designing the device

In this stage, designing the workflow is conducted which is described in the block diagram and flowchart. The block diagram in **Figure 4** illustrates the Arduino Uno as a data processing center that received input from infrared sensors, controlled by the buttons, and the output as a signal to adjust the angular velocity of a brushless motor as the driving component via the ESC motor driver and the LCD will show the magnitude of the angular velocity in rotation per minute (RPM). **Figure 5** shows the program flowchart for a device that further will be integrated with the Arduino Uno.

#### 3.2. Manufacturing the device

The schematic circuit diagram in **Figure 6** describes the use of Arduino Uno, buttons, infrared sensor, ESC, brushless motor, and LCD. There are eight Arduino pins, six digital, and two analog pins, which are used for the data path. Pin 4–7 on Arduino connected to four buttons. In connecting the ESC to Arduino, pins that support the pulse width modulation (PWM) are needed, so pin 3 was used on the Arduino. Infrared sensors require attach interrupt function on the program of pin 2. Then, to connect Arduino to LCD, I2C interface used to conserve the use of pins on the Arduino. From the circuit scheme, A4 pin on the Arduino is connected to the SLC in the I2C interface and A5 pin on the Arduino is connected to the ESC.

The used voltage source is an adapter of 12 V and 5 A. Most of the voltage source used to drive a brushless motor and ESC by using a voltage of 12 V and current of 5 A. Arduino gets voltage from the same source, but also need a resistor of 20  $\Omega$  on  $V_{\rm in}$  pin in order not to damage Arduino. While other components such as infrared sensors, I2C interface, and LCD can be run at a voltage of 5 V.



Figure 6. Circuit schematic.

After making a circuit scheme, the program code is conducted in accordance with the device workflow diagram that has been made at the designing stage. When the device circuit and the program code are completely made, it is necessary to merge the process of the device circuit with the program code so that the device can work in accordance with the flowchart. The incorporation using an application that matches to the Arduino device is Arduino IDE 1.6.8. Interface of Arduino IDE 1.6.8 application is shown in **Figure 7**.

#### 3.3. Testing the device

LCD displays the measurement of angular velocity and value rpm. As can be seen from **Figure 8**, the first line of LCD includes the word "Speed" that shows the measurement of the angular velocity in units of rpm. The second line of LCD is "Set' that shows the rpm setting value that users want in units of rpm as well. **Table 1** shows the measured voltages and currents between circuit blocks of the spin coater which explains that an infrared sensor will produce an output voltage of 4.92 V if detects black color and will produce an output voltage of 0.11 Vif detects another colors. Arduino circuit blocks will produce different output voltage according to the type of the use of the IC.

The next is the accuracy of angular velocity of the spin coater using tachometer type DT-2234C<sup>+</sup> as an angular velocity comparator (**Figure 9**). Angular velocities of the brushless motor are determined on the value from 1000 to 20,000 rpm.



Figure 7. Interface of Arduino IDE 1.6.8.



Figure 8. Test result.

Circuit blocks	V <sub>in</sub> (V)	$V_{out}$ (V)	I (mA)
ESC	12.01	~	5000
Infrared sensor			
Detects black color	4.92	4.92	3.3
Detects another colors	4.92	0.11	3.3
Arduino			
Set of 0 rpm	11.07	0.21	0.11
Set of 4000 rpm	11.07	0.23	0.11
Set of 5000 rpm	11.07	0.24	0.11
Set of 6000 rpm	11.07	0.25	0.11
Set of 7000 rpm	11.07	0.25	0.11
Set of 8000 rpm	11.07	0.27	0.11
Set of 9000 rpm	11.07	0.28	0.11
Set of 10,000 rpm	11.07	0.29	0.11
Set of 11,000 rpm	11.07	0.3	0.11
Set of 12,000 rpm	11.07	0.33	0.11
Set of 13,000 rpm	11.07	0.35	0.11
Set of 14,000 rpm	11.07	0.41	0.11
Set of 15,000 rpm	11.07	0.51	0.11
Set of 16,000 rpm	11.07	0.53	0.11
Set of 17,000 rpm	11.07	0.58	0.11
Set of 18,000 rpm	11.07	0.6	0.11
LCD			
Pin Vcc	4.91	-	3.3
Pin SDA	2.13	-	0.12
Pin SLC	2.58	-	0.01

Table 1. Measurements of voltage and current between circuit blocks.

From the experimental data, the brushless motor is only capable of producing the minimum angular velocity of 4000 rpm and the maximum of 18,000 rpm with no load. In addition, angular velocity on the spin coater has an average difference of 82.67 rpm obtained from the tachometer. The data can be seen in **Table 2** and **Figure 10**.

#### 3.4. Development analysis

A function menu is added in the program of development. In this function, users can choose the mode of use, i.e., manual and automatic modes. In automatic mode, users need to set

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Figure 9. Tachometer type DT-2234C<sup>+</sup>

the number of repetitions (step), the length of timer (timer), and the angular velocity (rpm set). The number of repetitions is only for a substrate. When the timer is up it is necessary to notify such as a sound, hence the buzzer circuit is added as a component to produce a sound as shown in **Figure 11(a)**. In addition, a button is also added, as shown in **Figure 11(b)**, as a supporter of the functions that will be created. The added button is useful for stop the button when the spin coater is started. The development of block diagram shown in **Figure 12** is not much different from the block diagram of before device development.

## 3.5. Development

The development of schematic circuit designing and flow of program are conducted in this stage. The developed schematic circuit shown in **Figure 13** is not much different from previous schematic, only different in add buzzer and button components. A buzzer and a button are connected directly to the Arduino via pins 9 and 8, respectively. Overall device development and its power supply can be seen in **Figure 14**.

A flow diagram in **Figure 15** shows the flow of the program code. First, the user is prompted to select the mode to be used. The available modes are manual and automatic modes are shown in **Figure 16**. If users select the manual mode, it will display a condition before the device was developed. When choosing the automatic mode, the user is prompted to set the number

Angular velocity (rpm)				
Set value	Spin coater (infrared sensor)	Tachometer		
4000	4200	4200		
5000	5280	5285		
6000	6360	6342		
7000	7380	7406		
8000	8340	8470		
9000	9540	9541		
10,000	10,500	10,504		
11,000	11,460	11,406		
12,000	12,360	12,442		
13,000	13,560	13,621		
14,000	14,220	14,428		
15,000	15,240	15,408		
16,000	16,200	16,367		
17,000	17,280	17,521		
18,000	18,060	18,135		

Table 2. The comparison results of angular velocity.



Figure 10. Angular velocity comparison.

of repetitions as shown in **Figure 17**, then adjust the angular velocity in rpm as shown in **Figure 18**, and set the length of time in seconds as shown in **Figure 19**. Once the setup process is complete, it will display a summary which is shown in **Figure 20** and then confirm to save the setting on Electrical Erasable Programmable Read-only Memory (EEPROM) on Arduino

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Figure 11. Buzzer (a) and button (b) component.



Figure 12. Development diagram.



Figure 13. Development circuit schematic.



Figure 14. Overall device development and its power supply.

semipermanently which is not lost when the power supply is not connected as in **Figure 21**. The save settings will display words of "Saving Data" as shown in **Figure 22**, after the save process is completed it will display the words of "Data saved" as shown in **Figure 23** and **a** buzzer will sound twice. If not saved then it will return to the setup process.

Once the data has been stored, the spin coater will begin the process of spin coating which displays some information such as repetition, duration, time remaining on the first line of the LCD, and the rpm setting value and measurement results of angular velocity on the second line of the LCD as in **Figure 24**. At each repetition process, the buzzer will sound once. If the spin coating process has been completed, it will display word of "Done" as shown in **Figure 25** and **a** buzzer will sound three times, after that confirmation of the spin coating reprocess will be also displayed as in **Figure 26**.

The aim of this stage is to improve the device accuracy by conducting device reconfiguration. The device reconfiguration will change the measurement of angular velocity, then retest must be done for the accuracy of device. The testing method as well as the testing method before development is compared to tachometer-type  $DT-2234C^+$ .

In the measurement of angular velocity of the brushless motor, the rpm setting value on a spin coater is determined which starts from 4000 to 18,000 rpm. The brushless motor only produces the minimum angular velocity of 4000 rpm and the maximum angular velocity of 16,637 rpm under no-load conditions. From data, the created spin coater has an accuracy rate of 98.9%. The results can be seen in **Figure 27** and **Table 3**.

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Figure 15. Program flowchart of a spin coater in the automatic mode.



Figure 16. Display of mode select.



Figure 17. Display of repetition setting.



Figure 18. Display of velocity setting.



Figure 19. Display of time setting.



Figure 20. Display of setting summary.



Figure 21. Display of set saving.

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Figure 22. Display of data saving.



Figure 23. Display of saved data.



Figure 24. Display of the spin coating process.



Figure 25. Display of the finished process.



Figure 26. Display of the spin coating reprocess.



Figure 27. Comparison results of angular velocity after development.

Testing the angular velocity (RPM)			Accuracy level of spin coater (%)	
Set value	Spin coater	Tachometer		
4000	3960	3916	99	
5000	4980	4977	99.6	
6000	5880	5887	98	
7000	6960	6938	99.42	
8000	7980	7998	99.75	
9000	8940	9002	99.33	
10,000	9960	9966	99.6	
11,000	10,980	10,932	99.82	
12,000	11,940	11,960	99.5	
13,000	12,960	12,996	99.69	
14,000	13,980	13,974	99.86	
15,000	15,000	15,027	100	
16,000	16,020	16,046	99.86	
17,000	16,560	16,587	97.41	
18,000	16,680	16,637	92.67	
Mean			98.9	

Table 3. Comparison data of angular velocity after development.

# 4. Results and applications

This method has been developed in our laboratory to fabricate thin films, especially ferroelectric thin films such as barium strontium titanate (BST), lithium tantalate (LiTaO<sub>3</sub>), lithium niobate (LiNbO<sub>3</sub>), and copper oxide (CuO) thin films. Specifically for BST ferroelectric thin films, its patent has been registered in Indonesia with a number of P00201201119 in 2013.

BST thin films of the modified spin coating method resulting in a dielectric constant of 2–18 and conductivity values of  $1.6 \times 10^{-6}$  to  $2.4 \times 10^{-9}$  S/cm at the voltages of 1–4 V [34]. In addition, the particle distribution size of BST 0.45 is 134.93 nm which is smaller than BST 0.25 which gives 186.26 nm, BST 0.35 gives a value of 467.86 nm, and BST 0.55 is 407.49 nm [34].

BST thin films have been developed in a number of applications such as temperature and light sensors that are applied into the automatic drying system [35], light sensors into the luxmeter system [36] and sensors in the blood sugar level system, its patent has been registered in Indonesia with a number of P00201508327 in 2015.

In the automatic drying system [35], light sensors have 0.176 mV/lux, which is the best sensitivity. While the best temperature sensor has a value range of 30–109°C, a sensitivity of 0.862 mV/°C, a film resolution of 1°C, an accuracy level of 92.2%, and small hysteresis [35]. These sensors, which are then integrated into microcontroller, have been successfully conducted on an ATMega8535 microcontroller based on our automatized drying system model.

In the luxmeter system [36],  $Ba_{0.25}Sr_{0.75}TiO_3$  (BST) thin films have been deposited on a Si (100) p-type substrate by a chemical solution deposition (CSD) method followed by the spin coating technique (at 3000 rpm rotational speed for 30 seconds). This BST has an electrical conductivity of  $2.79 \times 10^{-7}$  to  $5.3 \times 10^{-7}$  S/cm, which are in the range of semiconductor materials. The *I-V* measurement on the films which was carried out under dark and bright conditions results in convincing conclusion that the films are photodiodes. The maximum optical absorbance found for green light with a wavelength of around 550 nm.

The blood sugar level system also uses the modified spin coating method. The test results showed that the light intensity that was received by photodiode sensor, represented by the output voltage, will change in line with changes in the value of blood sugar levels, follows the equation  $y = 0.0014x^2 - 0.6652x + 139.34$ . The coefficient of  $R^2 = 0.9544$  indicates that x has a major effect on y, so that it can be concluded that the photodiode sensor can work well as a sensor of blood sugar level instrument. Accuracy and precision of the instrument are 98.92 and 97.41%, respectively.

BST thin films as solar cells enhanced by photonic crystals are currently being developed [37]. This enhancement needs higher angular velocity (>6000 rpm) than previous works in BST (3000 rpm). The second generation of modified spin coater is used for coating the thin films to fulfill the requirement. The optical characterization of BST ( $Ba_xSr_{1-x}TiO_3$ ) using a photonic crystal resulted in the average absorption percentages for mole fraction x = 0.25, 0.35, 0.45,

and 0.55 were 92.04, 83.55, 91.16, and 80.12%, respectively [37]. In addition, the BST thin film with the embedded photonic crystal exhibited a relatively significant enhancement on photon absorption, with increasing values of 3.96, 7.07, 3.04, and 13.33%, respectively.

Furthermore, BST thin films are worked both as sensors and solar cells can be applied to the more sophisticated fields such as temperature and light sensors in the satellite technology [38, 39], photodiode in satellite technology [40], as well as solar cells for substituting conventional battery in satellite technology [41].

LiTaO<sub>3</sub> thin films have also been developed by using the modified spin coating method as infrared sensors that are expected to be developed as an automatic switch in satellite technology [42]. These thin films have electrical conductivities of  $10^{-6}$ - $10^{-5}$  S/cm and the diffusion coefficient values of 57–391 nm<sup>2</sup>/s [43] as well as the energy gaps of 3.41–4.56 eV [42] while the LiTaO<sub>3</sub> thin films have energy gaps of 2.43–2.80 eV [44]. The LiNbO<sub>3</sub> thin films that were enhanced by a lanthanum dopant also use a velocity of 3000 rpm and have the energy gaps of 2.43–2.80 eV [45].

In addition to BST,  $LiTaO_3$ , and  $LiNbO_3$ , we are also develop other thin films, i.e., CuO thin films. This film is also developed as solar cells. CuO thin films were enhanced by photonic crystals that have absorbance in the visible region and energy gaps of 1.89–2.05 eV [46].

## 5. Conclusion

The modified spin coaters both first and second generation have given very good results on ferroelectric films, which are BST,  $LiTaO_{3'}$   $LiNbO_{3'}$  and CuO, as sensors and solar cells. In BST, the modified spin coater enhances the photon absorption percentages by using photonic crystals which need higher angular velocity (6000 rpm). Another ferroelectric thin film that use 3000 rpm also have given good results in energy gap, electrical conductivity, etc. From these data, they were succeed to be applied in an instrument or a device such as a blood sugar level, automatic drying, and luxmeter systems. In addition, these thin films also have potential to be applied in more sophisticated fields such as photodiode in satellite technology, temperature, and light sensors in the satellite technology, as well as solar cells for substituting conventional battery in satellite technology.

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# References

- Hamdani A, Komaro M, Irzaman. Development of Solar Cell based on Ferroelectric LiTaO<sub>3</sub> using Spin Coating Method for Green Electric Power, Scientific Report of Indonesia Institute of Science 2009 pp. 7. (in Indonesia)
- [2] Lee JS, Park JS, Kim JS, Lee JH, Lee YH, Hahn SR. Preparation of BST Thin Films with High Pyroelectric Coefficients an Ambient Temperatures. Jpn. J. Appl. 1999. **38**(5B), L574.
- [3] Irzaman, Darmasetiawan H, Hardhienata H, Erviansyah R, Akhiruddin, Hikam M, Arifin P. Electrical Properties of Photodiode BST Thin Film Doped with Ferrium Oxide using Chemical Deposition Solution Method. J. At. Indonesia, Batan. 2010. 6(2), 57–62. (in Indonesia).
- [4] Irzaman, Syafutra H, Darmasetiawan H, Hardhienata H, Erviansyah R, Huriawati F, Akhiruddin, Hikam M, Arifin P. Electrical Properties of Photodiode Ba<sub>0.25</sub>Sr<sub>0.75</sub>TiO<sub>3</sub> (BST) Thin Film Doped with Ferric Oxide on p-type Si (100) Substrate using Chemical Solution Deposition Method. At. Indonesia. 2011. **37**(3), 133–138. (in Indonesia).
- [5] I. Novianty, S. Yani, R. Chahyani, Z. Athiyah, Casnan, Fendi, S. Serah, J. Hartono, N. Rofiah, H. Syahfutra, Akhiruddin and Irzaman. Electrical Properties Fe2o<sub>3</sub> Doped Based Ba<sub>0.25</sub>Sr<sub>0.75</sub>TiO<sub>3</sub>. Thin Film As Light Sensor. Jurnal SainsMateri Indonesia. 2011 Vol. Materials for Sensor Special Edition, pp. 9–12.
- [6] Irzaman, Syafutra H, Rancasa E, Nuayi AW, Rahman TGN, Nuzulia NA, Supu I, Sugianto, Tumimomor F, Surianty, Muzikarno O, Masrur. The Effect of Ba/Sr ratio on Electrical and Optical Properties of  $Ba_xSr_{(1-x)}TiO_3$  (x = 0.25; 0.35; 0.45; 0.55) Thin Film Semiconductor. Ferroelectrics. 2013. **445**(1), 4–17.
- [7] Baumert BA, Chang LH, Matsuda AT, Tracy CJ. A Study of BST Thin Films for Use in bypass Capacitors. J. Mater. 1998. 13(1), 197.
- [8] Itskovsky MA. Kinetics of Ferroelectric Phase Transition: Nonlinear Pyroelectric Effect and Ferroelectric Solar Cell. Jpn. J. Appl. Phys. 1999. 38(8), 4812.

- [9] Darmasetiawan H, Irzaman, Indro MN, Sukaryo SG, Hikam M, Bo NP. Optical Properties of Crystalline Ta<sub>2</sub>O<sub>5</sub> Thin Films. Phys. Stat. Sol. (a), Germany. 2002. **193**, 53–60.
- Irzaman, Darvina Y, Fuad A, Arifin P, Budiman M, Barmawi M. Physical and Pyroelectric Properties of Tantalum Oxide Doped Lead Zirconium Titanate [Pb<sub>0.9950</sub>(Zr<sub>0.525</sub>Ti<sub>0.465</sub>Ta<sub>0.010</sub>)
   O<sub>3</sub>] Thin Films and Its Application for IR Sensor. Phys. Stat. Sol. (a), Germany. 2003. 199, 416–424.
- [11] Irzaman, Darmasetiawan H, Hikam M, Arifin P, Budiman M, Barmawi M. Pyroelectric Properties of Lead Zirconium Titanate (PbZr<sub>0.525</sub>Ti<sub>0.475</sub>O<sub>3</sub>) Metal-Ferroelectric-Metal Capacitor and Its Application for IR Sensor. In: International Conference on Materials for Advances Technology (ICMAT), Materials Research Society, Singapore. 2003. pp. 7–12.
- [12] Dahrul M, Syafutra H, Arif A, Irzaman, Indro, Siswadi MN. Synthesis and Characterizations Photodiode Thin Film Barium Strontium Titanate (BST) Doped Niobium and Iron as Light Sensor. In: The 4th Asian Physics Symposium, American Institute of Physics (AIP) Conference. 2010. 1325, pp. 43–46.
- [13] Hikam M, Sarwono E, Irzaman. Calculation on Spontaneous Polarization and Electric Quadrupole Moment of PIZT (PbInxZryTi1-x-yO3-x/2) Material. Makara, Sains. 2004. 8, 108–115. (in Indonesia)
- [14] Irzaman, Maddu A, Syafutra H, Ismangil A. Test on Electrical Conductivity and Dielectric of Lithium Tantalite (LiTaO<sub>3</sub>) Doped by (Nb<sub>2</sub>O<sub>5</sub>) using Chemical Deposition Method. In: Proceedings of National Workshop on Physics. 2010. pp. 175–183. (in Indonesia)
- [15] Umiati NAK, Irzaman, Budiman M, Barmawi M. Annelaing Effect on the Growth of PbZr<sub>0.625</sub>Ti<sub>0.375</sub>O<sub>3</sub> (PZT). Thin Film. Kontribusi Fisika Indonesia. 2001. **12**, 94–98 (in Indonesia).
- [16] Choi ES, Lee JC, Hwang JS, Yoon SG. Electrical Characteristics of The Contour Vibration Mode Piezoelectric Transformer with Ring/Dot Electrode Area Ratio. Jpn. J. Appl. Phys. 1999. 38(9B), 5317.
- [17] Momose S, Nakamura T, Tachibana K. Effects of Gas Phase Thermal Decompositions of Chemical Vapor Deposition Source Molecules on The Deposition of BST Films. Jpn. J. Appl. Phys. 2000. **39**, (9B), 5384.
- [18] Gao Y, He S, Alluri P, Engelhard M, Lea AS, Finder J, Melnick B, Hance RL. Effect of Precusors and Substrate Materials on Microstructure, Dielectric Properties and Step Coveage of (Ba, Sr)TiO<sub>3</sub> Films Grown by Metalorgic Chemical Vapor Deposition. J. Appl. Phys. 2000. 87, 124–132.
- [19] Auciello O, Scott JF, Ramesh R. The Physics of Ferroelectric Memories. Am. Inst. Phys. 1998. 51, 22–27.
- [20] Verma K, Sharma S, Sharma DK, Kumar R, Rai R. Sol-gel Processing and Characterization of Nanometersized (Ba,Sr)TiO<sub>3</sub> Ceramics. Adv. Mater. Lett. 2012. 3(1), 44–49.

- [21] Giridharan NV, Jayavel R, Ramasamy P. Structural, Morphological and Electrical Studies on Barium Strontium Titanate Thin Films Prepared by Sol-Gel Technique. Chennai: Crystal Growth Centre, Anna University; 2001.
- [22] Chen X, Cai W, Fu C, Chen H, Zhang Q. Synthesis and Morphology of Ba(Zr<sub>0.20</sub>Ti<sub>0.80</sub>)O<sub>3</sub> Powder Obtained by Sol-Gel Method. J. Sol-Gel Sci. Technol. 2011. 57, 149–156.
- [23] Wang F, Uusimaki A, Leppavuori S, Karmanenko SF, Dedyk AI, Sakharov VI, Serenkov IT. BST Ferroelectric Film Prepared with Sol-Gel Process and Its Dielectric Performance in Planar Capacitor Structure. J. Mater. Res. 1998. 13(5), 1243.
- [24] Tyunina M. Dielectric Properties of Atomic Layer Deposited Thin Film Barium Strontium Titanate. Integr. Ferroelectr. 2008. 102, 29–36.
- [25] Suherman PM. Comparison of Structural Microstructural and Electrical Analyses of Barium Strontium Titanate Thin Films. J Appl. Phys. 2009. 105, 1–6.
- [26] Kim S, Kang TS, Je JH. Structural Characterization of Laser Alblation Epitaxial BST Thin Films on MgO (001) by Synchrotron X-Ray Scattering. J. Mater. 1999. 14(7), 2905.
- [27] Zhu XH, Zheng DN, Peng JL, Chen YF. Enhanced Dielectic Properties of Mn Doped Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> Thin Films Fabricated by Pulsed Laser Deposition. Mater. Lett. 2005. 60, 1224–1228.
- [28] Izuha M, Ade K, Koike M, Takeno S, Fukushima N. Electrical Properties and Microstructure of Pt/BST/SrRuO<sub>3</sub> Capacitors. Appl. Phys. Lett. 1997. 70(11), 1405.
- [29] Purwanto R, Prajitno G. Speed and Rotation Time Variation in TiO<sub>2</sub> Coating Process for the Development of DSSC made from Garcinia Mangostana Extract as Dye Sensitizer. Jurnal Sains dan Seni POMITS. 2013. 2(1), 2337–3520 (in Indonesia).
- [30] Hikam M, Irzaman, Darmasetiawan H, Yogaraksa T. Study on Crystaline of PbZrxTi1xO3 made by Spin Coating method. J. Sains Mater. Indonesia. 2002. 4(1), 16–19. (in Indonesia).
- [31] Rahmawati E, Robiandi F, Didik LA, Rahayu S, Santjojo DJDH, Sakti SP, Masruroh. Effect of Xylene and Tetrahydrofuran on the Thickness of Polystyrene using Spin Coating Method. Natural. 2014. 2(4), 1–6. (in Indonesia).
- [32] Herrera MA, Mathew AP, Oksman K. Gas Permeability and Selectivity of Cellulose Nanocrystals Films (layers) Deposited by Spin Coating. Carbohydrate Polym. 2014. 112, 494–501.
- [33] Manikandan N, Shanti B, Muruganand S. Construction of Spin Coating Machine Controlled by Arm Processor for Physical Studies of PVA. Int. J. Electron. Electr. Eng. 2015. 3(4), 1–5.
- [34] Irzaman, Syafutra H, Arif A, Alatas H, Hilaluddin MN, Kurniawan A, Iskandar J, Dahrul M, Ismangil A, Yosman D, Aminullah, Prasetyo LB, Yusuf A, Kadri TM. Formation of Solar. Cells Based On Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> (BST) Ferroelectric Thick Film. AIP Proceeding, USA, 1586. 2014. 24–34.

- [35] Irzaman, Siskandar R, Aminullah, Irmansyah, Alatas H. Characterization of Ba<sub>0.55</sub>Sr<sub>0.45</sub>TiO<sub>3</sub> Films As Light and Temperature Sensors And Its Implementation on Automatic Drying System Model. Integr. Ferroelectr. 2016. **168** (1), 130–150.
- [36] Syafutra H, Irzaman, Indro MN, Subrata IDM. Development of Luxmeter Based on Ba<sub>0.25</sub>Sr<sub>0.75</sub>TiO<sub>3</sub> Ferroelectric Material. AIP Conf. Proc. 2010. **1325**, 75.
- [37] Abd. Wahidin Nuayi, H. Alatas, Irzaman, and M. Rahmat. Enhancement of Photon Absorption on Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> Thin-Film Semiconductor Using Photonic Crystal. Hindawi. 2014. 2014, 1–8.
- [38] Kurniawan A, Yosman, Arif A, Juansah J, Irzaman. Development and Application of Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub> (BST) Thin Film as Temperature Sensor for Satellite Technology. Procedia Environ. Sci. 2015. 24, 335–339.
- [39] Iskandar J, Syafutra H, Juansah J, Irzaman. Characterizations of Electrical and Optical Properties on Ferroelectric Photodiode of Barium Strontium Titanate (Ba<sub>0.5</sub>Sr<sub>0.5</sub>TiO<sub>3</sub>) Films Based on the Annealing Time Differences and Its Development as Light Sensor on Satellite Technology. Procedia Environ. Sci. 2015. 24, 324–328.
- [40] Setiawan A, Aminullah, Juansah J, Irzaman. Optical and Electrical Characterizations of Niobium-doped Ba<sub>0.25</sub>Sr<sub>0.75</sub>TiO<sub>3</sub> (BSNT) on p-type Silicon and Corning Glass Substrates and Its Implementation as Photodiode on Satellite of LAPAN-IPB. Procedia Environ. Sci. 2016. **33**, 620–625.
- [41] Irzaman, Putra IR, Aminullah, Syafutra H, Alatas H. Development of Ferroelectric Solar Cells of Barium Strontium Titanate (Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub>) for Subtituting Conventional Battery in LAPAN-IPB Satellite (LISAT). Procedia Environ. Sci. 2016. **33**, 607–614.
- [42] Ismangil A, Jenie RP, Irmansyah, Irzaman. Development of Lithium Tantallite (LiTaO<sub>3</sub>) for Automatic Switch on LAPAN-IPB Satellite Infra-red Sensor. Procedia Environ. Sci. 2015. 24, 329–334.
- [43] Ismangil A, Irmansyah, Irzaman. The Diffusion Coefficient of Lithium Tantalite (LiTaO<sub>3</sub>) with Temperature Variations on LAPAN-IPB Satellite Infra-red Sensor. Procedia Environ. Sci. 2016. **33**, 668–673.
- [44] Irzaman, Pebriyanto Y, Rosidah E, Apipah, Noor I, Alkadri A. Characterization of Optical and Structural of Lanthanum Doped LiTaO<sub>3</sub> Thin Films. Integrated Ferroelectr. 2015. 167(1), 137–145.
- [45] Irzaman, Sitompul H, Masitoh, Misbakhusshudur M, Mursyidah. Optical and Structural Properties of Lanthanum Doped Lithium Niobate Thin Films. Ferroelectrics. 2016. 502, 9–18.
- [46] Dahrul M, Alatas H, Irzaman. Preparation and Optical Properties Study of CuO Thin Film as Applied Solar Cell on LAPAN-IPB Satellite. Procedia Environ. Sci. 2016. 33, 661–667.

# Emission, Defects, and Structure of ZnO Nanocrystal Films Obtained by Electrochemical Method

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Additional information is available at the end of the chapter

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#### Abstract

ZnO nanocrystal (NC) films, prepared by electrochemical etching with varying the technological routines, have been studied by means of photoluminescence (PL), scanning electronic microscopy (SEM), energy dispersion spectroscopy (EDS), Raman scattering, and X ray diffraction (XRD) techniques. Raman and XRD studies have confirmed that annealing stimulates the ZnO oxidation and crystallization with the formation of wurtzite ZnO NCs. The ZnO NC size decreases from 250-300 nm down to 40-60 nm with increasing the etching time. Two PL bands connected with the near-band edge (NBE) and defect-related emissions have been detected. Their intensity stimulation with NC size decreasing has been detected. The NBE emission enhancement is attributed to the week quantum confinement and exciton-light coupling with polariton formation in small ZnO NCs. The luminescence, morphology, and crystal structure of ZnO:Cu NCs versus Cu concentration have been investigated as well. The types of Cu-related complexes are discussed using the correlation between the PL spectrum transformations and XRD parameters. It is shown that the plasmon generation in Cu nanoparticles leads to the surface enhanced Raman scattering (SERS) effect and to PL intensity increasing the defect-related PL bands. The comparison of ZnO and ZnO:Cu NC emissions has been done and discussed.

Keywords: ZnO NCs, ZnO:Cu NCs, photoluminescence, XRD, weak quantum confinement

# 1. Introduction

Porous semiconductor materials stimulate the scientific interest owing to the possibility for designing the properties not known in the bulk crystals [1]. The enormous attention in the last decades has been devoted to porous silicon (PSi) that was investigated for variety



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. of applications in electronics, as well as for chemical, biological, and medical sensing [1]. Recently, a great interest has been shown to the ZnO nanocrystals (NCs) obtained using electrochemical technology, earlier elaborated for PSi [1–3].

The wide band gap semiconductor, such as zinc oxide, which has a direct energy band gap (3.37 eV) and a great exciton binding energy (60 meV) at 300 K, promises a lot of applications in optoelectronic devices [4–8]. Actually ZnO nanowalls and wires can be applied in white light-emitting structures [5] and UV lasers [6]. ZnO nanoneedles demonstrate the field emission characteristics [7]. Field-effect transistors on the base of ZnO nanorods were presented in Ref. [8]. ZnO nanostructures have provoked great attention recently owing to their perspectives for low voltage and short-wavelength (368 nm) electro-optical devices, as well as for protection films with high UV transparency, in different gas sensors and structures for spintronic devices [9], for a room temperature ferromagnetism, a huge magneto-optic effect, and chemical sensing [5, 9, 10].

In addition, the ZnO NC structures are interesting for phosphor applications owing to the excellent emission in orange, yellow, green, and blue ranges of PL spectra. The high concentration of radiative defects obtained in ZnO NC films permits to expect a wide spectrum of luminescence bands that is important for "white" light emitting structures [11–14]. However, the relations between the defects and structural properties of ZnO NCs (nanosheets, nanorods, etc.) are not clear yet.

For growing ZnO NCs, the following methods were used: thermal evaporation technique [15], sol-gel deposition [16], metal organic chemical vapor deposition (MOCVD) [17], molecular beam epitaxy (MBE) [18], pulse laser preparation (PLD) [19], or spray pyrolysis [20]. All mentioned methods require very expensive equipment and do not produce ZnO NCs with bright PL bands that were demonstrated recently for the electrochemical technology [21, 22]. The anodization method permits to control the ZnO NC size by varying an electrolyte content, etching times, and voltages. Additionally, this method permits simple doping of ZnO NC films by different elements.

In this chapter, ZnO and ZnO:Cu NCs were created by the electrochemical method at varying etching times or etching voltages with film annealing at high temperature (400°C) in ambient air. Photoluminescence, scanning electronic microscopy (SEM), energy dispersion spectroscopy (EDS), Raman scattering, and X-ray diffraction (XRD) have been applied for the study of ZnO and ZnO:Cu NC films.

# 2. ZnO NC preparation and investigations

The electrochemical anodization of Zn foils was performed in an electrolyte using two Zn electrode systems with the distance between the electrodes being 10 mm. The electrolyte was a 1:10 volume mixture of HF acid (Aldrich) and deionized water. Ultrasonic cleaning of Zn foil pieces (Aldrich 99.99%) of 6 mm radius was performed in acetone and ethanol for 15 min before etching. To investigate the impact of etching times on ZnO NC parameters, the applied

voltage was 5 V and the varied times were 1, 3, 6, and 10 min. Then ZnO films were cleaned in deionized water and annealed at 400°C for 2 h in ambient air.

To investigate the influence of voltage, the etching time was kept at 6 min and the applied voltages varied as 1, 5, 10, 15, and 20 V. Obtained ZnO films were washed in deionized water and annealed at 400°C for 2 h in ambient air.

To investigate the effect of Cu doping on the structure and optical properties of ZnO:Cu NCs, and to compare it with those in ZnO NCs, the electrochemical anodization was performed with: (i) two Zn electrodes at the creation of ZnO NCs or (ii) cathode Zn and anode Cu electrodes at the growth of ZnO:Cu NCs. Zn (Aldrich 99.99%) and Cu (Aldrich 99.99%) foils were used. At etching, the applied voltage was 5 V and the times used were 1, 3, or 6 min. Then the films were annealed at 400°C for 2 h in ambient air.

SEM and EDS studies were done in JSM7800F-JEOL with an additional detector Apollo X 10 mark EDAX. The XRD equipment XPERT MRD, with a pixel detector, three-axis goniometry, a parallel collimator, and a resolution of 0.0001°, was applied to the crystal structure investigation. The Cu source with  $K_{\alpha 1}$  line  $\lambda$  = 1.5406 Å was used. XRD was performed for the angle range 20°–80° with a 0.05° step and a step duration of 10 s.

PL spectra, excited by a He-Cd laser with a wavelength of 325 nm and a beam power of 80 mW, were measured at 10–300 K using a PL setup based on a spectrometer SPEX500 described in references [23, 24]. Raman scattering spectra were studied in Jobin-Yvon LabRAM HR 800UV micro-Raman system using an excitation by a solid-state light-emitting diode with a light wavelength of 785 nm [25, 26].

# 3. The etching time impact on parameters of ZnO NC films

# 3.1. SEM and XRD studies

**Figure 1** presents the SEM images of ZnO NC films grown at different etching times after thermal annealing. It is clear that the size of ZnO NCs decreases versus etching times (**Figure 1d**): from 200–360 nm (for 1 min) down to 30–60 nm (for 10 min).

XRD results are summarized in **Figure 2**. As-grown ZnO films are characterized by the amorphous phase (**Figure 2a**) and the Zn substrate XRD peaks at the  $2\theta$  angles of 38.993, 43.233, and 70.058° have been seen (**Figure 2a**). These peaks owe to the diffraction from the (100), (101), and (103) crystal planes in the wurtzite Zn crystal lattice [27].

Thermal annealing at 400°C stimulates the ZnO oxidation and crystallization. A set of XRD peaks appears at the  $2\theta$  angles equaling to 31.770, 34.422, 36.253, 47.540, 56.604, and 62.865° after ZnO film annealing (**Figure 2b** and **c**). These XRD peaks correspond to the diffraction from the (100), (002), (101), (102), (110), and (103) crystal planes in the wurtzite ZnO crystal structure [27]. At first (1–6 min etching), the volume of crystalline ZnO phase enlarges that manifests itself in increasing the XRD peak intensities (**Figure 2d**). Then at higher etching time



**Figure 1.** SEM images of ZnO NCs after thermal annealing (a, b, c), obtained at the voltage of 5V and times of 1 min (a), 6 min (b), and 10 min (c). Widths and lengths of annealed ZnO NCs (d) for the etching durations of 1 min (A), 6 min (B), and 10 min (C) [22].

(10 min), ZnO NC films are characterized by smaller XRD peak intensities (**Figure 2d**) owing to, apparently, the material dissolution at the high anodization duration and increasing the volume of pores in the films.

#### 3.2. Raman scattering study

Raman scattering spectra of ZnO NC films are presented in **Figure 3**. Raman spectra of asgrown ZnO films do not demonstrate any Raman peaks (**Figure 3a**). The small Raman band

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Figure 2. XRD results for as-grown (a) and annealed (b, c) ZnO NCs obtained at etching durations of 1 (b) and 10 (a, c) min. Dependences (d) of (100) XRD peak intensity (1) and integrated PL intensity (2) for the PL band peaked at 3.1 eV in annealed films versus etching times [22].



Figure 3. Raman scattering spectra of as-grown (a) and annealed (b) ZnO films obtained at etching times: 1 min (curve 1), 6 min (curve 2), and 10 min (a) and (b), curve 3.

in the range of 400–500 cm<sup>-1</sup> is related to Raman scattering in the ZnO amorphous phase. The Raman study confirms that as-grown ZnO films are characterized by an amorphous phase mainly and it is consistent with the XRD data.

Annealing at 400°C stimulates the ZnO crystallization and four peaks at 327, 379, 434, and 549–556 cm<sup>-1</sup> appear in Raman spectra (**Table 1**). The Raman peak intensity rises versus etching time owing to the volume enlargement of the crystalline ZnO phase (**Figure 3b**).

The group theory predicts for the wurzite ZnO crystal structure the Raman active phonons in Brillouin zone center as:  $A_1$  and  $E_1$  symmetry polar phonons with two frequencies for the transverse (TO) and longitudinal (LO) optic phonons, and  $E_2$  symmetry nonpolar phonon mode with two frequencies  $E_2$  (low) and  $E_2$  (high).  $E_2$  (low) and  $E_2$  (high) modes are attributed to oxygen and zinc sublattices, respectively, in ZnO [28, 29].

Raman peaks at 327 and 437 cm<sup>-1</sup> are attributed, as a rule, to second-order Raman peaks arising from the zone boundary phonons  $3E_{2H}$ - $E_{2L}$  and  $E_{2H}$  modes in ZnO NCs [30]. Raman peaks at 379 and 434 cm<sup>-1</sup> can be attributed to the  $A_1$  (TO) and  $E_2$  (high) phonon modes in ZnO NCs (**Table 1**). The nature of the Raman peak at 549–556 cm<sup>-1</sup> is not clear. Its variable position in different samples (**Figure 3**, curves 2 and 3) and the location between TO and LO optic phonons permit to assign this Raman peak to the surface phonon (SP). The SP frequency ( $\omega_{sp}$ ) in ZnO NCs can be calculated using the formula [30, 31]:

$$\omega_{SP} = \omega_{TO} \sqrt{\frac{\varepsilon_0 l + \varepsilon_M (l+1)}{\varepsilon_{\infty} l + \varepsilon_M (l+1)}},$$
(1)

where  $\omega_{TO}$  is a frequency of TO phonon,  $\varepsilon_0$  and  $\varepsilon_\infty$  are the static and high-frequency dielectric constants in a bulk ZnO crystal,  $\varepsilon_M$  is a static dielectric constant of surrounding medium (air). Assuming  $\varepsilon_M = 1$  for air in pores of ZnO NCs and using  $\varepsilon_0$  and  $\varepsilon_\infty$  equal to 8.36 [32] and 3.77 [32], respectively, the SP frequency of 550 cm<sup>-1</sup> for the lowest (l = 1) mode has been estimated that is in a good agreement with detected values of 549–556 cm<sup>-1</sup> (**Table 1**).

#### 3.3. ZnO NC emission study

PL spectra of ZnO films obtained at different etching times in as-grown states are shown in **Figure 4**. PL spectra are presented as the superposition of three PL bands centered at 1.90–2.03, 2.49–2.51, and 2.80–2.85 eV (**Figure 4**, curves a, b, and c), which are attributed to the defect-related emission in an amorphous ZnO films. The PL intensity of the above-mentioned peaks increases with increasing anodization duration up to 6 min due to increasing the volume of ZnO amorphous phase. In samples prepared at 10 min (**Figure 4**, curve 3), the PL

Samples	E <sub>2</sub> (low)	3E <sub>2H</sub> -E <sub>2L</sub>	A <sub>1</sub> (TO)	E <sub>1</sub> (TO)	E <sub>2</sub> (high)	SP	A <sub>1</sub> (LO)	E <sub>1</sub> (LO)
	cm <sup>-1</sup>	cm <sup>-1</sup>	<b>cm</b> <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	cm <sup>-1</sup>	<b>cm</b> <sup>-1</sup>
Bulk ZnO [29] and ZnO NCs	102	327	379	410	434–439	549–556	574	591

Table 1. Raman peaks in ZnO crystals.
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**Figure 4.** PL spectra of as-grown ZnO NCs obtained at durations of 1 (1), 6 (2), and 10 (3) min. Dashed curves represent the deconvolution result on elementary PL bands (*a*, *b*, *c*).

intensity of the mentioned PL peaks decreases owing to decreasing the ZnO NC volume that is consistent with the XRD data (**Figure 2**).

Annealing at 400°C stimulates the ZnO crystallization, which is accompanied by the PL spectrum transformation (**Figure 5**). PL spectra of ZnO NCs are complex as well (**Figure 5**, curves 1, 2, and 3) and can be represented by a set of elementary PL bands (**Figure 5**, curves a, b, and c) with the peaks at 2.06–2.10, 2.52, and 3.10 eV. The defect-related PL band with the peak at 2.80 eV disappeared completely at the ZnO oxidation and crystallization, and the new PL band at 3.10 eV appeared in PL spectra of ZnO NCs. PL intensities of the mentioned PL bands (**Figure 5**) vary as XRD peak intensity changes, which is related to the changing crystalline ZnO volume versus anodization times (**Figure 2**d).



Figure 5. PL spectra of annealed ZnO NCs obtained at durations of 1 (1), 6 (2), and 10 (3) min. Dashed curves represent the deconvolution on elementary PL bands (a, b, c) [22].

The bulk ZnO crystals are characterized by the variety of luminescence bands in UV and visible spectral ranges [33, 34]. The origin of these emissions has not been conclusively established, and a number of hypotheses have been proposed for each emission band. NBE band at 3.1 eV is attributed to the optical transition between the shallow donor and valence band, to the phonon replicas of bound exciton, or free exciton (FE) emissions [34, 35]. The high intensity of NBE emission at 300 K and a small band half width in ZnO NCs permits to attribute the 3.1 eV PL band to a LO phonon replica of free exciton.

The blue PL band with the peak at 2.80 eV, which disappeared completely after the oxidation at annealing in ambient air, can be assigned to emission via the native defects in ZnO films [36, 37]. The defect-related green PL band in the range 2.40–2.50 eV is assigned to oxygen vacancies [36], Cu impurities [38], or surface defects [39] in ZnO. The PL intensity of 2.49–2.52 eV PL band does not change in the processes of oxidation and crystallization (**Figure 5**) that permits to assign this PL to some surface defects.

The PL band centered at 2.00–2.10 eV was assigned earlier to interstitial oxygen atoms (2.02 eV) [40] or hydroxyl groups (2.10 eV) [41, 42]. The PL intensity of 2.06–2.10 eV PL band increases at ZnO oxidation (**Figure 5**) and the assumption that corresponding defects are related to oxygen interstitials looks very reliable.

It is essential that ZnO NCs obtained by other methods, such as Zn powder thermal evaporation [43], sol-gel ZnO films [44], or MOCVD growth ZnO films [45], do not permit to obtain great variety of PL bands that have been demonstrated in the studied ZnO NCs.

# 4. Anodization voltage impact on the structure and emission of ZnO NC films

# 4.1. XRD and SEM study

The XRD study has shown that as-grown ZnO films are characterized by Zn substrate-related XRD peaks with highest XRD peak intensities at the angles  $2\theta$  equal to 38.993, 43.233, and 70.058° (**Figure 6a**). These peaks correspond to the diffraction from the (100), (101), and (103) crystal planes, respectively, in the hexagonal Zn crystal lattice with the lattice parameters of *a* = 2.6650 Å and *c* = 4.9470 Å [27]. Annealing at 400°C stimulates the crystallization of ZnO NCs and a set of XRD peaks appear at the angles  $2\theta$  equal to 31.770, 34.422, 36.253, 47.540, 56.604, and 62.865° (**Figure 6b**). These XRD peaks correspond to the X-ray diffraction from the (100), (002), (101), (102), (110), and (103) crystal planes in the wurtzite ZnO crystal structure [27].

The volume of crystalline ZnO phase enlarges versus anodization voltages up to 15 V that manifests itself by increasing the XRD peak intensities. However, ZnO NCs obtained at the voltage of 20 V are characterized by smaller intensity of XRD peaks that, apparently, connects with the ZnO dissolution in an electrolyte at higher anodization voltages and increases the volume of the pores.

SEM images after thermal annealing of ZnO NCs, obtained at voltages of 1, 5, and 15 V, are presented in **Figure 7(a)–(c)**. The dimension of ZnO NCs does not change essentially versus

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Figure 6. XRD results for as-grown film (a) and annealed (b) ZnO NCs prepared at etching voltage 15 V and etching time 6 min [24].

voltages at the anodization (**Figure 7d**). The sizes estimated from SEM images vary in the range 45–60 nm up to 85–105 nm. Anodization voltage increase leads to a raise in the thickness of ZnO NC layers mainly.

#### 4.2. Emission study of ZnO NCs

PL spectra of ZnO NCs prep ared at different anodization voltages and annealed at 400°C are complex and can be presented as a set of PL bands. The deconvolution procedure permits to obtain the PL bands centered at: 3.18, 3.02, 2.94, 2.55, and 1.98 eV (**Figure 8**).

Elementary PL bands with the peaks at 2.55 and 1.98 eV were attributed earlier to the defect-related emissions in ZnO NCs [33–36]. The intensity of defect-related PL bands enlarges with increase in the anodization voltages due to increase in the volume of ZnO NC layers. The high energy PL bands (3.18, 3.02, and 2.94 eV) were assigned to NBE emission in ZnO [31].

PL spectra of ZnO NCs measured in the temperature range 10–300 K are presented in **Figure 9**. The intensities of defect-related PL bands (1.98 and 2.55 eV) decrease significantly in this temperature range. Integrated PL intensities versus temperature have been presented in Arrhenius coordinates in **Figures 10** and **11** with the aim to estimate the activation energies of PL thermal decays.



**Figure 7.** SEM images of annealed ZnO NCs obtained at anodization voltages 1 (a), 5 (b), and 15 V(c) for etching time 6 min. Widths and lengths of annealed ZnO NCs (d) obtained at different etching voltages of 10, 15, and 20 V [24].



Figure 8. PL spectra of ZnO NCs prepared at voltages: 1 (1), 15 (2), and 20 (3) V.

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Figure 9. PL spectra of ZnO NCs obtained at 15 V and measured at 10-300 K with the step of 30 K.



Figure 10. Dependences of integrated PL intensities versus temperature presented in Arrhenius coordinates for defectrelated PL bands.



Figure 11. Dependences of integrated PL intensities versus temperature presented in Arrhenius coordinates for NBE emission bands.

PL thermal decays in the range 10–150 K for all PL bands realize with the same activation energy (8.6–8.8 meV) due to the activation, apparently, of some nonradiative recombination centers. Thermal quenching of all PL bands starts at higher temperatures (150–300 K). The 2.94 and 3.06 eV PL bands, which demonstrate the PL thermal decay with the activation energy of 18meV, are related, apparently, to the LO phonon replicas of bond-exciton emission. The 3.18 eV PL band, with highest PL decay activation energy (50 meV), is connected, probably, with the LO phonon replicas of FE emission.

# 5. Size-dependent effects in emission of ZnO NC films

The impact of NC sizes on PL spectra has been studied using ZnO NCs prepared at a voltage of 5 V, times: 1 (1), 3 (2), 6 (3), and 10 (4) min and annealed at 400°C. These ZnO NCs have been discussed in Section 3 and their sizes are summarized in **Table 2**. PL spectra of these ZnO NCs are a superposition of PL bands with the peaks at 2.05, 2.45, and 3.11 eV (**Figure 12**, dashed lines).

**Figure 13** shows the variation of NBE emission in ZnO NCs of different sizes. The 3.10 eV PL band at 300 K belongs to the FE phonon-assisted replica in ZnO NCs [21, 22]. The deconvolution procedure has been applied to PL spectra and its result is presented by dashed curves in **Figure 13**. PL bands centered at 3.010, 3.082, 3.154, and 3.226 eV were chosen for the deconvolution, which can be attributed to the LO phonon replicas (FE-5LO, -4LO, -3LO, and -2LO) of A exciton (3.373 eV). The energy difference between these PL transitions is close to some numbers of LO phonons (72 meV) in ZnO [46].

Integrated PL intensities of 2.45, 3.010, 3.082, 3.154, and 3.226 eV PL bands increase significantly with diminishing the ZnO NC size and with enlarging the surface-to-volume ratio (**Figure 14a** and **b**).

Additionally, the main PL peak of NBE emission shifts to higher energy owing to the PL intensity enlargement of 3LO and 2LO phonon replicas mainly (**Figure 13**). Note that PL spectra of ZnO NCs, typically, do not reveal any FE peaks or phonon replicas owing to poor material quality and high concentrations of structural defects.

Sample numbers	Average NC width (nm)	Average NC length (nm)	Lattice parameter, "a" (Å)	Lattice parameter, "c" (Å)	Porosity, $c_0$ (%)
Bulk ZnO [27]			3.2495	5.2069	
1	308	600	3.2504	5.2071	25
2	253	459	3.2534	5.2119	28
3	170	316	3.2564	5.2167	37
4	67	131	3.2584	5.2199	50

Table 2. The size of ZnO NCs from SEM images and hexagonal crystal lattice parameters estimated from XRD data.

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Figure 12. Normalized PL spectra of ZnO NCs obtained at times of 1 (1), 3 (2), 6 (3), and 10 (4) min. Dashed curves present the deconvolution of the PL spectrum (4) [26].

The defect-related green PL band, detected traditionally in the spectral range of 2.40–2.50 eV in ZnO, has been assigned to the oxygen vacancies [36], Cu impurities [38], or surface defects [22, 39]. In our experiments, the intensity of 2.45 eV PL band increases significantly (**Figure 14a**) in PL spectra at decreasing the ZnO NC size and increasing the surface-to-volume ratio in NCs. Thus, it can be supposed that emission centers, responsible for the 2.45 eV PL band, relate to the surface defects and their concentration enlarges with increasing the surface-to-volume ratio in ZnO NCs.

#### 5.1. NBE intensity stimulation at ZnO NC size decreasing

The intensity of 3.082–3.226 eV PL bands, related to FE phonon-assisted replicas, increases significantly with decreasing the ZnO NC size (**Figure 14b**). Since the process of reduction in size is accompanied by increasing the interplanar distances in ZnO NCs (**Table 2**), the FE-related PL bands have to shift to lower energy in small NCs (4). But the main PL peak of NBE emission shifts to high energy (**Figure 13**) from 3.08 eV (1) to 3.14 eV (4). It means that some other physical mechanism is responsible for the PL intensity enlargement and spectral transformation of NBE emission band.

The PL intensity  $W_{PL}$  of ZnO NCs can be represented by the formula [47]:

$$W_{p_{L}} = I_{0} (1 - R)^{2} (1 - c_{0}) [1 - \exp(-\alpha d)] \eta$$
<sup>(2)</sup>

where  $I_0$  is the excitation light intensity, d is the ZnO NC layer thickness, R and  $\alpha$  are the reflection and absorption coefficients, and  $\eta$  is the internal quantum emission efficiency that is  $(\eta = \frac{\tau_R^{-1}}{\tau_R^{-1} + \tau_{NR}^{-1}})$ ,  $\tau_R$  and  $\tau_{NR}$  are radiative and nonradiative recombination times, respectively,



**Figure 13.** NBE emission bands in annealed ZnO NCs obtained at the durations of 1 (1), 3 (2), 6 (3), and 10 min (4). Dashed curves present the deconvolution of PL spectra on LO phonon-assisted PL bands [26].

and  $c_0$  is the porosity of ZnO layers (**Table 2**). At high porosity, the ZnO volume, which absorbs the excitation light, decreases.

Let us consider the coefficients of relative varying the integrated PL intensities in the studied structures, in comparison with the structure 1, at permanent parameters of the excitation light intensity ( $I_0$ ) and R coefficient. Actually, the excitation intensity  $I_0$  was the same in our experiments and the reflection coefficient decreases a little versus NC sizes in the range 60–600 nm. The relation of PL intensities can be presented as:

$$K_{ex} = \frac{W_{PL}^{\#i}}{W_{PL}^{\#1}} = \frac{(1 - c_{oi})}{(1 - c_{o1})} \frac{[1 - \exp(-\alpha d_i)]\eta_i}{[1 - \exp(-\alpha d_1)]\eta_1}$$
(3)

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**Figure 14.** The variation of integrated PL intensities versus sizes of ZnO NCs for PL bands: (a) 2.05 (1) and 2.45 (2) eV and (b) 3.226 (1), 3.154 (2), 3.082 (3), and 3.010 (4) eV [26].

The values of  $K_{ex}$  parameters are summarized in **Table 3**. Some rising in exciton PL intensity in ZnO NCs at the NC size variation from 308 × 600 nm (1) down to 253 × 459 nm (2) can be explained by increasing the NC layer thickness and excitation light absorption. However, the PL intensities of all PL bands enlarge significantly (**Figure 14**, **Table 3**) when the size of ZnO NCs decreases down to 67 × 131 nm (4). To explain the reasons of such PL stimulation, the factors that influent on the internal quantum efficiency and radiative recombination rates have to be discussed.

The stimulation of internal quantum efficiency in small ZnO NCs (3, 4) can be attributed to exciton recombination rate increasing owing to the realization of the weak exciton confinement. The theoretical consideration of this effect was presented in references [48, 49] and two regimes of weak exciton confinement are discussed. The first regime deals with NCs of the size "bigger" than the Bohr exciton radius, but "smaller" than a wavelength of emitted light in ZnO. Oscillator strength increase in the first case is a result of oscillator strength enhancement for localized excitons in proportion to spreading their wave functions, predicted for the bound exciton early [50].

N	PL K <sub>ex</sub>	Average NC width,				
	3.226	3.155	3.083	3.010	2.45	
	eV	eV	eV	eV	eV	nm
1	1.0	1.0	1.0	1.0	1.0	308
2	2.9	2.6	2.1	2.3	3.7	253
3	7.8	7.5	5.4	5.8	8.6	170
4	16.0	14.0	9.5	10.7	31.6	67

**Table 3.** Experimental rations  $K_{ex}$  for integrated PL intensities  $W_i/W_1$  of studied PL bands.

The second weak confinement regime is connected with exciton-light coupling with the formation of polaritons, which becomes strong if the size of NCs approaches to light wavelength in ZnO. The exciton recombination rate G, at the assumption of exiton-light coupling was considered as the product of photon and exciton eigenstates early in [48, 49]:

$$G = K \left[ \int dr \cos(kr) \Phi(r) \right]^2, \text{ with } k = \sqrt{\varepsilon_{\infty}} k_{\alpha}$$
(4)

where *k* is the wave vector of light in a material with the high frequency dielectric constant,  $\varepsilon_{\infty}$ , that equals to  $\varepsilon_{\infty} = 3.77$  [32] in ZnO,  $k_0 = 2\pi/\lambda_0$  is the wave vector of light at an exciton resonance frequency and *K* is a characteristic of long-range exchange energy splitting for exciton in NCs [48]. The  $\Phi(r)$  in Eq. (4) was taken as a Gaussian function to get an analytical formula and formulas for the exciton recombination rate *G* and exciton recombination time  $\tau_R$  were obtained as [48, 49]:

$$G = \frac{\sqrt{2\pi}}{12} \omega_{LT} \left(\frac{2\pi}{\lambda_o}\right)^3 \langle r \rangle^3 \exp\left(-8 \varepsilon_{\infty} \frac{\pi^2 \langle r \rangle^2}{\lambda_o^2}\right)$$
(5)

$$\tau_{R} = \frac{1}{G} \tag{6}$$

The radiative recombination rates (**Figure 15**) and corresponding radiative lifetimes (**Figure 16**) have been numerically estimated using Eqs. (5) and (6) for the quant energy of FE phonon-assisted replicas (3.226, 3.154, 3.082, and 3.010 eV) in ZnO NCs of different sizes.

The recombination rates approach to maximum in ZnO NCs with diameters of 59–64 nm for the exciton-light coupling model (**Figure 15**) and starting from 59 to 64 nm the radiative recombination rate decreases (radiative lifetime increases) versus NC sizes (**Figures 15** and **16**).

The estimation of exciton recombination rates (**Figure 15**) has been done for the spherical shape of NCs. In the studied films, the ZnO NCs have a rhomb shape (**Figure 1**). The exciton



Figure 15. Numerically simulated exciton recombination rates for LO phonon-assisted PL bands in ZnO NCs of different sizes [26].

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Figure 16. Numerically simulated exciton radiative lifetimes for LO phonon-assisted PL bands in ZnO NCs of different sizes [26].

recombination rate decreases fast versus sizes (**Figure 15**) and due to this is reasonable to consider only the smallest NC parameter (width), because the recombination rate along the largest NC sizes (length) will be some orders smaller. Thus, the variation of PL intensity in ZnO NCs is reasonable to present versus NC widths, as shown in **Figure 14**.

The exciton-light coupling model predicts well the ZnO NC size (59–64 nm), where the maximum of PL intensity can be expected. This size correlates with the NC width (67 nm) in the structure 4 with highest detected PL intensity. However, the PL intensities of FE phononassisted PL bands enlarge 15- or 10-fold with decreasing NC widths from 250 down to 67 nm (**Table 3**). At the same time, the estimated recombination rate has to increase 90-fold or even more in the proposed model (**Figure 15**). This difference can be attributed to the following reasons: (i) the enlargement of nonradiative recombination rate in smallest ZnO NCs due to increasing significantly the concentration of surface defects and (ii) the exciton-light coupling and polariton orientation partially along the length of ZnO NCs, where the exciton recombination rate is smaller. Thus, the stimulation of both recombination in ZnO NCs lead to smaller internal quantum efficiency,  $\eta$ , and integrated PL intensity,  $W_{pL'}$  than it is predicted by the exciton-light coupling model.

We need to discuss as well increasing the integrated PL intensity of FE-2LO and FE-3LO replicas in comparison with the intensity of FE-4LO and FE-5LO bands (Figure 13, Table 3) in small ZnO NCs. This effect, probably, deals with decreasing the exciton-phonon coupling strength in the smallest ZnO NCs that were predicted early for ZnO QDs [51]. The effect was attributed to diminishing exciton polarity in small NCs and to decreasing Frohlich polar intraband scattering that induces phonon-assisted emission bands [52–54].

# 6. Impact of Cu-doping on the structure and emission properties of ZnO NC films

To the adjustment of ZnO NC characteristics the doping by different metals Al [55], Co [56], Ni [57], Cu [58, 59], or Ag [60] can be used. Cu atoms are most impotent impurities due to the low toxicity and large source content. ZnO:Cu NCs have demonstrated excellent electrical, magnetic, and photoelectrical characteristics and gas sensing [58, 59]. The Cu atoms are well known as emission activators for semiconductors that can change essentially the emission intensity in ZnO NCs [58, 59].

A lot of papers related to doping ZnO films by Cu in different concentrations were published recently [61–64]. A systematic change of XRD parameters with Cu content increasing in the ZnO crystal lattice was observed in Ref. [63], together with decreasing the ZnO energy band gap versus Cu contents [63]. NBE intensity enhancement in ZnO films with Cu doping at 2.0 at% and emission quenching at Cu doping 4.4 at% was reported in Ref. [56].

A set of published papers are devoted to the defect study if the ZnO:Cu crystals [64, 65]. The green PL band at 2.45 eV with the LO phonon-related structure and zero-phonon line was assigned to the optical transition via  $Cu_{Zn}$  acceptors [64, 65]. The structure-less green emission was assigned to the recombination of electron from a shallow donor with hole bounds to Cu+ ions [65].

The assumptions concerning the Cu defect structure have been presented, but only some of them look as reliable. The purpose of our work is connected with the investigation of correlated varying the XRD parameters and PL spectra of ZnO Cu NCs versus Cu contents with the aim to analyze the Cu-related defects. The parameters of the studied ZnO and ZnO Cu NCs are summarized in **Table 4**.

# 6.1. SEM and XRD studies

SEM images of ZnO and ZnO Cu NCs obtained at the adonization duration of 3 min with thermal treatment at 400°C are presented in Figure 17(a) and (b). ZnO NCs have a rhomb

Sample number	Type of NCs	Etching duration (min)	Etching voltage (V)	NC size (nm)	Integrated PL intensity of all bands at 10 K (arb. un.)
1	ZnO	1	5	308 × 548	$1.0 \times 10^{5}$
2	ZnO	3	5	273 × 459	$2.0 \times 10^{5}$
3	ZnO	6	5	170 × 316	$2.4 \times 10^{5}$
4	ZnO Cu	1	5	$300 \times 540$	$1.3 \times 10^{5}$
5	ZnO Cu	3	5	282 × 510	$3.3 \times 10^{5}$
6	ZnO Cu	6	5	200 × 320	$1.7 \times 10^{5}$

Table 4. The average NC sizes obtained from SEM images.

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Figure 17. SEM images of N2 ZnO NCs (a) and N5 ZnO Cu (b) NCs obtained at an anodization time of 3 min after thermal annealing.

shape and we used width and length for the size characterization (**Table 4**). The size of ZnO NCs decreases versus etching times from 308 × 548 nm to 170 × 316 nm (**Table 4**).

At first, the XRD investigation of ZnO and ZnO Cu NCs has been done with the aim to confirm that Cu atoms are incorporated in ZnO NCs. The five XRD peaks have been detected in both types of NCs (**Figures 18** and **19**), related to the diffraction from the (100), (002), (101), (110), and (103) crystal planes in the wurtzite ZnO crystal lattice [27].



Figure 18. XRD results for the N2 (a) and N3 (b) ZnO NCs (Table 4) after thermal annealing [66].



Figure 19. XRD results for the N5 (a) and N6 (b) ZnO Cu NCs (Table 4) after thermal annealing [66].

The decreasing ZnO NC size stimulates the shift of XRD peaks to lower angles (**Table 5**) that testify on larger interplane distances in small ZnO NCs. It was supposed early that this effect is related to compressive strain decreasing in small ZnO NCs [26].

At the XRD study of ZnO:Cu NCs with small Cu concentration of  $\leq 2.28$  at% [67] (samples N4 and N5), the XRD peaks shift to bigger diffraction angles (2 theta) in comparison with ZnO NCs (samples N1, N2), together with decreasing the NC sizes (**Table 5**). This effect testifies on smaller interplanar distances in ZnO:Cu NCs. At the Cu concentration higher than 2.28 at% (sample N6), XRD peaks shift to smaller 2 theta values even more essential than those are detected in ZnO NCs (sample N3). The last effect corresponds to increasing the interplanar space in ZnO Cu NCs of N6.

Sample number	ZnO	ZnO	ZnO	Cu	ZnO	ZnO
	(100)	(002)	(101)	(111)	(110)	(103)
1	31.7622	34.4022	36.2322		56.5422	62.8922
2	31.7322	34.4022	36.2321		56.5422	62.8922
3	31.7022	34.3722	36.2022		56.5222	62.8822
4	31.7713	34.4663	36.2793		56.6143	62.8473
5	31.7813	34.4763	36.2893	43.2963	56.6733	62.8963
6	31.6891	34.3351	36.1481	43.2531	56.4831	62.8041

Table 5. XRD peaks for studied ZnO NCs and ZnO Cu NCs [66].

The valence of Cu could be +1 or +2 and the radius of Cu<sup>+</sup>, Cu<sup>+2</sup>, and Zn<sup>+2</sup> ions are 0.096, 0.072, and 0.074 nm, respectively, in ZnO [68–72]. Substitution ions Cu<sup>+</sup> and Cu<sup>+2</sup> and interstitial Cu<sup>+2</sup> ions can be incorporated in ZnO. Lattice constants in ZnO:Cu NCs increase, in comparison with those in undoped ZnO NCs, when Cu<sup>+</sup> substituted Zn<sup>+2</sup> ions, together with compressive strain enlarging [68, 69]. In ZnO:Cu nanowires (NWs), a decrease in lattice parameter was detected and interpreted as Cu<sup>+2</sup> ions substituted of Zn<sup>+2</sup> ions in ZnO [70]. In addition, Cu atoms can form the complex defects [Cu<sub>2n</sub> Zn<sub>i</sub>]<sub>x</sub> as well [70].

In our study of ZnO and ZnO:Cu NCs three XRD effects have been revealed:

- **1.** A low angle shift of XRD peaks in ZnO NCs at decreasing NC sizes (**Table 5**) owing to compressive strain decreasing that can be accompanied by decreasing the energy band gap.
- **2.** A higher angle shift of XRD peaks at small Cu content (2.28 at%) in ZnO:Cu NCs (**Table 5**) owing to, probably, the Cu<sup>+2</sup> ion substitution of Zn<sup>+2</sup> ions in ZnO.
- **3.** A low angle shift of XRD peaks at higher Cu content (≥2.28 at%) in ZnO Cu NCs (**Table 5**) owing to Cu<sup>+</sup> ion substituting the Zn<sup>+2</sup> ion or the formation of Cu-related complexes.

In ZnO:Cu NCs the XRD peak intensity increases versus etching durations (**Figure 19**) due to thickness increasing of the ZnO Cu NC layers. Simultaneously, the new XRD peak ( $2\theta = 43.2963^\circ$ ) related to the diffraction from (111) crystal planes in metallic Cu nanoparticles with a cubic crystal lattice [73] has been revealed (**Table 5**, **Figure 19**).

# 6.2. Comparative PL study of ZnO and ZnO Cu NCs

PL spectra of ZnO and ZnO Cu NCs obtained at different etching times (3 and 6 min) and measured at 10 K are presented in **Figure 20(a)** and **(b)**. PL spectra are complex and include two wide PL bands well known in ZnO:NBE emission in the spectral range 2.80–3.37 eV [34] and defect-related emission in the range 1.70–2.80 eV [37–39]. The intensity of NBE luminescence rises versus anodization time owing to enlarging the thickness of ZnO NC layers (**Figure 20a** and **b**).

Simultaneously, the NBE band shifts to lower energy in PL spectra (**Figure 20a** and **b**) that is caused by decreasing the NC sizes, compressive strains, and the energy band gap of ZnO NCs [26].

The variation of Cu concentrations in ZnO:Cu NCs influent mainly on the intensity and shape of defect-related PL bands in the range 1.7–2.8 eV. PL band intensity increases when the Cu concentration approaches to 2.28 at% and then decreases at higher Cu contents (**Figure 20a** and **b**). At high Cu concentration, the new PL band centered at 2.61–2.70 eV at 10 K has been detected in PL spectra of ZnO Cu NCs (**Figure 20b**, curve 2).

To make the conclusion concerning the light-emitting mechanisms of visible PL bands in ZnO:Cu NCs, PL spectra have been studied in the range of 10–300 K (**Figure 21**).

Normalized PL spectra of ZnO and ZnO:Cu NCs for the visible spectral range measured at different temperatures are presented in **Figure 22(a)** and **(b)**. It is clear that four PL bands (A, B, C, D) have composed PL spectra in the orange-yellow-green-blue ranges of ZnO Cu NCs, which are characterized by different kinetics of PL intensity thermal decays.



Figure 20. PL spectra of N2 (curve 1) and N3 (curve 2) ZnO NCs (a) and N5 (curve 1) and N6 (curve 2) ZnO Cu NCs (b).

The deconvolution procedure was applied to PL spectra of **Figure 22(a)** and **(b)** that permits to obtain three- and four-elementary PL bands in ZnO and ZnO Cu NCs, respectively, peaked at 10 K: 1.95–2.00 eV(A), 2.15–2.23 eV(B), 2.43–2.50 eV(C), and 2.61–2.69 eV(D).

The PL intensity of bands A, B, and C decreases faster (N6) versus etching duration in comparison with the PL intensity of band D (**Figure 20b**, curve 2). The variation of integrated PL intensities of all PL bands versus temperatures in ZnO and ZnO Cu NCs is presented in **Figure 23(a)** and **(b)**. The band D intensity decreases at low temperatures (starting from 70 K). PL thermal decays of the bands A, B, and C are similar in ZnO and ZnO Cu NCs. PL intensities of bands (A, B, C) fall down slowly in the range 10–100 K, and only at higher temperatures (100–300 K) their PL thermal decays become faster.

To estimate the activation energies of PL thermal decay in different temperature ranges, the Arrhenius plots have been designed (**Figure 24**). At low temperatures, the activation energies of PL intensity decays are estimated as: 9 meV in ZnO or 16 meV in ZnO Cu NCs. These small activation energies of PL decay are related to the thermal activation of some nonradiative recombination centers (NRC). At higher temperatures PL intensities of A, B, and C bands decay with activation energies: 44meV (A) and 35 meV (B and C) in ZnO NCs (**Figure 24a**) as well as 37 meV (A) and 27 meV (B and C) in ZnO Cu NCs (**Figure 24b**). The PL band D intensity decreases with the activation energy of 20 meV (**Figure 24b**, curve 4).

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Figure 21. PL spectra of ZnO:Cu NCs measured in the range 10–300K.



Figure 22. Normalized PL spectra in the range of defect-related PL bands for ZnO NCs (a) and ZnO Cu NCs (b).



Figure 23. Thermal dependences of integrated PL intensities in ZnO (a) and ZnO Cu NCs (b) [66].



Figure 24. Arrhenius plots obtained for different PL bands for ZnO (a) and ZnO Cu NCs (b) [67].

#### 6.3. Orange-yellow-green PL bands

The orange PL band (1.95–2.05 eV) in ZnO was assigned to oxygen interstitials,  $O_i$  (2.02 eV) [40], to shallow donor-deep acceptor pairs [11], or to hydroxyl groups (2.10 eV) [41]. The yellow band (2.15–2.23 eV) in undoped and doped (with N or Ga) ZnO layers [11, 74] was

attributed to the electron transitions from shallow donors to deep acceptors with an energy level of 0.7 eV above the valence band, connected with the zinc vacancy,  $V_{Zn'}$  or  $V_{Zn}$ -shallow donor complex [11]. The green PL band (2.43–2.50 eV) is complex and includes five PL bands connected with different defects in undoped ZnO NCs [75–78]. The types of corresponding defects and optical transitions are not clear yet.

The ZnO and ZnO:Cu NC layers were annealed at 400°C in air that is the O- and N-rich condition. The defects favored for this condition are  $V_{Zn'} O_{i'}$  and  $O_{Zn}$  [79] that act as deep acceptors in ZnO [79]. However, the probability of forming  $O_{Zn}$  defects is low due to the high value of its formation energy in ZnO. The PL intensity of 2.40–2.50 eV band increases with NC size decreasing and surface-to-volume ratio rising [26], which permits to attribute the green radiative centers to native defects (zinc vacancy or surface defects) in ZnO NCs (**Figure 20a**).

Cu doping with the concentration  $\leq 2.28$  at% stimulates significantly the intensity of orangeyellow-green PL bands in ZnO:Cu NCs (**Figure 20b** and **Table 4**). Simultaneously, the XRD study has detected a high angle shift of all XRD peaks in ZnO Cu NCs owing to, apparently, the substitution of Zn<sup>+2</sup> ions by Cu<sup>+2</sup> ions in ZnO. Thus, the radiative centers connected with structureless green PL band (2.43–2.50 eV) in ZnO:Cu NCs can be attributed to Cu<sub>Zn</sub><sup>+2</sup> defects [64, 65].

The high PL intensity of green band is detected together with the high intensities of orange and yellow PL bands in the ZnO Cu NCs (**Figure 20b**). It can be supposed that the process of Zn<sup>+2</sup> ion substitution by Cu<sup>+2</sup> ions at the thermal treatment (400°C) is accompanied by appearing other native acceptors: zinc vacancies, oxygen interstitials, or their complexes. Zinc vacancies,  $V_{Zn'}$  are the deep acceptors with the transition energy levels  $E^{(0/-)} = 0.18$  eV and  $E^{(-/2-)} = 0.87$  eV above the valence band according to the calculations reported in [79]. Oxygen interstitials are characterized by deep acceptor transition levels  $E^{(0/-)} = 0.72$  and  $E^{(-/2-)} = 1.59$  eV above the valence band [79]. Cu atoms act as deep acceptors in ZnO as well [80]. Thus, all these deep acceptors can be responsible for the stimulation of orange-yellow-green PL bands in ZnO:Cu NCs.

Small activation energies of emission thermal decays (**Figure 24**) for bands (A, B, C) permit to attribute the corresponding centers to the shallow donor-deep acceptor pars (DAPs). Note that PL thermal decays of B and C bands are characterized by the same activation energies owing to, apparently, the formation of corresponding DAPs from the same shallow donors, for example,  $Zn_{r'}$  and different deep acceptors.

Note that the defect concentration in ZnO:Cu NCs is higher than its value in ZnO NCs. Defect concentration increasing leads to the stimulation of the PL intensities of A, B, and C bands. Simultaneously, the activation energies of PL decays decrease in ZnO Cu NCs that is a result of distance decreasing between donors and acceptors in DAPs. The last effect provokes attractive interaction increasing in DAPs and, as a result, the shift of donor and acceptor energy levels closer to the conduction (valence) bands. In this case, the PL thermal decays in ZnO:Cu NCs are characterized by smaller activation energies that actually has been revealed: 37 meV (A) and 27 meV (B and C) (Figure 24).

The energy position of  $Zn_i^{+1/0}$  donor levels was estimated early as 50 meV [81]. A shallow donor with ionization energy of 30 meV was detected at high-energy electron irradiation experiments [82]. The authors suggested that these shallow donors owe to Zn-sublattice

defects: Zn interstitialses or Zn-interstitial-related complex [83]. In addition, under the N-rich ambient condition the shallow donors,  $Zn_i-N_O$ , can be obtained as it was supposed in [84]. Thus, it can be assumed that in ZnO NCs the orange (A), yellow (B), and green (C) emissions are related to DAPs, which include the deep acceptors, such as oxygen interstitials and zinc vacancies, and shallow donors, like zinc interstitials or their complexes. In ZnO Cu NCs the substitutional  $Cu_{Zn}$  atoms form the DAPs with shallow donors that are responsible on the structureless green PL band.

# 6.4. Blue PL band

The blue PL band D (2.61–2.70 eV) appears in PL spectra of ZnO:Cu NCs (sample N6, **Figure 20b**) at higher Cu contents ( $\geq$ 2.28 at%). Simultaneously, the intensities of other PL bands decrease (**Table 4**) and the band D dominates in the PL spectrum (**Figure 20b**, curve 2). At higher Cu concentrations in ZnO:Cu NCs, the nonradiative recombination centers (NRC), probably, appear that provokes decreasing the PL intensity of the bands (A, B, C). At the same time, the D band intensity decreases slowly that testifies on concentration increasing of D band emitting defects. In this case, a low angle shift of XRD peaks has been revealed at XRD study. This fact testifies on increasing the lattice parameters and interplanar distances owing to the formation of some Cu-related complexes in the ZnO matrix. Cu-complex defects can be attributed to [Cu<sub>7n</sub> Zn<sub>i</sub>]<sub>x</sub> complexes proposed in [65].

# 7. Plasmon-related effects in ZnO Cu NC films with metallic Cu nanoparticles

The purpose of this part deals with the study of another effect related to Cu doping of the ZnO NCs. In the earlier mentioned papers [11, 58–63], the ZnO NCs were doped by Cu in low concentrations, when Cu atoms substituted Zn atoms in the ZnO crystal lattice. However, the method of Zn etching technology with thermal treatment permits to prepare ZnO:Cu NCs with metallic Cu nanoparticles located at the ZnO NC surface (**Figure 19**, **Table 5**). In this ZnO:Cu films, as expected, it is possible to generate plasmon by light in Cu nanoparticles that permit to study its impact on optical properties [80].

At first, the XRD (**Figure 19**) and EDS (**Figure 25**) methods have been used for the confirmation that Cu atoms and Cu nanoparticles exist in ZnO Cu NC films (**Table 6**).

**Figure 25(b)** clearly demonstrates the  $Cu_{K}$  line in the high resolution insertion for ZnO:Cu NCs. The EDS analysis and estimated element concentrations are presented in **Table 6**.

XRD comparative investigations of ZnO and ZnO Cu NCs have been presented early in **Figures 18** and **19** and analyzed in Section 6. In addition to the above discussed Cu peak at 2 theta equal to 43.2963° (**Figure 19**), which corresponds to the diffraction from the (111) crystal planes in the cubic crystal lattice of metallic Cu nanoparticles [73], the second Cu (200) peak at the 2 theta equaling to 50.4308° has been revealed in ZnO Cu NCs as well (**Figure 26a** and **b**) [85].

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**Figure 25.** EDS spectra of N3-ZnO (a) and N6-ZnO Cu (b) NC samples obtained at an anodization time 6 min after thermal annealing [85]. The insertions present the high resolution EDS spectra in the range 7.8-8.3 keV for ZnO (a) and ZnO:Cu (b) NCs.

In ZnO:Cu NCs obtained with the etching time of 6 min, the concentration of Cu NCs enlarges, which manifests itself by increasing the intensity of the Cu (111) and Cu (200) XRD peaks (**Figures 19b** and **26b**). The oxidation of Cu nanoparticles can be realized, partially as well, at annealing in ambient air. The small peculiarities in XRD diagrams (**Figure 19**) for the sample M6 in the range 38–40° can be related to the CuO or Cu<sub>2</sub>O phases.

### 7.1. Raman scattering study

Raman peaks at 331, 379, 437, and 572–575 cm<sup>-1</sup> have been detected in Raman scattering spectra measured in the 100–650 cm<sup>-1</sup> range in ZnO and ZnO:Cu NCs (**Figure 27**). The nature of these Raman peaks has been discussed in Section 3.2. The increase in etching time leads to the enlargement of Raman peak intensities owing to the growth of ZnO NC volume and varying the geometry of Raman scattering measurement in small ZnO NC films (**Figure 27**). The intensity of all Raman peaks in ZnO Cu NCs is threefold higher than its value in ZnO NCs (**Figure 27a** and **b**). The studied NCs are characterized by the identical crystal structure and NC sizes (**Table 4**). The difference in the Raman scattering intensity can be attributed to the surface-enhanced Raman scattering (SERS) effect in ZnO Cu NCs [72].

Element	wt%	at%
0 <sub>K</sub>	19.87	50.29
Cu <sub>k</sub>	3.58	2.28
Zn <sub>K</sub>	76.55	47.42
Sum	100	100

Table 6. Analysis of K-lines in EDS results for N5 ZnO Cu NCs.



Figure 26. XRD results for the ZnO Cu NCs obtained at an anodization times of 3 min (a) and 6 min (b) after thermal annealing in the XRD range 50–51° [85].

The light-enhanced electric field and the SERS effect are attributed to the plasmon resonance at the material interface with metallic nanoparticles. In the studied case, apparently, the excitation light used at Raman scattering study stimulates the plasmon generation in metallic Cu nanoparticles at the surface of ZnO:Cu NCs with corresponding wavelength for plasmon-polariton resonance that is needed for SERS effect.

#### 7.2. ZnO emission study

PL spectra of ZnO and ZnO Cu NCs are presented in **Figure 28** for the comparison. The PL intensity of defect-related PL bands (2.08 and 2.50 eV) increases, in comparison with the NBE emission intensity, when the NC size falls down in ZnO and ZnO Cu NCs together with the surface-to-volume ratio rising (**Figure 28**, **Table 4**). It is known that 2.02–2.08 eV PL band



**Figure 27.** Raman scattering spectra of thermal annealed ZnO NCs (a) and ZnO Cu NCs (b) obtained at the etching times: 1 (1), 3 (2), and 6 min (3) [85].

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**Figure 28.** PL spectra of ZnO NCs (a) and ZnO Cu NCs (b) obtained at the anodization durations of 1 (1), 3 (2), and 6 min (3). Dashed curves represent the deconvolution of experimental PL spectrum on the elementary PL bands (curves 4, 5, 6) [85].

increased significantly its intensity after oxidation at annealing in ambient air [21, 22] that is accompanied by the oxygen interstitial content enlargement in ZnO. The detection of identical orange emission peaks in ZnO and ZnO Cu NCs permits to attribute the PL band (2.08 eV) to radiative defects included the oxygen interstitials.

The influence of metallic Cu nanoparticles on the PL band intensities in PL spectra of ZnO:Cu NCs is different significantly.

The influence of Cu nanoparticles on the intensities of PL bands in ZnO NCs is different. **Figure 28** shows that the PL intensity of defect-related PL bands is higher by twofold in ZnO Cu NCs than it value in ZnO NCs. This fact can be assigned to the plasmon-enhancing recombination via these defects [1]. However, NBE emission in ZnO Cu NCs is less effective in comparison with ZnO NCs (**Figure 28**). The last effect can be explained by the destruction of excitons by locally enhanced electric field in Cu nanoparticles at the ZnO Cu NC surface and due to this diminish the exciton-related emission.

# 8. Conclusion

The morphology, crystal structure, Raman scattering, and multicolor emission have been comparatively studied in ZnO and ZnO:Cu NCs. XRD study confirms the wurtzite structure of ZnO NCs obtained by electrochemical method. The PL intensity enhancement of exciton emission is detected in NCs with the size of 67–170 nm and attributed to the week quantum confinement and exciton light coupling with the formation of polaritons. It is shown that metallic Cu nanoparticles on the surface of ZnO:Cu NCs stimulate the SERS effect and PL intensity rising the visible PL bands owing to, apparently, the plasmon generation in Cu NCs. Simultaneously, NBE emission decreases in ZnO:Cu NCs due to the exciton destruction by plasmon-enhanced electric field.

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# References

- T.V. Torchynska, Nanocrystals and Quantum Dots. Some Physical Aspects, in "Nanocrystals and Quantum Dots of Group IV Semiconductors", Eds: T.V. Torchynska and Y. Vorobiev, American Scientific Publisher, Stevenson Ranch, CA, pp. 1–42 (2010).
- [2] L. Schacht Hernandez, T.V. Torchynska, J.A. Hernandez, G. Polupan, Y. Goldstein, A. Many, et al., Microelectronic Eng. 66, 83 (2003).
- [3] T.V. Torchinskaya, N.E. Korsunskaya, B. Dzumaev, B.M. Bulakh, O.D. Smiyan, A.L. Kapitanchuk, S.O. Antonov, Semiconductors 30, 792 (1996).
- [4] S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, T. Steiner, Prog. Mater. Sci. 50, 293 (2005).
- [5] N.H. Alvi, S. Hussain, O. Nur, M. Willander, Scripta Mater. 64, 697 (2011).
- [6] M.H. Huang, S. Mao, H. Feick, Science 292, 1897 (2001).
- [7] Y.B. Li, Y. Bando, D. Golberg, Appl. Phys. Lett. 84, 3603 (2004).
- [8] W.I. Park, J.S. Kim, G.C. Yi, M.H. Bae, H.J. Lee, Appl. Phys. Lett. 85, 5052 (2004).
- [9] K. Keis, E. Magnusson, H. Lindstrom, Sol. Energy Mater. Sol. Cells 73, 51 (2002).
- [10] D. Gruber, F. Kraus, J. Muller, Sens. Actuators B 92, 81 (2003).
- [11] M.A. Reshchikov, H. Morkoc, B. Nemeth, J. Nause, J. Xie, B. Hertog, A. Osinsky, Physica B. Condensed Matter 358, 401 (2007).
- [12] F. Benharrats, K. Zitouni, A. Kadri, B. Gil, Superlat. Microstruct. 47, 592 (2010).
- [13] T. Saidani, M. Zaabat, M.S. Aida, A.B. Aboud, S. Benzitouni, A. Boudine, Superlat. Microstruct. 75, 47 (2014).
- [14] S.S. Shinde, C.H. Bhosale, K.Y. Rajpure, J. Photoch. Photobiol. B 120, 1 (2013).

- [15] S. Xiang-Bing, F. Lin, J. Xian-Wei, Chin. Phys. B 20, 067804 (2011).
- [16] N. Kumar, R. Kaur, R.M. Mehra, J. Lumines. 126, 784 (2007).
- [17] X. Zhou, S. Gu, Z. Wu, S. Zhu, J. Ye, S. Liu, R. Zhang, Y. Shi, Y. Zheng, Appl. Surf. Sci. 253, 2226 (2006).
- [18] L. Esaki, C.L. Chang, Thin Solid Films 36, 285 (1976).
- [19] A.V. Singh, R.M. Mehra, A. Yoshida, A. Wakhara, J. Appl. Phys. 90, 5661 (2001).
- [20] W. Tang, D.C. Cameron, Thin Solid Films 238, 83 (1994).
- [21] A.I. Diaz Cano, B. El Filali, T.V. Torchynska, Physica E 51, 24 (2013).
- [22] A.I. Diaz Cano, B. El Falali, T.V. Torchynska, J. Phys. Chem. Solids 74, 431 (2013).
- [23] N. Korsunska, L. Khomenkova, M.K. Sheinkman, T. Stara, V. Yuhimchuk, T.V. Torchynska, A. Vivas Hernandez, J. Lumines. 115, 117 (2005).
- [24] T.V. Torchynska, J. Palacios Gomez, G.P. Polupan, F.G. Becerril Espinoza, A. Garcia Borquez, N.E. Korsunskaya, L.Y. Khomenkova, Appl. Surf. Science 167, 197 (2000).
- [25] A. Diaz Cano, S. Jiménez Sandoval, Y. Vorobiev, F. Rodriguez Melgarejo, T.V. Torchynska, Nanotechnology 21, 134016 (2010).
- [26] T.V. Torchynska, B. El Filali, J. Lumines. 149, 54 (2014).
- [27] PDF2 XRD database, Reference code: 00-004-0831 (Zn) and 00-036-1451 (ZnO).
- [28] N. Ashkenov, B.N. Mbenkum, C. Bundesmann, V. Riede, M. Lorenz, D. Spemann, E.M. Kaidashev, A. Kasic, M. Schubert, M. Grundmann, G. Wagner, H. Neumann, V. Darakchieva, H. Arwin, B. Monemar, J. Appl. Phys. 93, 126 (2003).
- [29] J.F. Scott, Phys. Rev. B 2, 1209 (1970).
- [30] A.V. Fedorov, A.V. Baranov, K. Inoue, Phys. Rev. B 56, 7491 (1997).
- [31] G. Polupana, T.V. Torchynska, Thin Solid Films 518, S208 (2010).
- [32] V.A. Coleman, C. Jagadish, Basic Properties and Applications of ZnO, in "Zinc Oxide Bulk, Thin Films and Nanostructures", Eds: C. Jagadish and S. Pearton, Elsevier, Amsterdam, pp. 2–20 (2006).
- [33] S. Ghoopum, N. Hongsith, P. Mangkorntong, Physica E 39, 53 (2007).
- [34] A.B. Djurišic, A.M. Ng, X.Y. Chen, Prog. Quantum Electron. 34, 191 (2010).
- [35] T. Voss, C. Bekeny, L. Wischmeier, H. Gafsi, S. Borner, W. Schade, A.C. Mofor, A. Bakin, A. Waag, Appl. Phys. Lett. 89, 182107 (2006).
- [36] M.K. Patra, K. Manzoor, M. Manoth, N. Kumar, J. Lumin. 128, 267 (2008).
- [37] D.H. Zhang, Z.Y. Xue, Q.P. Wang, J. Phys. D Appl. Phys. 35, 2837 (2002).
- [38] N.Y. Garces, L. Wang, N.C. Giles, G. Cantwell, Appl. Phys. Lett. 81, 622 (2002).

- [39] A.B. Djurišic, W.C.H. Choy, V.A.L. Roy, Y.H. Leung, C.Y. Kwong, K.W. Cheah, T.K. Gundu Rao, W.K. Chan, H.F. Lui, C. Surya, Adv. Funct. Mater. 14, 856 (2004).
- [40] X. Liu, X. Wu, H. Cao, R.P.H. Chang, J. Appl. Phys. 95, 3141 (2004).
- [41] J. Qiu, X. Li, W. He, S.-J. Park, H.-K. Kim, Y.-H. Hwang, J.-H. Lee, Y.-D. Kim, Nanotechnology 20, 155603 (2009).
- [42] R.B.M. Cross, M.M. De Souza, E.S. Narayanan, Nanotechnology 16, 2188 (2005).
- [43] S. Xiang-Bing, F. Lin, J. Xian-Wei, Chin. Phys. B 20, 067804 (2011).
- [44] N. Kumar, R. Kaur, R.M. Mehra, J. Lumines. 126, 784 (2007).
- [45] X. Zhou, S. Gu, Z. Wu, S. Zhu, J. Ye, S. Liu, R. Zhang, Y. Shi, Y. Zheng, Appl. Surf. Sci. 253, 2226 (2006).
- [46] C. Klingshirn, Phys. Status Solidi (a) 71, 547 (1975).
- [47] T.V. Torchynska, A.I. Diaz Cano, J.A. Yescas Hernandez, Y. Shcherbyna, J. Nanoparticle Res. 14, 19 (2011).
- [48] B. Gil, A.V. Kavokin, Appl. Phys. Lett. 81, 748 (2002).
- [49] S.V. Gupalov, E.L. Ivchenko, A.V. Kavokin, J. Exp. Theor. Phys. 86, 388 (1998).
- [50] E.I. Rashba, G.E. Gurgenishvili, Sov. Phys. Solid State 4, 759 (1962).
- [51] W.-T. Hsu, K.-F. Lin, W.-F. Hsieha, Appl. Phys. Lett. 91, 181913 (2007).
- [52] D.M. Bagnall, Y.F. Chen, M.Y. Shen, T. Goto, Appl. Phys. Lett. 73, 1038 (1998).
- [53] T. Makino, C.H. Chia, N.T. Tuan, Y. Segawa, M. Kawasaki, A. Ohtomo, K.Tamura, H. Koinuma, Appl. Phys. Lett. 76, 3549 (2000).
- [54] C.H. Ahn, S.K. Mohanta, H.K. Cho, Appl. Phys. Lett. 94, 261904 (2009).
- [55] M.H. Mamat, M.Z. Sahdan, Z. Khusaimi, A. Zain Ahmed, S. Abdullah, M. Rusop, Optical Mater. 32, 696 (2010).
- [56] S.A. Ansari, A. Nisar, B. Fatma, W. Khan, A.H. Naqvi, Mater. Sci. Eng. 177, 428 (2012).
- [57] M. ElHilo, A. Dakhel, A. Ali-Mohamed, Magnet. Magn. Mater. 321, 2279 (2009).
- [58] S. Singhal, J. Kaur, T.S. Namgyal, R. Sharma, Physica B. 407, 1223 (2012).
- [59] H. Liu, J. Yang, Z. Hua, Y. Zhang, L. Yang, Appl. Surf. Sci. 256, 4162 (2010).
- [60] E. Velázquez, L.T. Torchynska, J.L. Casas, Espinola Physica B 453, 111 (2014).
- [61] Y. Zhao, M. Zhou, Z. Li, et al., J. Lumines. 131, 1900 (2011).
- [62] X.B. Wang, C. Song, K.W. Geng, et al., Appl. Surf. Sci. 253, 6905 (2007).
- [63] Q.A. Drmosh, S.G. Rao, Z.H. Yamani, et al., Appl. Surf. Sci. 270, 104 (2013).

- [64] R. Dingle, Phys. Rev. Lett. 23, 579 (1969).
- [65] N.Y. Garces, L. Wang, L. Bai, N.C. Giles, L.E. Halliburton, G. Cantwell, Appl. Phys. Lett. 81, 622 (2002).
- [66] T.V. Torchynska, B. El Filali, I.C. Ballardo Rodríguez, Physica E 75, 156 (2016).
- [67] T. V. Torchynska, B. El Filali, L. Shcherbyna, Phys. Stat. Sol. (c) 13, 594 (2016).
- [68] B. Kulyk, B. Sahraoui, V. Figà, B. Turko, J. Alloys Compounds. 481, 819 (2009).
- [69] M. Ligang, M. Shuyi, H. Chen, X. Ai, X. Huang, Appl. Surf. Sci. 257, 10036 (2011).
- [70] L. Chowa, O. Lupana, G. Chaia, H. Khallaf, L.K. Ono, B. Roldan Cuenya, I.M. Tiginyanu, V.V. Ursaki, V. Sontea, A. Schulte, Sensors Actuators A 189, 399 (2013).
- [71] Y. Yan, M.M. Al-Jassim, S.H. Wei, Appl. Phys. Lett. 89, 181912 (2006).
- [72] X. Peng, J. Xu, X. Zang, et al., J. Lumines. 128, 297 (2008).
- [73] PDF2 XRD data base, Reference code: 00-004-0836.
- [74] H. Morkos, U. Ozgur, Zinc Oxide. Fundamentals, Materials and Device Technology, Wiley-VCH, Weinheim, 469 p (2009).
- [75] R.B. Lauer, J. Phys. Chem. Solids 34, 249 (1973).
- [76] D.C. Reynolds, D.C. Look, B. Jogai, H. Morkoc, Sol. St. Commun. 101, 643 (1997).
- [77] D.C. Reynolds, D.C. Look, B. Jogai, J.E. Van Nostrand, R. Jones, J. Jenny, Solid State Commun. 106, 701 (1998).
- [78] B. Lin, Z. Fu, Y. Jia, Appl. Phys. Lett. 79, 943 (2001).
- [79] A. Janotti, C.G. Van de Walle, Rep. Prog. Phys. 72, 126501 (2009).
- [80] F.J. Garsia Rodriguez, et al., J. Raman Spectrosc. 29, 763 (1998).
- [81] F.A. Kröger, The Chemistry of Imperfect Crystals. 2nd Edn, North Holland, Amsterdam, p. 73 (1974).
- [82] D.C. Look, J.W. Hemsky, J.R. Sizelove, Phys. Rev. Lett. 82, 2552 (1999).
- [83] A. Janotti, C.G. Van de Walle, Appl. Phys. Lett. 87, 122102 (2005).
- [84] D.C. Look, G.C. Farlow, P. Reunchan, S. Limpijumnong, S.B. Zhang, K. Nordlund, Phys. Rev. Lett. 95, 225502 (2005).
- [85] B. El Filali, T.V. Torchynska, A.I. Diaz Cano, J. Lumines. 161, 25 (2015).

**Optimization Parameters in the Thin Film Science** 

# Lab-on-a-Tube Surface Micromachining Technology

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Additional information is available at the end of the chapter

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#### Abstract

In this chapter, the lab-on-a-tube surface micromachining technology will be used to fabricate a flexible implantable microtemperature sensor for hyperthermia application and a three-electrode system on a polymer tube surface for glucose monitoring application. This micromachining process is based on two homemade equipments: a spray coating equipment and a programmable UV 3D projection lithography system with alignment. In the spray coating system, there is a heater nozzle next to the spray nozzle for real-time heating. Pure nitrogen is flowed through the heater nozzle, warmed up and sprayed onto the tube substrate surface. The programmable UV lithography equipment for cylindrical substrate mainly consists of four parts: a uniform illumination system, a reduced projection lithography system, a synchronized motion stage system, and a Charge-Coupled Device (CCD) multilayer alignment system which is used to observe simultaneously the projected mask's patterns and those ever fabricated on the tube. Using the developed labon-a-tube surface micromachining technology, an implantable flexible microtemperature sensor and a three-electrode microstructure are successfully fabricated on the flexible polymer tube with 330 µm outer diameter, respectively. The test temperature coefficient of resistance (TCR) of the temperature sensor is 0.0034/°C. The measured cyclic voltammetry curve shows that the three-electrode system has a good redox property.

**Keywords:** micromachining, lab-on-a-tube, thin film, flexible cylindrical substrate, 3D lithography

# 1. Introduction

With the development of the Internet of Things (IoT), wearable devices, and implantable biomedical components, the flexible sensors, actuators, and electrical circuits have been demanded more and more widely. However, the traditional silicon-based surface micromachining technologies are difficult to meet this requirement due to natural brittle structure. With regard to this, we developed a novel micromachining method that mainly includes



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. spray coating, lithography pattering, and multilayer alignment on the flexible cylindrical substrate, such as fiber, polymer tube, capillary, and other tubes. It can realize the integrated fabrication of many sensors and actuators with different functional materials on an ultrathin (hundreds of micrometers) flexible cylindrical substrate, which is very promising to wearable devices and biomedical applications in the future. Here, we called it "lab-on-a-tube surface micromachining technology."

In this chapter, the equipments used for lab-on-a-tube surface micromachining will be described in detail. Firstly, a spray coating system for cylindrical substrate will be introduced, and the effect of process parameters on the quality of the coated photoresist (PR) film on tube surface will be also discussed. Then, the UV projection lithography system for cylindrical substrate is developed, and its working principle is described in detail. Finally, two application examples of the developed lab-on-a-tube surface micromachining technology will be shown, one is the flexible implantable microtemperature sensor on a polymer tube surface, another is flexible implantable microneedle with three-electrode system for glucose sensor.

# 2. Equipments for lab-on-a-tube surface micromachining

### 2.1. Spray coating system for cylindrical substrate

A homemade equipment was built, as shown in **Figure 1**, which can realize the spray coating of PR film on the tube surface. In order to complete real-time heating for the tube with coated film, a heater nozzle was used, where nitrogen gas ( $N_2$ ) will be flowed. The temperature of  $N_2$  gas was controlled by using two temperature sensors at the inside and outlet of the heater nozzle. The scan speed of the spraying nozzle, the rotation speed of the tube, and the distance between spray nozzle and the tube can be all independently controlled. They are main process parameters in the current system [1].

In the present work, the photoresist (PR) solution including a positive photoresist S1830 and a thinner AZ 5200 was used as the PR film coated on the tube surface. In the solution, their weight ratio is 1:1. **Figure 2** shows the effect of the nozzle/tube distance on the thickness of coated PR film when using the real-time heating or not. **Figure 3** is the measured variations of the PR film thickness versus the rotation speed when using different weight ratios and



Figure 1. Homemade spray coating system for tube substrate and its schematic setup [3].



Figure 2. Measured effects of the real-time heating process on the variation of the PR film thickness versus the nozzle tube distance.



Figure 3. Measured variations of the PR film thickness versus the rotation speed under different weight ratios and cycle scanning speeds.

cycle scanning speeds. It can be found that the quality of the coated PR films is not good if there is no real-time heating during spray coating. The thinner PR film would be obtained if increasing the rotation speed and thinner concentration. Because that the centrifugal force will become larger when the rotation speed of the tube increases. So PR solution particles will be thrown away more from the tube surface. Finally, the PR films become thinner when increasing the rotation speed.

These experimental results about the spraying PR film on the tube surface are generally in accordance with the previous reports [1, 2]. However, considering the size of tube is very small compared to those of the spray jet and the nozzle/tube distance. So its basic principle is different from the traditional coating process, where the size of wafer is usually planar shape with several inches. A so-called impinging region existing below the nozzle will cover the tube spraying area. Moreover, considering the spraying PR particles (about 10–20  $\mu$ m) is usually only one-tenth of the tube diameter, the influence of the rotation speed is more obvious than the real-time heating during the spray coating. Especially for that using low-volatility

thinner, the real-time heating is more important. Otherwise, it is difficult to obtain continuous and smooth PR film surface. In addition, the effect of process parameters in the spray coating on the quality of PR film on tube surface has been fully studied in our previous work [3, 4].

### 2.2. UV projection lithography system for cylindrical substrate

**Figure 4** shows the sketch of the developed UV lithography system for tube surface. The whole system mainly consists of four units: a synchronized motion stage, a reduced projection exposure unit, a CCD multilayer alignment part, and a uniform illumination unit. After through a reduced mask image, the UV light used as exposure source will be focused onto the bottom surface of the tube with coated PR film. The wavelength of the used UV light is 250–600 nm. With regard to this, a 436 ± 10 nm interference filter was used to eliminate the aberration. Finally, the magnifying power of the objective lens will determine the amplification factor of the whole lithography system. In the present work, the overall reduced factor is 0.5 when the pattern of mask is transferred to the surface of the tube. This is reasonable and enough for our current research. By the abovementioned setting, a focal depth of ±45 µm can be realized in the developed UV lithography system that will be used to exposure and patterning the tube surface with coated PR film. Two chucks in the rotation stages are used to fix the tube in order to make sure the coaxial rotation. In addition, for adjusting the coaxiality conveniently, a laser was also used as a reference.

The final whole lithography system that includes five degrees of freedom (DOFs) is shown in **Figure 5(a)**. The patterns on mask and tube can be seen simultaneously by using two CCD, which can help to complete the secondary or multilayer alignment in the exposure. The side



Figure 4. Schematic illustration of programmable UV lithography system with alignment for cylindrical substrates [4].



**Figure 5.** Optical photo of (a) final developed lithography equipment and CCD for alignment and (b) side view and (c) top view in the programmable operation window.

view and top view in the programmable operation window are shown in **Figure 5(b)** and **(c)**, respectively. The programmable software can automatically control motorized XYZ- $\theta$  stages and exposure time. The movement and the rotation accuracies are 0.1 µm and 0.01° in the axial direction and the  $\theta$ -direction, respectively. By using PC operation window and doing those programmable sentences, the PR film on the tube surface can be patterned according to the design. Finally, the PR patterns with expected microstructures will be obtained on the tube surface after the development. This equipment can be used not only for tube exposure but also for those similar cylindrical substrates, such as optical fibers, capillary, metal or fabric wires, etc. The working principle of the developed lithography system can be found in our previous works [4, 5].

Micropatterning on the tube surface can be easily realized by using the developed programmable lithography equipment. Firstly, you can decompose the designed pattern into sequential programmable sentences in the PC operation window. Then, the software will automatically control the movements of stage, mask, and tube; the UV light will complete the exposure to the tube surface with coated PR film according to the programmable sentences. For example, you can complete an oblique line pattern on the tube by controlling the tube to parallel translation and rotate simultaneously. Of course, the final angle of the oblique line will be determined together by their two speed values in the respective directions. In the exposure, we can conveniently tune the intensity by changing the quantity of projection light and movement speed of the tube. Figure 6 is the preview patterns of some microstructures after completing the programmable sentences, such as (a) micro-heater and (b) resonator. These micropatterns will be firstly drawn by programmable operation window in our developed lithography system shown in Figure 5. Then, they will be fabricated on the silica glass tube surface. After the exposure of these cylindrical tubes with coated PR film by the above programmable lithography system, the development was carried out subsequently. As a result, the PR films on the tube surfaces have been successfully patterned as those expected program patterns in Figure 6(a) and (b), which are as shown in Figure 6(a') and (b').

After sputtering Pt film and subsequent lift-off process, the two kinds of microstructures are clearly seen, including zigzag micro-heater and partial patterns of resonator, which are



**Figure 6.** Planar previews of the programmed (a) micro-heater and (b) resonator patterns and (a'-b') obtained micropatterns on silica glass tube after exposure and development according to corresponding programmed patterns.



Figure 7. SEM of fabricated (a) zigzag structures of micro-heater and (b) resonator.

shown in **Figure 6** (a') and (b'). **Figure 7** shows the Scanning Electron Microscope (SEMs) of these microstructures. The PR film thickness and the line width are ~2 and 20  $\mu$ m, respectively. As so far, the line width of 10  $\mu$ m has been obtained by using special fabrication process in our developed lithography system.

# 3. Application examples

### 3.1. Flexible implantable microtemperature sensor

The hyperthermia is still considered as an effective way for the cancer treatment, which has been proven in many clinical studies. In the treatment, the microwave was used to heat the lesion to above 42°C in order to kill tumors. At the same time, we have to make sure the normal tissue not to be damaged [6]. So, in the hyperthermia it is necessary to develop a microtemperature sensor for measuring the temperature precisely. Although many researchers have fabricated some microtemperature sensors, they cannot be used as a flexible device to implant into the objects due to its fabrication based on silicon process [6-8]. Its natural brittle feature is not beneficial. Therefore, some researchers try to develop thinner sensor based on the cylindrical substrate in order to implant into the tissue. For example, a microcoil on the capillary surface for magnetic resonance imaging (MRI) interventional treatment has been reported in Ref. [9]. Similarly, in Refs. [10, 11], a radio frequency (RF) coil has also been developed on the cylindrical surface for portable nuclear magnetic resonance (NMR) diagnosis. In addition, the soft lithography technology was used to realize patterning on the curved surface in Ref. [12]. Even, in order to fabricate microstructures on the thin cylindrical substrate, an automatic wire bonder was also utilized in the work [13, 14]. However, in these methods the devices are usually fabricated on glass capillary or metal stick surface. The whole flexibility of the sensor is poor, and corresponding fabrication resolution and sensitivity are neither not good. In addition, in these methods only one kind of material can be used and fabricated because the multilayer alignment cannot be realized. As a result, their applications have been subjected to a lot of limitations.

In the present work, using the developed programmable UV lithography system, a flexible implantable microtemperature sensor for hyperthermia application will be designed and fabricated. Finally, the fabricated microtemperature sensor will be also evaluated in detail.

In this work, we design a flexible implantable microtemperature sensor on a polymer tube with only  $330 \ \mu m$  outer diameter for hyperthermia application. This sensor will be fabricated
using the above developed lithography system. The design sketch of the temperature sensor and its corresponding general working principle is shown in **Figure 8(a)**. In the future practical application, you can implant the part of the sensor into the tumor and monitor its temperature. The doctor can make a right decision and precise operation by referring the measured result from the microtemperature sensor. The material of the sensing element in the sensor is platinum (Pt) considering its good resistance-temperature effect. The sensing element and its geometric parameters are shown in **Figure 8(b)** and **(c)**, respectively.

ANSYS was used to do the simulation of the microtemperature sensor. **Figure 9** is the 2D model of the sensor, which only contains one Pt line and pitch unit because of its symmetry. The polymer tube from Furukawa Electric Co., Ltd. was used as the substrate because of its excellent physical and chemical stabilities. It is substantially a kind of commercial polyimide (PI) material. Especially, this tube can withstand the temperature up to 200°C. Before simulation the related boundary conditions need to be determined according to application environment. The temperature of tube surface was set as 37°C, which was considered as the normal tissue. Here, 42°C is set as the highest temperature in the hyperthermia. The transient simulation was carried out for dynamic response of the designed microtemperature sensor. **Figure 9(b)–(g)** shows the simulated results. It can be seen that the temperature didn't continue to spread along the vertical direction of the tube surface until the moment about 2–4 ms, which means the response time of the sensor.



Figure 8. (a) Sketch of the flexible microtemperature sensor on the polymer tube for hyperthermia, (b) sensing element, and (c) its structural parameters [4].



Figure 9. Dynamic simulation of microtemperature sensor used in hyperthermia. (a) FE model and (b)–(g) transient temperature field distributions [4].

The general fabrication process of the temperature sensor is described in Figure 10, as follows:

- **a.** Cleaning the polymer tube. Using a UV ozone treatment unit (VX-0200HK-002, ACingTec, Japan) to clean the surface and modification.
- **b.** Spray coating ~2.5  $\mu$ m PR on the tube substrate by developed homemade coating system.
- **c.** Exposure and patterning of the polymer tube with coated PR film by developed cylindrical lithography method.
- **d.** Magnetron sputtering Pt film (~0.13  $\mu$ m) onto the patterned tube surface.
- e. PR film was removed by lift-off.
- f. Again spray coating PR film (~2 µm) on the tube with patterned Pt microstructures.
- g. Secondary exposure and development were done to pattern the PR film again.
- **h.** SiO<sub>2</sub> layer ~0.3  $\mu$ m was deposited on the Pt film for electric isolation.
- **i.** Obtaining the microtemperature sensor after removing the residual PR film by acetone solution. The detailed fabrication process steps of the sensor can be found in our previous report [15].

The polymer tube substrates used in this work were all cleaned by immersing in the  $H_2SiO_4/H_2O_2$  solution at 115°C for 15 min and then rinsed with purified water. The PR film was depositing on the tube surface by homemade spray coating setup. During the spray coating, the real-time heating was used always. The thickness of coated PR film can be controlled by cycle spray coating number and tube rotation speed. In the fabrication of Pt sensing element in the



Figure 10. Main fabrication processes of flexible microtemperature sensor on the polymer tube.

sensor, the quality of the Pt film is very important considering it is used as the critical sensitive material. The sputtering condition is the vacuum  $7.0 \times 10^{-4}$  Pa, the purity of Ar gas 99.9%, the purity of Pt target 99.99%, and sputtering power 100 W. The fabrication process steps of the microtemperature sensor are described in our previous work [15].

The optical photo of the final fabricated flexible microtemperature sensor is shown in **Figure 11**. It can be seen that the sensor has a good flexibility. The Pt sensing element in the sensor can be also seen clearly in the right picture in the figure. Also, the line patterns of the fabricated sensing element on the polymer tube are clearly shown in **Figure 12**.

Platinum (Pt) film temperature sensing will experience a change in resistance with environmental temperature according to the following formula:

$$R_{t} = R_{0} [1 + \alpha (T - T_{0})]$$
<sup>(1)</sup>

where  $R_t$  is the resistance at the working temperature T and  $R_0$  is the resistance at the reference temperature  $T_0$ . And,  $\alpha$  is the temperature coefficient of resistance (TCR). By slowly increasing and reducing the temperature from room temperature to 90°C, we can obtain the TCR, as shown in **Figure 13**. It is generally 0.0034/°C. This measured value is lower than the theoretical value of bulk pure Pt (0.0039/°C) because the electron scattering would be cause grain not be density during the film sputtering [16]. Of course, the deviation will also be caused by fabrication parameters, testing method, etc.



Figure 11. Optical photo of the fabricated flexible microtemperature sensor next to a coin for reference and its sensing element micropattern.



Figure 12. SEM photograph of the fabricated flexible microtemperature sensor on polymer tube surface.

#### 3.2. Flexible implantable microneedle with three-electrode system for glucose sensor

As another example of the developed programmable UV lithography system, a threeelectrode system will be designed and fabricated on a polymer tube surface. As a result, the tube with three-electrode microstructure can be used as a flexible microneedle, which could be promising in the implantable glucose sensor for human body in the future. **Figure 14(a)** is the sketch of the designed system and its configuration. The one end of the microneedle can be used as an implantable sensor considering its flexibility and thin size. In addition, the hollow structure of the tube may be as a convenient path for potential drug delivery. The three-electrode structure is as follows: counter electrode (CE), reference electrode (RE), and working electrode (WE). **Figure 14(b)** and **(c)** shows the corresponding geometric parameters and configurations. Some external measuring and controlling systems are also necessary if the microneedle would be used in the glucose monitoring and insulin injecting.

**Figure 15** generally describes fabrication steps of the three-electrode structure on the polymer tube, as follows:

- a. Polymer tube substrate ready and cleaning the surface of the tube using plasma.
- **b.** Spray coating PR film ~2  $\mu$ m on the polymer tube surface by developed spray coating system.



Figure 13. Test TCR of the flexible microtemperature sensor fabricated on the polymer tube surface.



Figure 14. (a) Sketch of the interventional flexible implantable microneedle with three-electrode system for continuous glucose monitoring and drug delivery, (b) distributions, and (c) main structural parameters [17].

- **c.** Patterning the tube with coated PR film according to the programmable micropattern of three-electrode pattern using the developed programmable UV lithography equipment.
- **d.** Magnetron sputtering of 120 nm thick Pt film onto the tube surface with patterned PR. Lift off and remove the residual PR and obtaining three-electrode patterns.
- e. The second spray coating PR and lithography with alignment.
- **f.** Sputtering Ag layer and AgCl layer preparation; remove residual PR film by lift-off process. Finally, the three-electrode pattern was completed. The detailed fabrication process steps of the microneedle can be found in our previous reports [17, 18].

In the above fabrication of the three-electrode structure, the Ag/AgCl electrode must be completed according to programmable patterns as shown in **Figure 16**. In addition, the second lithography with alignment in the experiment is very critical. The related operation can be found in our previous work [17]. **Figure 16** shows the programmable micropattern of the three-electrode system (left) and the three-electrode structure obtained by programmable lithography equipment with multilayer alignment: PR boundaries in  $-40^{\circ}$  and  $-10^{\circ}$  views after the development by secondary alignment (right). So far, we have realized the ±1 µm alignment precision using the developed lithography system.

**Figure 17** is the final fabricated three-electrode structure on the polymer tube surface. The whole structure can be used as an implantable flexible microneedle because of its good flexibility property. Generally, this proposed device shows better overall property than other similar reports [19–24]. The novel design including a three-electrode structure on a thin hollow tube will be very useful for some applications in the micro-total analysis systems ( $\mu$ TAS) in the future.



Figure 15. Main fabrication process of the three-electrode structure in flexible microneedle on polymer tube surface.



**Figure 16.** Programmable micropattern of the three-electrode system (left) and three-electrode structure obtained by programmable lithography equipment with multilayer alignment: PR boundaries in  $-40^{\circ}$  and  $-10^{\circ}$  views after the development by secondary alignment (right).



Figure 17. SEM and optical photo of the fabricated three-electrode system on a polymer tube surface as a flexible microneedle.



Figure 18. Measured cyclic voltammetry curve of the three-electrode pattern on the fabricated prototype microneedle on polymer tube surface.

Next, the fundamental electrochemical property of the fabricated three-electrode structure was measured. The detailed measuring method, conditions, and related equipment used can be found in our previous work [17]. The measured cyclic voltammetry (CV) curve is shown in **Figure 18**. It indicates the device has a good redox property. But the peak of the test current is not very evident. Very small reaction area in the three-electrode pattern is considered as a main reason because of thin tube diameter. In addition, the quality of the sputtering Pt film is another affected factor. We can obtain an estimated peak current density according to the above measured result, about 0.8 mA/dm<sup>2</sup>, which is sufficient for subsequent circuit signal processing in the glucose sensor application. In addition, our fabricated flexible microneedle device can be more easily implanted into the objects compared to other reported ones [23–26].

## 4. Conclusion

In this chapter, a lab-on-a-tube surface micromachining technology for cylindrical substrates has been built for the first time based on the developed programmable UV lithography system with alignment. The related equipments used in the lab-on-a-tube surface micromachining,

including a homemade spray coating system and a projection exposure system for cylindrical substrate, have been introduced, and corresponding working principle and process parameters have been also explained. Then, as the application examples, an implantable flexible microtemperature sensor and an implantable microneedle with integrated three-electrode system on the tube surfaces have been proposed, fabricated, and characterized. The magnetron sputtering Pt film is used as the sensing material in the temperature sensor. The test TCR of the fabricated sensor is 0.0034/°C. The fabricated three-electrode structure on the polymer tube in CV measurement shows a good performance. The developed microneedle with the integrated three-electrode pattern will be very promising in the implantable glucose sensor for the human body in the future.

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# References

- [1] N. P. Pham, J. N. Burghartz and P. M. Sarro, "Spray coating of photoresist for pattern transfer on high topography surfaces," *J. Micromech. Microeng.*, vol. 15, pp. 691–697, 2005.
- [2] V. K. Singh, M. Sasaki, K. Hane, Y. Watanabe, H. Takamatsu, M. Kawakita and H. Hayashi, "Deposition of thin and uniform photoresist on three-dimensional structures using fast flow in spray coating," *J. Micromech. Microeng.*, vol. 15, pp. 2239–2345, 2005.
- [3] Y. Lu, Y. Zhang, J. Lu, A. Mimura, S. Matsumoto and T. Itoh, "Three-dimensional photolithography technology for fiber substrate by using microfabricated exposure module," *J. Micromech. Microeng.*, vol. 20, 125013(10pp), 2010.
- [4] Z. Yang, Y. Zhang, T. Itoh and R. Maeda, "Flexible implantable microtemperature sensor fabricated on polymer capillary by programmable UV lithography with multilayer alignment for biomedical applications," J. Microelectromech. Syst., vol. 23, no. 1, pp. 21–29, 2014.

- [5] Z. Yang, S. Liu, F. Xue, Y. Zhang, X. Zhao, J. Miao and L. K. Norford. "Micro anemometer by a MEMS compatible lab-on-a-tube technology", 18th International Conference on Solid-State Sensors Actuators and Microsystems (TRANSDUCERS 2015), 2015.
- [6] L. Lin, Q. Pei, J. Xu and H. Guo, "A microfabricated temperature sensor for hyperthermia," in 5th IEEE International Conference on Nano/Micro Engineering and Molecular Systems (NEMS), Xiamen, China, 2010.
- [7] S. Y. Xiao, L. F. Che, X. X. Li and Y. L. Wang, "A novel fabrication process of MEMS devices on polyimide flexible substrates," *Microelectron. Eng.*, vol. 85, pp. 452–457, 2008.
- [8] D. Resnik, D. Vrtačnik, M. Možek, B. Pečar and S. Amon, "Experimental study of heattreated thin film Ti/Pt heater and temperature sensor properties on a Si microfluidic platform," J. Micromech. Microeng., vol. 21, no. 2, p. 025025, 2011.
- [9] D. Mager, V. Badilita, U. Loeffelman, P. J. Smith and J. G. Korvink, "Micro-MR coil construction by combining metal-on-glass inkjetting and MEMS techniques," in *Proc. Int. Soc. Mag. Reson. Med.*, West Yellowstone, USA, 2009.
- [10] V. Demas, A. Bernhardt, V. Malba, K. L. Adams, C. Harvey, R. S. Maxwell and J. L. Herberg, "Electronic characterization of lithographically patterned microcoils for high sensitivity NMR detection," *J. Magn. Reson.*, vol. 200, pp. 56–63, 2009.
- [11] S. Goto, T. Matsunaga, Y. Matsuoka, K. Kuroda, M. Esashi and Y. Haga, "Development of high-resolution intraluminal and intravascular MRI probe using microfabrication on cylindrical substrates," in 20th IEEE International Conference on Micro Electro Mechanical Systems (MEMS), Kobe, Japan, 2007.
- [12] J.G. Kim, N. Takama, B.J. Kim and H. Fujita, "Optical-softlithographic technology for patterning on curved surfaces," J. Micromech. Microeng., vol. 19, no. 5, p. 055017, 2009.
- [13] K. Kratt, M. Seidel, M. Emmenegger, U. Wallrabe and J. G. Korvink, "Solenoidal micro coils manufactured with a wire bonder," in 21st IEEE International Conference on Micro Electro Mechanical Systems (MEMS), Tucson, USA, 2008.
- [14] D. L. Olson, T. L. Peck, A. G. Webb, R. L. Magin and J. V. Sweedler, "High-resolution microcoil <sup>1</sup>H-NMR for mass-limited, nanoliter-volume samples," *Science*, vol. 270, pp. 1967–1970, 1995.
- [15] Z. Yang, Y. Zhang and T. Itoh, "A flexible implantable microtemperature sensor on polymer capillary for biomedical applications", 26th International Conference on Micro Electro Mechanical Systems (IEEE MEMS 2013), 2013.
- [16] G. Fischer, H. Hoffmann and J. Vancea, "Mean free path and density of conductance electrons in platinum determined by the size effect in extremely thin films," *Phys. Rev. B*, vol. 22, no. 12, pp. 6065–6073, 1980.
- [17] Z. Yang, Y. Zhang, T. Itoh and R. Maeda, "New fabrication method of three-electrode system on cylindrical capillary surface as a flexible implantable microneedle," *Surf. Rev. Lett.*, vol. 22, 1350027(8pp), 2013.

- [18] Z. Yang, A. Toda, Y. Zhang, T. Itoh and R. Maeda. "An interventional flexible microneedle with three-electrode system on the capillary for continuous glucose monitoring and drug delivery", 2013 Transducers & Eurosensors XXVII: The 17th International Conference on Solid-State Sensors Actuators and Microsystems (TRANSDUCERS & EUROSENSORS XXVII), 2013.
- [19] H. Huang and C. Fu, "Different fabrication methods of out-of-plane polymer hollow needle arrays and their variations", J. Micromech. Microeng., vol. 17, pp. 393–402, 2007.
- [20] L. J. Fernández, A. Altuna, M. Tijero, G. Gabriel, R. Villa, M. J. Rodríguez, M. Batlle, R. Vilares, J. Berganzo and F. J. Blanco, "Study of functional viability of SU-8 based microneedles for neural applications", J. Micromech. Microeng., vol. 19, p. 025007, 2009.
- [21] A. Altuna, G. Gabriel, L. M. De La Prida, M. Tijero, A. Guimerá, J. Berganzo, R. Salido, R. Villa and L. J. Fernández, "SU-8-based microneedles for *in vitro* neural applications", *J. Micromech. Microeng.*, vol. 20, p. 064014, 2010.
- [22] S. J. Moon and S. S. Lee, "A novel fabrication method of a microneedle array using inclined deep x-ray exposure", J. Micromech. Microeng., vol. 15, pp. 903–911, 2005.
- [23] M. Kimura, K. Bundo, Y. Imuro, Y. Sagawa and K. Setsu, "Chronoamperometry using integrated potentiostat consisting of poly-Si thin-film transistors", *IEEE Electron. Device Lett.*, vol. 32, pp. 212–214, 2011.
- [24] J. D. Zahn, D. Trebotich and D. Liepmann, "Microdialysis microneedles for continuous medical monitoring", *Biomed. Microdevices*, vol. 7, pp. 59–69, 2005.
- [25] S. Zimmermann, D. Fienbork, B. Stoeber, A. W. Flounders and D. Liepmann, in 12th International Conference on Solid-State Sensors, Actuators and Microsystems (Transducers'03), Boston, USA, 2003 99.
- [26] K. E. Toghill and R. G. Compton, "Electrochemical non-enzymatic glucose sensors: A perspective and an evaluation", *Int. J. Electrochem. Sci.*, vol. 5, pp. 1246–1301, 2010.

# Efficient Optimization of the Optoelectronic Performance in Chemically Deposited Thin Films

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Additional information is available at the end of the chapter

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#### Abstract

Chemical deposition methodology is a well-understood and highly documented category of deposition techniques. In recent years, chemical bath deposition (CBD) and chemical vapor deposition (CVD) have garnered considerable attention as an effective alternative to other deposition methods. The applicability of CVD and CBD for industrial-sized operations is perhaps the most attractive aspect, in that thin-film deposition costs inversely scale with the processing batch size without loss of desirable optoelectronic properties in the materials. A downside of the method is that the optoelectronic characteristics of these films are highly susceptible to spurious deposition growth mechanisms. For example, increasing the temperature of the chemical deposition bath can shift the deposition mechanisms from ion-by-ion (two dimensional) precipitation to bulk solution cluster-by-cluster (three dimensional) formation which then deposit. This drastically changes the structural, optical, and electrical characteristics of CBD-deposited thin films. A similar phenomenon is observed in CVD deposited materials. Thus, it is of great interest to study the coupling between the deposition parameters and subsequent effects on film performance. Such studies have been conducted to elucidate the correlation between growth mechanisms and film performance. Here, we present a review of the current literature demonstrating that simple changes can be made in processing conditions to optimize the characteristics of these films for optoelectronic applications.

**Keywords:** chemical bath deposition, chemical vapor deposition, performance optimization, perovskites, optoelectronic performance



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# 1. Introduction

The intent of this chapter is to cover the most recent advances achieved in optimization of chemically deposited thin films. The most prominent and widely used chemical deposition processes are chemical bath deposition (CBD) and chemical vapor deposition (CVD) methods. Recent breakthroughs in film optimizations relating to these methods will be the focus of this monograph.

Advanced thin films are the key enabler of the modern high-tech explosion. These materials find uses in military, defense, private, and commercial products with a truly limitless potential. It can be argued that every piece of electrical equipment, tool, hardware, and device commercially available relies, to some extent, on advanced processing of thin-film materials and our ability to scale those processes for cost-effective mass production.

Although CBD and CVD methods have been known since the 1940s and 1950s, respectively, the pursuit of cost reductions has driven recent research efforts in these fields [1, 2]. Specifically, the past decade has seen developments in the performance optimization of thin films by altering the deposition parameters. This has allowed for improved film characteristics without additional cost and spurred research into the growth and optimization of organic semiconductors [3–6]. Further, CVD and CBD have facilitated efficient device manufacturing by enabling systematic film layer depositions. Additional layers of a single material or of multiple materials may be deposited as necessary to grow monolithic structures for advanced applications. Such mesoscopic assemblies opened new doors for device manufacturing and optimization. These novel approaches are expected to further expand the capabilities of the current technology in a wide range of applications.

The recent advances in this particular field of science are far-reaching and extend beyond the scope of this chapter. This chapter reviews only the mainstream and high-impact achievements in chemically deposited thin films. Some of the current challenges and limitations of these methods are also addressed. This chapter is divided into two sections: the first section addresses the chemical bath deposition technique, structural and optoelectronic characterization, and performance of CBD deposited thin films; the second section deals with the chemical vapor deposition and performance and tunability of CVD deposited thin films. Tunability and deposition parameter optimization of film performance are addressed in both sections.

# 2. Chemical bath deposition (CBD)

The roots of chemical bath deposition extend back over a century [7]. It was initially shown that high-quality chalcogenides and oxides could be deposited using this simple cost-effective technique [8]. At the time, however, the semiconductor theory was decades away. Thus, only a few enthusiasts exhibited initial interest in the method. As the power of thin-film semiconductors was realized, the demand for such high-performance materials exploded. The market demand required a cost-effective method, which could sustain the production of high-quality

thin films. By this time, CBD was already a well-established process shown to produce highly crystalline structures and, thus, was a natural choice for such an application [9]. Research at that time showed that the method could also be applied for the deposition of metals, metallic alloys, chalcogenides, oxides, carbonates, and halides, all of which are an inherent part of next-generation organic semiconductors [10–12]. In more recent years, the process has been extended to deposit electron and hole transport layers (ETL and HTL, respectively), transparent conducting oxides (TCO), nanotubes, copper indium gallium selenide (CIGS) devices, and numerous other applications [13–17]. Further, the CBD method is inexpensive, easy to implement, convenient for large area depositions, and associated with highly favorable optoelectronic and structural properties [18, 19]. The power and the usefulness of the method cannot be overstated. Because of its broad applicability, CBD became a focus of numerous research groups.

### 2.1. CBD theoretical considerations

The underlying concept behind CBD is the rearrangement of the chemical constituents in the bath or already deposited on a substrate into functional crystalline structures during the chemical reactions. The original size of the chemical constituents can range from subatomic particles to microscale molecules. CBD finds a broad range of applications because it can be applied to a wide variety of chemicals. This concept is demonstrated further in the following examples.

(a) Electron exchange (redox)

Changes in oxidation numbers in elements during a chemical reaction indicate a redox reaction taking place. Such reactions take place in the CBD formations of metal, nonmetallic compounds, and oxide films, through direct oxidation or oxidative redux in which the electron exchange takes place among more than two elements. Insoluble lead dioxide [PbO<sub>2</sub>], for example, forms from the oxidative redux of peroxydisulfate ion [ $S_2O_8^{2-}$ ] in water, as shown in Eq. (1) [20]:

$$Pb^{2+} + S_2 O_8^{2-} + 2H_2 O \rightarrow PbO_2 + 2SO_4^{2-} + 4H^+$$
 (1)

## (b) Ligand exchange

This type of reaction involves the exchange of ligands in a complex ion. Highly desired silicon dioxide  $[SiO_2]$  is precipitated using reaction 2 through the exchange of oxygen and fluorine ions. In general, this reaction holds an advantage in that it is generally more specific, allowing high selectivity in the produced compounds to be achieved [20]:

$$SiF_{4}^{2-} + 4H^{+} + BO_{3}^{3-} \rightarrow SiO_{2} + H_{2}O + BF_{4}^{-}$$
 (2)

## (c) Complex reaction

This type of reaction occurs by a coordinated exchange of complexes in a chemical bath, as illustrated in Eq. (3). Because of the potential for additional reactions, complex exchange reactions can have drawbacks that require advanced consideration. For example, due to its availability and low cost, thiourea  $[SC(NH_2)_2]$  is a common sulfur source used in CBD. Exchange

of sulfur from the thiourea requires complex decomposition and reaction. Although the stable molecule cyanamide  $[CN_2H_2]$  is a common by-product of the thiourea decomposition, formation of reactive and toxic cyanide  $[CN^-]$  has also been reported [21]. Such undesirable decompositions can have adverse effects on the overall deposition process:

$$Cd(NH_3)_4^{2+} + SC(NH_2)_2 + 2OH^- \rightarrow CdS + CN_2H_2 + 2H_2O$$
(3)

The existence of numerous approaches to growing films in solutions is illustrated in the basic reactions discussed in Eqs. (1)–(3). It should also be inferred that careful consideration of each chemical reaction by-product is necessary to prevent contamination of the film or undesired waste products. The structural properties, precipitation rates, crystallinities, and—of greater interest—optical and electrical performance of materials can thus be controlled with careful planning. Perhaps, the most promising category of materials derived from a theoretical understanding of CBD has been organic semiconductors. Recently, CBD was used to crystallize CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite powders for use in highly efficient organic-inorganic perovskite solar cells [22]. This would not have been possible without a deep theoretical understanding of the chemical reaction.

Reliably predicting film performance and controlling the deposition mechanisms is a formidable challenge. Charge carrier mobilities, for example, depend on the grain size, layer composition, porosity, interstitial trapping, doping, contaminants, diffusion lengths, substrate, bond lengths, and a plethora of other factors [23–25]. Recent deviations between continuum and atomistic level simulations stress this point further [26, 27].

However, it has been shown that it is possible to conduct an in situ study of the deposition parameters, deduce growth mechanisms, and reproduce the film performance from such simulations [28]. Accumulated experimental data are then utilized to converge atomistic models for accurate computational predictions [29]. The remainder of this section will discuss the accumulated experimental data on the corporeal control of the CBD process and its effects on film performance.

## 2.2. CBD experimental data

Two main deposition mechanisms dominate thin-film growth during CBD. The first, ion-by-ion (two dimensional) mechanism is the sequential reaction between ions to form clusters, shown in **Figure 1(a)**. Typically, this method produces highly stoichiometric crystals and can be finely controlled by the bath pH, temperature, and constituent concentrations. The second mechanism utilizing precipitation taking place in the bulk of the solution and known as cluster-by-cluster (three dimensional) growth is shown in **Figure 1(b)**. In general, there is less control over this latter mechanism, with the resulting structures deviating from stoichiometry calculations, often containing interstitial traps and producing unique optical and electrical material properties.

It is widely reported that the optoelectronic performance of chemically grown thin films is strongly dependent on the deposition mechanisms [30]. To evaluate this, the nonintrusive method of spectroscopic ellipsometry (SE) could be used to analyze the role of bath parameters on the deposition mechanisms. The films could then be subsequently analyzed using more intrusive methods to better understand the full scope of the relationship.

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**Figure 1.** (a) Ion by ion and (b) cluster by cluster are the two dominating deposition mechanisms during chemical bath deposition. Ions permeate the solution precipitating on top of the substrate during growth in the ion-by-ion mechanism. As opposed to the cluster agglomerations forming in the bulk of the solution prior to attaching themselves to the substrate in the cluster-by-cluster mechanism.

SE analysis revealed three growth stages. The first stage was a short induction time, during which time little or no observable growth took place. Some of the material was observed to precipitate in the solution (although negligible amount showed adhesion to the substrate). The masses forming in the solution at this stage have not reached the critical diameter for crystallization. The second stage was a fairly linear growth period, dominated by the ion-by-ion mechanism.

This steady epitaxial growth produced highly compact stoichiometric films. The third stage was then dominated by the cluster-by-cluster mechanism in which clusters formed in the solution reached a critical size and could precipitate, producing a porous layer on top of the film. The porous layer typically established the surface roughness of the film. In some instances, this layer could be minimized by immediate washing following the chemical bath deposition [30]. Three distinct layers deposited by CBD are visible in the scanning electron microscope (SEM) images shown in **Figure 2**.

The nonintrusive SE measurements were used to study the effects of bath temperatures on the thickness of each layer. Data were collected on the films deposited at bath temperatures ranging from 55°C to 95°C. Physical models representative of the film structures were constructed consisting of three layers of quartz glass. The porosity and chemical composition of each layer were adjusted until a high correlation between the experimental and measured data was achieved [28].

It was found that at low bath temperature (i.e., 55°C) nearly 85% of the structure consisted of a highly stoichiometric and compact thin film. The porous surface layers in such films were

~1% of the entire structure thickness. This is indicative of substantial growth through the ionby-ion deposition mechanism, which overwhelmingly dominates at low bath temperatures. Increase in the bath temperature was accompanied by a steady transition to the cluster-bycluster mechanism. At a bath temperature of 95°C, the compact layer constituted ~60% of the entire structure thickness.



Figure 2. (a) Planar and (b) cross-sectional SEM reveal tight crystalline structure with three distinct layers.

The porous layer made up the majority of the rest of the film assembly [28]. These results indicate the coexistence of the two deposition mechanisms taking place in the bath during film formation. At lower temperatures, the ions are less likely to saturate the solution allowing the two-dimensional mechanism to dominate the film growth. As the temperature rises, the ion concentrations saturate and begin to form particulates in solution, causing the ion-by-ion mechanism to be supplemented by cluster-by-cluster growth.

It was realized that if a clear correlation between the optoelectronic performance of films and their growth mechanisms could be established, optimization of film performance through efficient means in the bath could be achieved. The high-impact nature of establishing this correlation prompted a significant amount of research on the topic.

One research topic of interest was the oxidation of the dangling bonds on the surface of stoichiometric crystalline films, which could be studied using X-ray photoelectron spectroscopy (XPS). XPS spectra of a CdS thin film as deposited on an n-InP substrate and a corresponding film after a 1-minute treatment with a buffer oxide etch (BOE) are shown in **Figure 3(a)** and **(b)**, respectively. The ratio of S:Cd prior to the 1 min BOE etch is found to be ~0.6 and increases to ~0.85 after the etch. These results reveal a thin (~30 nm) passivation CdO layer forming on top of the films [31]. Similar results have been widely reported in various materials deposited by CBD method [19]. Such stoichiometric structures are explained by the dangling bonds on the surface of the materials.

In general, the valence electrons deep in the bulk of the material are committed to the covalent bonds between the elements. Electrons near the film surface are less constrained, resulting in the dangling bonds. This allows for the ambient oxygen to oxidize the materials at or near the surface, resulting in a thin layer of oxide being formed [19]. This thin oxidation layer prevents degradation of the films and introduces passivation properties in high-speed field-effect transistors. During subsequent depositions the layer acts as a buffer [31]. Oxidation removal from nanocrystalline thin films becomes an important step in efficiency enhancement of the monolithic structures, such as in CIGS. Similar passivation layer formations are not observed under three-dimensional (cluster by cluster) deposition mechanisms [28].



Figure 3. XPS spectra of an n-InP sample with (a) 2 min CdS deposition at 75°C and (b) CdO removal with 1 min of BOE immersion.

Optoelectronic performance of films is known to be heavily dependent on the crystalline structure of the materials [32, 33]. Crystallinity is of great interest for lattice matching in thinfilm devices such as CIGS. Extensive X-ray diffraction (XRD) studies of film structures have been conducted and revealed that crystallinities are highly dependent on deposition temperatures. As an example, XRD data of CdS films deposited at various bath temperatures are shown in **Figure 4**. Lower deposition temperatures tend to deposit highly symmetric crystals—zinc blende (cubic) in the case of the CdS. As the bath temperatures are increased, a noticeable shift from symmetric to asymmetric structures is observed—wurtzite (hexagonal) structures in the case of CdS.



Figure 4. XRD patterns for CdS samples deposited at various bath temperatures. Spectra reveal a shift towards the hexagonal structures at higher deposition temperatures.

Under the three-dimensional deposition mechanism, much of the cluster agglomeration takes place in the bulk of the solution. These irregularly shaped clusters form the asymmetrical structures that attach themselves to the substrate. This is in contrast to the two-dimensional deposition mechanism which creates a uniform lateral expansion of the crystals. This contrast in film growth causes the structural differences produced by the two methods.

The cluster agglomeration, i.e., three-dimensional deposition mechanism, is expected to force interstitial trapping of the large cations in the bath. These trapped ions then act as dopants in the semiconductor, either releasing free electrons or introducing holes to the material. This drastically changes the optoelectronic performance of the films. Several groups pursued solid-state nuclear magnetic resonance (NMR) studies that substantiate this hypothesis. NMR analysis of three-dimensional deposited films reveals an increase in the peak intensity corresponding to cations intrinsic in the solution [28, 34].

These studies validate that the typically large cations of the inorganic thin films are trapped during the three-dimensional cluster agglomeration. Careful consideration of this phenomenon may be used to optimize film performance without the use of extrinsic dopants. Conversion efficiencies have been shown to improve nearly 5% by the careful use of interstitial trappings [34]. There is an additional challenge, however, that needs to be considered in order to achieve effective doping. Transition metals with large numbers of valence electrons are widely used as dopants in various inorganic thin films [35, 36].

However, work in this field demonstrated a limit in the doping efficiency for these metals [37, 38]. This is mainly due to formation of polyoxometalates between the transition metals and other ions in the chemical bath. The valence electrons that otherwise would be donated to the material are instead localized into formed complexes [39], which limit the doping efficiencies to ~1 donated electron per ion. This phenomenon is observed even in the materials with upward of seven valence electrons [37, 38]. Unpublished results from an ongoing study at the University of Virginia use interstitial iridium trapping to prove the possibility of overcoming theoretical doping efficiency limits.

Building on the aforementioned research, it is of great interest to tie the optoelectronic performance of the films to the growth mechanisms in the bath. Highly stoichiometric films grown by the ion-by-ion deposition mechanisms possess properties typical of intrinsic materials. Deviation from stoichiometry (i.e., introduction of the cluster-by-cluster mechanisms) noticeably changes the film characteristics. A case study of CdS is presented below.

Thin films of CdS fabricated under various deposition mechanisms were widely studied to show that the cluster-by-cluster growth mechanism produces a blend of crystalline structures. As previously mentioned, the XRD data revealed the formation of a blended cubic/ hexagonal structures as temperature increased (**Figure 4**) [40, 41].

The refractive index (*n*) and extinction coefficient (*k*) over the range of deposition temperatures were obtained utilizing multiwavelength ellipsometer and are shown in **Figure 5(a)** and **(b)**, respectively. Two maxima in the refractive index located at ~280 and ~410 nm are visible in the films deposited at 55°C bath temperatures. There is a noticeable shift in the location of the maxima at higher bath temperatures. The two maxima in the latter cases are found at ~475 and ~275 nm wavelengths. These maxima are well studied and understood to be the fundamental absorption peaks in the transition along  $\Gamma \rightarrow A$  Brillouin zone (BZ) boundaries in the CdS structure [42]. The shift in the locations of the maxima, however, testifies to the structural changes taking place in the crystals. At low bath temperatures, the location of the maxima is found to match expectations for the cubic structured CdS.

At higher deposition temperatures, however, the maxima are located slightly below the expected locations for the hexagonal structures [43, 44]. A noticeable variation in the change of the onset of the extinction coefficient is also observed. This is suggestive of a change in the optical band gap. Such a shift has been widely reported and is attributed to the cubic-hexagonal transitions taking place in the CdS film structure [45]. In a greater context, the multiwave-length analysis testifies that the ion-by-ion deposition mechanism favors the crystallization of highly symmetric structures, whereas the cluster-by-cluster deposition mechanism tends to produce asymmetry in crystallization and deviation from stoichiometry. However, the resulting structures are rarely of a single phase, and even at higher bath temperatures, the two-dimensional deposition mechanism contributes significantly to the overall structure of the film.

Changes in the crystallinity of the materials have a significant impact on the overall optical properties. Optical performance of the aforementioned CdS films was studied in an effort to understand the growth mechanism/optical performance relationship. Significant changes in

the reflectance and absorbance spectra are observed with the rise of the hexagonal phase in the film, as shown in **Figure 5(c)** and **(d)**, respectively. The three observed dips in the reflectance and absorbance data coincide with the valence band splits in  $\Gamma_{g'}$   $\Gamma_{\tau'}$  and  $\Gamma_5$  previously reported for CdS [46]. Reflectance is significantly higher in three-dimensionally grown films. The absorbance curve shows a steeper slope for the low deposition temperatures and a fairly flat absorption tail. These results suggest lower reflectance and higher absorbance of the symmetric structures deposited by two-dimensional mechanisms. Such results would be expected in the epitaxially grown films. The random distribution of the clusters produced by the three-dimensional mechanisms scatters light resulting in less favorable optical properties.



Figure 5. (a) Refractive index (n), (b) extinction coefficient (k), (c) reflectance, and (d) absorbance over a range of deposition temperatures.

Analysis of the electrical performance of CdS films deposited under different conditions was also conducted. Summary of the film's electrical properties is shown in **Table 1**. Cd:S ratios were computed from the XPS spectra and validated using energy-dispersive spectroscopy (EDS). Cd and S constituted the majority of the film composition. Traces of C, Ca, and Na contaminants were also observed but in negligible amounts. As can be seen from the data, the films deposited at low bath temperatures are highly stoichiometric.

This is evident from the 1:1 ratio between the  $Cd^{2+}$  and  $S^{2-}$  ions. Films deviate significantly from stoichiometry at higher bath temperatures, reaching ~1.67  $Cd^{2+}$  ions per one  $S^{2-}$ . This is

understood from the previous discussion of the interstitial trapping. The large  $Cd^{2+}$  ions are caught in the lattice, offsetting the Cd:S ratio; correspondingly, the electrical performance was observed to be enhanced.

	Deposition temperatures (°C)		
	55	75	95
Ratio Cd:S	1:1	1:0.90	1:0.59
Optical band gap (eV)	2.43	2.45	2.49
n (cm <sup>-3</sup> ) × 10 <sup>17</sup>	1.1	5.9	8.1
μ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	8.2	10.0	32.5
ę (Ω cm)	33.5	30.7	9.3

Table 1. Deposition temperatures and film parameter summary [28].

For example, the carrier concentrations (*n*) increase over sevenfold. This is achieved without sacrificing the carrier mobility ( $\mu$ ) which also rises nearly four times. Resistivity ( $\rho$ ) decreases over threefold as well. This phenomenon is contrary to the common empirical relationship between carrier concentrations and mobility [47, 48]. This is partially due to the larger grain sizes in the cluster-by-cluster grown lattices. More importantly, however, this is suggestive that unlike extrinsic doping, the interstitially trapped dopants contribute carriers without following the inverse proportional relationship between carrier concentrations and mobility. This is a significant result, allowing for semiconducting thin films to overcome current limitations.

## 2.3. CBD conclusions

From the presented research, it is evident that the growth mechanism during chemical bath deposition can follow several routes during the fabrication of thin film, which can affect their performance. Careful study of the deposition mechanisms allows for a controlled deposition of the film with the desired optoelectronic properties. Furthermore, control of the growth mechanism can allow for the theoretical doping limits to be overcome and for the exploitation of novel film regimes. All of this can be achieved simply by controlling the deposition temperature with negligible changes in the deposition costs.

## 3. Chemical vapor deposition (CVD)

CVD is another promising chemical deposition method for the production of high-quality thin films. Although this method was developed and studied since the 1960s, the recent interest in organic and two-dimensional semiconductors has reinvigorated the field. Perhaps, the most attractive characteristic of CVD is just how effective and versatile it can be [49]. Nanostructured

graphene, carbon nanotubes, CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskites with applications in optoelectronics, solid oxide fuel cells, batteries, sensors, and high-performance organic photovoltaics are all manufactured using CVD [50–52]. Moreover, this method has been shown to be adaptable for the deposition of a single-layer material and scalable for mass production [53, 54]. Another advantage of CVD is the conformity of the deposited films (i.e., the thicknesses and grain sizes near the substrate edges are comparable across the sample) [55]. Hence, such films can be deposited on elaborate shapes, inside underlying features, and in high aspect ratio holes. Thus, there are virtually no limits to the types of films that may be deposited using this method. CVD does not discriminate between transition metals, heavy metals, organics, and inorganics and has the ability to deposit all of these without distorting the structures of the films. Additionally, cost-effective distillation of the precursors allows for deposition of high-purity films. The power of this method cannot be overstated. Chemical vapor methods yield to chemical bath only in the areas of deposition surface size and the equipment cost.

### 3.1. CVD theoretical considerations

CVD is influenced by numerous factors. For example, the type, shape, size of the reactor, gas flow, flow rates, flow order, arrangements coating, and substrates all affect the overall deposition results and mechanisms. The deposition reactions themselves may require complicated reaction schemes, involving pyrolysis, reduction, oxidation, disproportionation, hydrolysis, or some combination of each [56]. Despite the various approaches to CVD, in general, the results are achieved in a linear sequence. First, reagents are applied to the substrate to create an initial kinetic barrier. This barrier needs to be permeated by the gaseous diffusion prior to the preliminary reactions. Initial absorption then takes place on the substrate surface followed by reactions among the chemical constituents which results in nucleation. As with the CBD study, careful consideration of the CVD experiments allows for an effective tunability of the film characteristics. Here, we present a short theoretical discussion.

In general, the flow of the gases is assumed to be laminar, with zero velocity near the surface of the substrate, and increasing linearly to a constant value at some distance from the substrate. In such an approximated case, the boundary layer theory (BLT) is used for the study of the reaction dynamics [57]. This approach couples the chemical and mass transport processes on the heated substrate surface with a gas flow.

The free energy of the chemical reaction is analogous to Gibbs free energy and may be easily shown to be

$$\Delta G = \sum_{i=1}^{\text{\#products}} \Delta G_{\text{products}} - \sum_{i=1}^{\text{\#reactants}} \Delta G_{\text{reactants}}$$
(4)

where  $\Delta G$  is related to the equilibrium constant  $k_{n}$ :

$$\Delta G = 2.3RT \log(k_p) \tag{5}$$

Due to vapors utilized in the CVD process, the equilibrium constant is related to the partial pressures of the reactants and products. It is of greater interest, however, to relate the equilibrium constant in terms of concentrations. This is achieved using the ideal gas law [58]. The resulting free energy of the system consisting of *g* gaseous and *s* solid phases is thus

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$$\Delta G = \sum_{i=n_s}^{g} \left[ n_g \Delta G_g + RT \ln(P) + 2T \ln\left(\frac{n_g}{N_g}\right) \right] + \sum_{i=1}^{s} n_s \Delta G_s$$
(6)

where  $n_g$  and  $n_s$  are the number of moles of a particular reagent in the gaseous and solid state, respectively, and  $N_g$  is the total number of moles of all gaseous components. P and T are the total pressure and temperature, respectively. The  $\Delta G_g$  and  $G_s$  are the free energy of formation at specific temperatures for the gaseous and solid species, respectively. Thus, the equation can be solved iteratively for the free energy minima, i.e., the point at which nucleation will commence. An analysis of the equation also reveals that the reagent concentrations can be offset by the pressure and temperature in the CVD chamber.

Hypothetically, it should be possible to conduct thin-film growth at low pressures and temperatures with high reagent concentrations; although such an approach would not be most efficient from the chemical perspective, it would, however, help alleviate the requirement for sophisticated equipment. Further, the low-temperature approach allows for the deposition of highly sought organic materials. Of course, there is also a limit to the operability temperatures, since at some pressure and temperature the molecular gases will liquefy.

The analogousness between the CBD and CVD methods should be obvious from the brief theoretical introduction. The free energy of the chemical reaction, Eq. (6), shows that reagent concentrations, pressure, and temperature are the control parameters of interest in CVD. Thus, similar to CBD method, the optoelectronic performance of the CVD grown films will depend heavily on the deposition parameters and mechanisms.

## 3.2. CVD experimental data

Low vapor temperatures result in less random scattering of reagents; thus, clusters, ~10  $\mu$ m in diameter, form in the flowing gas prior to reaching the substrate. These clusters then coalesce on the surface of the substrate. The formation of CH<sub>4</sub>/H<sub>2</sub> clusters is shown in **Figure 6(a)** and **(b)** [59]. The semisolid state of the clusters allows for coagulation with other clusters as they hit the substrate. In this case thermal diffusivity of the materials will determine the final structure of the materials [60]. In materials with low thermal diffusivity, e.g., organics, the structure resulting from the cluster-by-cluster deposition is similar to that of epitaxial growth. Consequently, materials with low thermal conductivity can be deposited at low temperatures. Thus, it follows that theoretically it may be possible to achieve firm crystalline structures and optimal optoelectronic performance of the films without the need for high deposition temperatures.



Figure 6. SEM images of carbon cluster formations on mirror-polished substrates.

Reagent concentrations also greatly affect the structural quality of the materials and their optoelectronic performance. For example, graphene deposited under high reagent concentrations showed high disorder, requiring synthesis of additional layers [61]. Raman analysis of graphene deposited under various methane concentrations partially reveals the causes behind the phenomenon, as shown in **Figure 7**. The data reveal an upshift of ~5 cm<sup>-1</sup> and a downshift of ~6 cm<sup>-1</sup> in the D and 2D peaks, respectively. Extensive research on such peak dispersions was shown to be caused by the formation of additional graphene layers [62].



Figure 7. Raman spectra of CVD synthesized graphene with a Cu catalyst and SiO<sub>2</sub> substrates.

Furthermore, a significant increase in the D peak intensity is observed. This is typical of an increase in disorder [63]. The types of the disorders, whether layer or defect related, remain to be determined. Cumulatively, the results show that an increase in reagent concentrations produces mismatched layers and film defects. This causes anharmonic interactions between the phonons and electron-hole pairs [64], having a significant impact on the performance of such films. It is of great interest to conduct further research in minimizing layer mismatches and film defects. At present, this work is ongoing.

Preliminary results of the CVD flow rates and gas purity studies also show an effect on the optoelectronic performance of chemically deposited films. This research, however, is in the infancy stage and requires further analysis and effort.

There is a great potential for the efficient optimization of the optoelectronic performance of CVD deposited materials. Significant additional research into the deposition parameters and their effects on the growth mechanisms and optoelectronic performance will be required to fully understand the effects of each deposition parameter. It is expected that these issues will be resolved in the near future, allowing for effective optimization of these types of advanced materials.

## 3.3. CVD conclusions

In the optimization of CVD materials, thus far, the growth mechanisms have not been completely elucidated. There is, however, a strong correlation between the optoelectronic performance and

the deposition parameters. Much more research in the field of CVD modern-advanced materials is required but, once solved, will allow for an efficient optimization of such films.

# 4. Conclusion

This chapter discussed the growth mechanics, characteristics, and optimization of the optoelectronic performance in the chemically deposited materials. Two methods of interest are the chemical bath and chemical vapor depositions. Much more work has been completed in the field of CBD, but CVD is showing great promise in the deposition of novel advanced materials. The growth mechanisms are well understood for the chemical bath but remain to be elucidated for chemical vapor.

Once the growth mechanics are firmly established, it is possible to manipulate the chemical composition and other deposition parameters to efficiently optimize the optoelectronic film performance. Such results are abundant for the chemical bath, as is evident from the CdS case presented above, while for chemical vapor deposition, the research is ongoing. Each of these technologies is continuing to find uses in increasingly complicated manufacturing applications. It is expected that the ongoing research will enable new technologies for a wide variety of applications.

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# References

- [1] Dobkin D., Zuraw M. K. Principles of Chemical Vapor Deposition: What's Going on Inside the Reactor. 1st ed. NY: Springer Science; 2013. 242 p. DOI: 10.1007/978-94-017-0369-7.
- [2] Nielsen A. E. Kinetics of Precipitation (International Series of Monographs on Analytical Chemistry). 1st ed. NY: Pergamon Press; 1964.
- [3] Schwartz R. W. Chemical solution deposition of perovskite thin films. Chemistry of Materials. 1997;9:2325–2340. DOI: 10.1021/cm970286f.
- [4] Tavakoli M. M., Gu L., Gao Y., Reckmeier C., He J., Rogach A. L., Yao Y., Fan Z. Fabrication of efficient planar perovskite solar cells using a one-step chemical vapor deposition method. Scientific Reports. 2015;4:14083. DOI: 10.1038/srep14083.
- [5] Taima T., Shahiduzzaman M., Yamamoto K., Furumoto Y., Kuwabara T., Takahashi K. Planar heterojunction type perovskite solar cells based on TiO<sub>x</sub> compact layer fabricated by chemical bath deposition. Proceedings SPIE 9749. Oxide-based Materials and Devices VII. 2016.
- [6] Chow L., Wang H., Kleckley S., Daly T. K., Buseck P. R. Fullerene formation during production of chemical vapor deposited diamond. Applied Physics Letters. 1995;66:430. DOI: 10.1063/1.114046.
- [7] Puscher C., Water glass as a solvent for coralline. Chemical News. 1870;21:239.
- [8] Lincot D., Hodes G. Overview of history and present trends in chemical bath deposition of thin solid films and structures. ChemInform. 2008;39. DOI: 10.1002/chin.200809234.
- [9] Goldstein A. W., Rostoker W., Schossberger F., Gutzeit G. Structure of chemically deposited nickel. Journal of the Electrochemical Society. 1957;104:104–110. DOI: 10.1149/1.2428503.
- [10] Chopra K. L., Kainthla R. C., Pandya D. K., Thakoor A. P. Chemical solution deposition of inorganic films. Physics of Thin Films. 1982;12:167–235. DOI: 10.1016/S0079-1970(13)70010-0.
- [11] Lincot D., Froment M., Hubert C. Chemical deposition of chalcogenide thin films from solution. In: Alkire R. C., Kolb D. M., editors. Advances in Electrochemical Science and Engineering. Wiley Online Library; 2008. pp. 165–235. DOI: 10.1002/9783527616800.ch3.
- [12] Verdieck R. G., Yntema L. F. The electrochemistry of baths of fused aluminum halides. IV. The Journal of Physical Chemistry. 1944;48:268–279. DOI: 10.1021/j150437a005.
- [13] Yu X., Marks T. J., Facchetti A. Metal oxides for optoelectronic applications. Nature Materials. 2016;15:383–396. DOI: 10.1038/nmat4599.
- [14] Steirer X. K., Chesin J. P., Widjonarko N. E., Olson D. C. Solution deposited NiO thinfilms as hole transport layers in organic photovoltaics. Organic Electronics. 2010;11:1414– 1418. DOI: 10.1016/j.orgel.2010.05.008.
- [15] Elen K., Capon B., De Dobbelaere C., Dewulf D., Peys N., Detavernier C., Hardy A., Van Bael M. K. Transparent conducting oxide films of group V doped titania prepared by

aqueous chemical solution deposition. Thin Solid Films. 2014;555:33–38. DOI: 10.1016/j. tsf.2013.05.104.

- [16] Zhang H., Ma X., Xu J., Yang D. Synthesis of CdS nanotubes by chemical bath deposition. Journal of Crystal Growth. 2004;263:372–376. DOI: 10.1016/j.jcrysgro.2003.11.090.
- [17] Nakada T., Kunioka A. Direct evidence of Cd diffusion into Cu(In,Ga)Se<sub>2</sub>Cu(In,Ga) Se<sub>2</sub> thin films during chemical-bath deposition process of CdS films. Applied Physics Letters. 1999;74:2444. DOI: 10.1021/cm9703511.
- [18] Moutinho H. R., Albin D., Yan Y., Dhere R. G., Li X., Perkins C., Jiang C. S., To B., Al-Jassim M. M. Deposition and properties of CBD and CSS CdS thin films for solar cell application. Thin Solid Films. 2003;436:175–180. DOI: 10.1016/S0040-6090(03)00646-1.
- [19] Slonopas A., Alijabbari N., Saltonstall C., Globus T., Norris P. Chemically deposited nanocrystalline lead sulfide thin films with tunable properties for use in photovoltaics. Electrochimica Acta. 2015;151:140–149. DOI: 10.1016/j.electacta.2014.11.021.
- [20] Mindt W. Electroless deposition of certain metal oxides. Journal of the Electrochemical Society. 1970;117:615–618. DOI: 10.1149/1.2407588.
- [21] Mitzi D. B., Yuan M., Liu W., Kellock A. J., Chey J. S., Deline V. A high-efficiency solution-deposited thin-film photovoltaic device. Advanced Materials. 2008;20:3657–3662. DOI: 10.1002/adma.200800555.
- [22] Slonopas A., Foley B. J., Choi J. J., Gupta M. C. Charge transport in bulk CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite. Journal of Applied Physics. 2016;119:074101. DOI: 10.1063/1.4941532.
- [23] Law M. E., Lian M., Burk D. E. Self-consistent model of minority-carrier lifetime, diffusion length, and mobility. IEEE Electron Device Letters. 2002;12:401–403.
- [24] Liu Y., Gibbs M., Puthussery J., Gaik S., Ihly R., Hillhouse H. W., Law M. Dependence of carrier mobility on nanocrystal size and ligand length in PbSe nanocrystal solids. Nano Letters. 2010;10:1960–1969. DOI: 10.1021/nl101284k.
- [25] Takagi S., Toriumi A., Iwase M. On the universality of inversion layer mobility in Si MOSFET's: Part I—effects of substrate impurity concentration. IEEE Transactions on Electronic Devices. 1994;41:2357–2362. DOI: 10.1109/16.337449.
- [26] Weinan E., Zhongyi H.. Matching conditions in atomistic-continuum modeling of materials. Physical Review Letters. 2001;87:135501. DOI: 10.1103/PhysRevLett.87.135501.
- [27] Stukowski A. Computational analysis methods in atomistic modeling of crystals. The Journal of The Minerals: Metals & Materials Society (TMS). 2014;66:399–407. DOI: 10.1007/s11837-013-0827-5.
- [28] Slonopas A., Ryan H., Foley B., Sun Z., Sun K., Globus T., Norris P. Growth mechanisms and their effects on the optoelectronic properties of CdS thin films prepared by chemical bath deposition. Materials Science in Semiconductor Processing. 2016;52:24–31. DOI: 10.1016/j.mssp.2016.05.011.

- [29] Frost J. M., Butler K. T., Brivio F., Hendon C. H., Van Schilfgaarde M., Walsh A. Atomistic origins of high-performance in hybrid halide perovskite solar cells. Nano Letters. 2014;14:2584–2590. DOI: 10.1021/nl500390f.
- [30] Hodes G. Chemical Solution Deposition of Semiconductor Films. NY: Marcel Dekker Inc; 2002.
- [31] Dauplaise H. M., Vaccaro K., Davis A., Ramseyer G. O., Lorenzo J. O. Analysis of thin CdS layers on InP for improved metal-insulator-semiconductor devices. Journal of Applied Physics. 1996;80:2873. DOI: 10.1063/1.363139.
- [32] Shinde S. S., Shinde P. S., Bhosale C. H., Rajpure K. Y. Optoelectronic properties of sprayed transparent and conducting indium doped zinc oxide thin films. Journal of Physics D: Applied Physics. 2008;41:105109.
- [33] Sebastian P. J., Calixto M. E., Bhattacharya R. N., Noufi R. CIS and CIGS based photovoltaic structures developed from electrodeposited precursors. Solar Energy Materials and Solar Cells. 1999;59:125–135. DOI: 10.1016/S0927-0248(99)00037-9.
- [34] Neuschitzer M., Sanchez Y., Olar T., Thersleff T., Lopez-Marino S., Oliva F., Espindola-Rodriguez M., Xie H., Placidi M., Izquierdo-Roca V., Lauermann I., Leifer K., Perez-Rodriguez A., Saucedo E. Complex surface chemistry of kesterites: Cu/Zn reordering after low temperature postdeposition annealing and its role in high performance devices. Chemistry of Materials. 2015;27:5279–5287. DOI: 10.1021/acs.chemmater.5b01473.
- [35] Sebastian P. J. p-type CdS thin films formed by *in situ* Cu doping in the chemical bath. Applied Physics Letters. 1993;62:2956. DOI: 10.1063/1.109181.
- [36] Goudarzi A., Aval G. M., Park S. S., Choi M. C., Sahraei R., Ullah H. M., Avane A., Ha C. S. Low-temperature growth of nanocrystalline Mn-doped ZnS thin films prepared by chemical bath deposition and optical properties. Chemistry of Materials. 2009;21:2375– 2385. DOI: 10.1021/cm803329w.
- [37] Lozano O., Chen Q. Y., Wadekar P. V., Seo H. W., Chinta P. V., Chu L. H., Tu L. W., Lo I., Yeh S. W., Ho N. J., Chuang F. C., Jang D., Wijesundera D., Chu W. K. Factors limiting the doping efficiency of transparent conductors: a case study of Nb-doped In<sub>2</sub>O<sub>3</sub> epitaxial thin-films. Solar Energy Materials and Solar Cells. 2013;113:171–178. DOI: 10.1016/j. solmat.2013.02.006.
- [38] Slonopas A., Melia M., Xie K., Globus T., Fitz-Gerald J. M., Norris P. Factors limiting doping efficiency of Iridium in pulsed laser deposited TiO<sub>2</sub> transparent conducting oxide. Journal of Material Science. 2016;51:8995–9004. DOI: 10.1007/s10853-016-0152-9.
- [39] Siedle A. R., Newmark R. A., Brown-Wesley K. A., Skarjune R. P., Haddad L. C., Hodgson K. O., Roe A. L. Solid-state organometallic chemistry of molecular metal oxide clusters: carbon-hydrogen activation by an iridium polyoxometalate. Organometallics. 1988;7: 2078–2079. DOI: 10.1021/om00099a037.
- [40] Joint Committee on Powder Diffraction Standards (JCPDS). Card 10–0454, CdS (cubic), 1999.

- [41] Joint Committee on Powder Diffraction Standards (JCPDS). Card 6–0314, CdS (hexagonal), 1999.
- [42] Zelaya-Angel O., Hernandez L., De Melo O., Alvarado-Gil J. J., Lozada-Morales R., Falcony C., Vargas H., Ramirez-Bon R. Band-gap shift in CdS: phase transition from cubic to hexagonal on thermal annealing. Vacuum. 1995;46:1083–1085. DOI: 10.1016/0042-207X(95)00111-5.
- [43] Jensen B., Torabi A. Refractive index of hexagonal II–VI compounds CdSe, CdS, and CdSexS1-x. Journal of the Optical Society of America B. 1986;3:857–863. DOI:10.1364/ JOSAB.3.000857.
- [44] Al Kuhaimi A. S. Influence of preparation technique on the structural, optical and electrical properties of polycrystalline CdS films. Vacuum. 1998;51:349–355. DOI:10.1016/ S0042-207X(98)00112-2.
- [45] Pal U., Silva-Gonzales R., Martinez-Montes G., Gracia-Gimenez M., Vidal M. A., Torres S. Optical characterization of vacuum evaporated cadmium sulfide films. Thin Solid Films. 1997;305:345–350. DOI:10.1016/S0040-6090(97)00124-7.
- [46] Seto S. Photoluminescence, reflectance and photoreflectance spectra in CdS epilayers on Si(111) substrates. Japanese Journal of Applied Physics. 2005;44.
- [47] Hilsum C. Simple empirical relationship between mobility and carrier concentration. Electronics Letters. 1974;10:259–260.
- [48] Masetti G., Severi M., Solmi S. Modeling of carrier mobility against carrier concentration in arsenic-, phosphorus-, and boron-doped silicon. IEEE Transactions on Electron Devices. 1983;30. DOI:10.1109/T-ED.1983.21207.
- [49] Liu Y., Liu M. A highly sensitive and fast-responding SnO<sub>2</sub> sensor fabricated by combustion chemical vapor deposition. Chemistry of Materials. 2005;17:3997–4000. DOI:10.1021/ cm0504510.
- [50] Liu Y., Zha S., Liu M. Novel nanostructured electrodes for solid oxide fuel cells fabricated by combustion chemical vapor deposition (CVD). Advanced Materials. 2004;16:256–260. DOI:10.1002/adma.200305767.
- [51] Liu Y., Zha S., Liu M. Nanocomposite electrodes fabricated by a particle-solution spraying process for low-temperature SOFCs. Chemistry of Materials. 2004;16:3502–3506. DOI:10.1021/cm049583s.
- [52] Leyden M. R., Ono L. K., Raga S. R., Kato Y., Wang S., Qi Y. High performance perovskite solar cells by hybrid chemical vapor deposition. Journal of Materials Chemistry A. 2014;2:18742–18745. DOI: 10.1039/C4TA04385E.
- [53] Gomez L., Zhang Y., Kumar A., Zhou C. Synthesis, transfer, and devices of single- and few-layer graphene by chemical vapor deposition. IEEE Transactions on Nanotechnology. 2009;8:135–138. DOI:10.1109/TNANO.2009.2013620.
- [54] Kumar M., Ando Y. Chemical vapor deposition of carbon nanotubes. Journal of Nanoscience and Nanotechnology. 2010;10:3739–3758. DOI:10.1166/jnn.2010.2939.

- [55] Thomann A. L., Vahlas C., Aloui L., Samelor D., Caillard A., Shaharil N., Blanc R., Millon E. Conformity of aluminum thin films deposited onto micro-patterned silicon wafers by pulsed laser deposition, magnetron sputtering, and CVD. Chemical Vapor Deposition. 2011;17:366–374. DOI:10.1002/cvde.201106936.
- [56] Yee K. K. Protective coatings for metals by chemical vapour deposition. International Metals Review. 2013;23:19–42. DOI:10.1179/imtr.1978.23.1.19.
- [57] Spear K. E. Principles and applications of chemical vapor deposition (CVD). Pure and Applied Chemistry. 1982;54:1297–1311.
- [58] Petrucci R. H., Harwood W. S., Herring G. E., Madura J. General Chemistry: Principles and Modern Application. 9th ed.. Newark, NJ: Prentice Hall; 2016.
- [59] Melnikova V. The cluster growth mechanism of nanostructured diamond. In: Veziroglu T. N., Zaginaichenko Y. S., Schur V. D., Baranowski B., Shpak P. A., Skorokhod V. V. Hydrogen Materials Science and Chemistry of Carbon Nanomaterials. NY: Springer; 2007. pp. 557–562. DOI:10.1007/1-4020-2669-2\_64.
- [60] Murakami T. N., Kijitori Y., Kawashima N., Miyasaka T. Low temperature preparation of mesoporous TiO<sub>2</sub> films for efficient dye-sensitized photoelectrode by chemical vapor deposition combined with UV light irradiation. Journal of Photochemistry and Photobiology A: Chemistry. 2004;164:187–191. DOI:10.1016/j.jphotochem.2003.11.021.
- [61] Bhaviripudi S., Jia X., Dresselhaus M. L., Kong J. Role of kinetic factors in chemical vapor deposition synthesis of uniform large area graphene using copper catalyst. Nano Letters. 2010;10:4128–4133. DOI:10.1021/nl102355e.
- [62] Pocsik I., Hundhausen M., Koos M., Ley L. Origin of the D peak in the Raman spectrum of microcrystalline graphite. Journal of Non-Crystalline Solids. 1998;227–230:1083-1086. DOI:10.1016/S0022-3093(98)00349-4.
- [63] Tuinstra F., Koenig J. L. Raman spectrum of graphite. The Journal of Chemical Physics. 1970;53:1126. DOI:10.1063/1.1674108.
- [64] Ferrari A. C., Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. Physical Review B. 1999;61:14095. DOI:10.1103/PhysRevB.61.14095.

# Thin Films as a Tool for Nanoscale Studies of Cement Systems and Building Materials

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Additional information is available at the end of the chapter

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#### Abstract

Many efforts have been made over the last decades to improve and develop new technologies for cement and chemical industries that can provide materials that are more durable and cost efficient, stronger and less environmentally harmful. Studies at small scale in cementitious materials usually require special sample preparation, which can damage the material and mislead the analysis. In nanoscale experiments, several techniques require samples to be extremely thin, while others need the samples to be very flat. The possibility of using thin films of clinker phases in cement research opens far-reaching opportunities for the development of this material and the materials associated to this. Testing different evaporation parameters, the deposition of films with a few tens of nanometers in thickness was achieved for all the clinker phases individually. This chapter will present the attempts for synthesizing thin films of all main clinker phases by the use of electron beam evaporation technique, as well as data on the hydration of the calcium silicate thin, flat and homogeneous samples. Changes are tracked chemically and mineralogically. This study redirects cement science to new perspectives of understanding the nanostructure of cement products. This leads to basis for developing stronger and more durable cement-based materials.

Keywords: cement, clinker phases, thin films, electron beam evaporation

# 1. Introduction

The Portland cement is an inorganic material, which results from burning and grounding of a raw material containing CaO,  $SiO_2$ ,  $Al_2O_3$  and small quantities of other materials. Its mixture with water results in a cement paste that sets and hardens due to a reaction called hydration. The result is a strong material that is stable even under aqueous conditions.



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. Cement hydration reactions take place simultaneously and in a very complex way, and understanding the behavior of such systems, with the ultimate purpose of improving durability, strength, cost and environmental impact, often requires studies at nanoscale [1].

These experiments in cementitious materials normally involve special sample preparation that can damage the material, change its properties or make it difficult to run analysis due to certain morphological characteristics of the material.

X-ray photoelectron spectroscopy (XPS) requires no special sample preparation for measurements, allowing progressive ion milling and analysis of flat surfaces to follow the progress of surface reactions [2]. In addition, in situ analyses of samples provide information not only about chemical composition but also changes in the coordination state of the elements; this has been successfully used to follow the progress of cement hydration reactions and subsequent polymerization of the materials [3–11].

Clinker is composed mainly of calcium silicates, calcium aluminate and calcium aluminoferrite. Its hydration is a very complex process, involving several phases and the formation of secondary products. Subsequently, properties of concrete are governed by processes at a molecular level with single-crystal formation. Thus, the durability and behavior of concrete during its service life strongly depend on its nanostructure.

Here, electron beam evaporation methods have been used to evaporate different clinker phases individually to synthesize thin films in an effort for producing samples suitable for nanoscale studies of cementitious materials and avoiding typical problems of sample preparation when studying these materials. This kind of sample permits elemental studies intending to design the behavior of each phase individually and the cement itself, at nanoscale, providing tools for understanding and changing the materials characteristics, looking forward to obtain better performance and durability.

Thin films techniques are widely used to produce ceramic films in the semiconductor, aerospace and optics industry, but thus far have not been applied to clinker phases. This study is an effort to develop integrated tools that allow improving the knowledge of early stage clinker phases' hydration at the molecular level and with this to better understand the behavior of these materials. With this, this work is aimed at producing clinker phase thin films suitable for hydration studies using electron beam evaporation techniques. Evaporation of each phase was repeated several times in order to optimize the most favorable experimental conditions and assess the reproducibility of the process.

# 2. Synthesis of clinker phases' thin films

This session describes the attempt to synthesize thin films of the four main clinker phases by means of electron beam evaporation and the outcomes. Clinker is the product from the sintering of limestone and clay during the cement manufacturing, composed mainly of four components: tricalcium silicate (C<sub>3</sub>S),  $\beta$ -dicalcium silicate (C<sub>2</sub>S), tricalcium aluminate (C<sub>3</sub>A) and ferrite (C<sub>4</sub>AF). Notation is the standard used in cement chemistry. Commercially available

clinker phases were used here as bulk material. All the components were  $3600 \text{ cm}^2/\text{g}$ , with free lime content below 0.5%.

Thin films were prepared with electron beam evaporation by sending a current through a tungsten filament outside the deposition zone to avoid any contamination. The filament is heated until the start of the electrons thermionic emission. Magnets focus and direct the electrons toward the bulk material that is in a constantly cooled crucible. When the electron beam hits the evaporant's surface, kinetic energy is converted into heat, releasing high energy. The evaporant boils and evaporates, condensing on the substrate and all surfaces inside the vacuum chamber. Thicknesses of the films are a function of irradiation time, estimated by an in situ quartz deposition controller.

The bulk powder phases were placed in crucibles previously cleaned with isopropyl alcohol and mounted in a vacuum chamber Univex 450B Oerlikon Leybold in a clean room. A power supply controller Telemark with a beam generating system and beam deflection unit with electromagnetic deflection for the x- and y-axis was used in the electron beam evaporator.

Sample	Crucible	Pressure (mbar)	Power (%)	I (Amp)	Voltage (Kv)	Vel <sub>0</sub> (Å/s)
C <sub>3</sub> S	Graphite	$3.6 - 3.7 \times 10^{-4}$	3–6	0.016-0.030	7.37–7.40	0.4–1.2
C <sub>2</sub> S	Graphite	$3.6 - 3.8 \times 10^{-4}$	6–10	0.022-0.050	7.30–7.42	1.1–2.5
C <sub>3</sub> A	Graphite	$3.6\times10^{-4}$	8–9	0.030-0.037	7.28–7.33	1–2.4
C <sub>4</sub> AF	Boron nitride	$3.8 - 4.2 \times 10^{-4}$	6–11	0.018-0.056	7.26–7.32	0.1–4

Table 1. Parameters for each evaporation.

Silicon wafers with a 100 crystallographic orientation were used as deposition substrate, placed in a plate 30 cm above the crucible and held by metallic clips, and kept at ambient temperature. At a stable pressure, 4 sccm of a mix of 50% oxygen and 50% argon was inserted into the chamber to compensate the possible oxygen lost. Parameters used for each evaporation are listed in **Table 1**. The temperature in the silicon wafers was monitored and showed to be constant at room temperature during all the process; however, it is not possible to confirm the temperature achieved in the bulk sample during the evaporation.

Sample	Thickness (nm)	
C <sub>3</sub> S	280	
$C_2S$	200	
C <sub>3</sub> A	200	
C <sub>4</sub> AF	60	

Table 2. Thicknesses of the thin films.

Each sample behaved differently when bombarded by the electron beam: calcium silicate powders sublimated and did not liquefy, while during the evaporation of calcium aluminates,

the powder seemed to liquefy and higher intensities caused blasts. The resulting thin films had the thickness described in **Table 2**, measured with a profilometer.

X-ray diffraction (XRD) investigations of the bulk material were carried out in a Bruker D83 Advanced diffractometer operated at an accelerating voltage of 40 keV on a CuK $\alpha$  anode, irradiation intensity of 40 mA and 40 scans in steps of 0.02°/s, and results are described in the next section.

Sample	Peak position (eV) and (FWHM)						
	Ca 2p 1/2	Ca 2p 3/2	Si 2p	O 1s	Al 2p	Fe 2p	
C₃S bulk	350.2 (2.5)	346.8 (2.46)	101.0 (2.83)	530.1 (2.35)			
				531.6 (2.80)			
$C_3S$ thin film	350.2 (1.85)	346.8 (2.07)	98.2 (1.81)	529.8 (1.69)			
	351.1 (1.85)	347.5 (2.41)	100.6 (1.83)	531.2 (2.57)			
			102.4 (2.48)				
C <sub>2</sub> S bulk	350.3 (2.41)	346.7 (2.28)	101.0 (2.68)	530.1 (2.23)			
				531.6 (2.75)			
C <sub>2</sub> S thin film	350.4 (2.24)	346.8 (2.13)	100.8 (2.08)	530.0 (1.59)			
			101.7 (2.70)	531.3 (3.02)			
C <sub>3</sub> A bulk	350.3 (2.43)	346.8 (2.28)		531.4 (2.15)	73.2 (2.48)		
$C_3A$ thin film	350.6 (2.17)	347.0 (2.05)		531.5 (2.24)	-		
				533.4 (2.19)	-		
C <sub>3</sub> A crucible	350.4 (2.03)	346.9 (2.05)		529.7 (1.5)	73.6 (1.72)		
				530.6 (2.92)	74.1 (2.25)		
C₄AF bulk	350.4 (2.25)	346.9 (2.11)		529.0 (1.95)	73.1 (2.32)	710.2 (2.60)	
						711.8 (3.33)	
				531.1 (2.68)		723.8 (2.29)	
						725.2 (3.43)	
C <sub>4</sub> AF thin film	351.1 (2.24)	347.6 (2.44)		529.8 (1.45)	-	710.4 (2.91)	
						712.6 (2.92)	
				530.7 (2.82)		723.9 (2.57)	
						725.8 (3.80)	
C <sub>4</sub> AF crucible	349.9 (2.51)	346.4 (2.51)		529.4 (2.13)	73.2 (1.92)	709.8 (3.70)	
				531.4 (2.12)		723.0 (3.41)	

Table 3. Peak position and (FWHM) for all samples.

On the other hand, due to the small diffracting volumes, which result in low intensities compared to the substrate and background, mineralogical phases on thin films are difficult to be identified. GIXRD allows increasing the intensity of the signal produced from the film by increasing the path length of the incident X-ray beam through it, so that conventional phase identification analysis can be run [12–14]. GIXRD experiments were performed using a Bragg-Brentano Siemens D-500 X-ray diffractometer at 45 kV accelerating voltage, on a CuK $\alpha$  anode, with 40 mA irradiation intensity and 0.05°/s steps, with an incident angle of w = 0.4°. No monochromator was used to increase the signal. Different detector apertures were used for each sample, depending on their size.

Chemical composition of a material's surface was assessed by XPS, which works by irradiating the sample with a X-rays beam and measuring both the kinetic energy and the number of electrons escaping from its surface.

Chemical composition of the thin films was verified using a SPECS<sup>TM</sup> X-ray photoelectron spectroscopy system equipped with an XR50 Al anode source operating at 150 W and a Phoibos MCD-9 detector. Spectra were recorded with pass energy of 25 eV at 0.1 eV steps at a pressure below  $10^{-9}$  mbar.

For analysis of the bulk material, powder was pressed into pellets and fixed onto holders with a copper tape, same fixing as the silicon wafers with the thin films. For each sample, general scan was repeated three times, and specific high-resolution scans were carried out for elements of interest, such as calcium, silicon, carbon, oxygen, iron and aluminum. Data were extracted from the spectra via peak fitting using CasaXPS<sup>TM</sup> software. Shirley background was assumed in all cases. The adventitious carbon peak at 284.8 eV was used for correction of the charging effects. Three scans with a passing energy of 5 eV were carried out for the acquisition of each pattern.

XPS binding energies (BEs) and full width half maximum (FWHM) peak parameters are shown in **Table 3**.

## 2.1. Calcium silicates

The similarity between the GIXRD patterns of the bulk material and the XRD of the thin film (**Figure 1a**) strongly suggests that the evaporated and recondensed material keeps the mineralogical composition of the original bulk material. Even with the relatively faint signal observed due to the thickness of the film and the high noise level, the presence of the most intense peaks of  $C_3S$  (at 32.07°, 34.29° and 32.33°) is clearly noticed as a broad peak in the pattern. This broadening in the peaks has been observed in several other researches when working with thin films, specially using Bragg-Brentano configuration [15–17]. This is likely due to the thin film's poor crystallinity.

Similarly to  $C_3S$ , the  $C_2S$  samples show a strong match between the diffraction patterns of bulk material and thin film (**Figure 1b**). The same low signal and high noise are observed, but the presence of the most intense peaks of  $C_2S$  (at 31.98°, 32.38° and 40.55°) is coincident with the broad peak in the thin film spectrum, suggesting that the evaporated material keeps the bulk mineralogical composition. Even the broad peak at low degrees is observed in both spectra,

which can be either due to the presence of amorphous material or an artifact of the technique due to the small size of the sample.



**Figure 1.** (a)  $C_3S$  powder (top) and grazing incident angle (bottom) XRD from the bulk and thin film samples, respectively. (b)  $C_2S$  powder (top) and grazing incident angle (bottom) XRD from the bulk and thin film samples, respectively.



Figure 2. Top: XPS spectra of the  $C_3S$  (top) and  $C_2S$  (bottom) bulk material and thin film. Thick lines are the spectra collected, while the thin lines are the background and the result of peak fitting.
On the other hand, a comparison between XPS patterns from bulk material and the thin film shows that the elements are present in the same elemental coordination state. Some changes are noticed though, as an additional calcium peak at 351.1 eV, which can be related to pre-hydration on the surface due to the contact with the atmosphere. The same behavior was observed in previous researches [3, 4]. This is confirmed by the silicon peak, which presents a split into two peaks at 102.4 and 100.6 eV. This shift to higher BE is related to pre-hydration and the formation of C-S-H [18]. At the same time, there is the presence of a peak related to the metallic silicon from the thin film (98.2 eV), which is associated with the substrate and is probably due to the porosity of the layer, despite its thickness (**Figure 2**); hence, reaction with the substrate cannot be totally discarded [19]. Changes in the oxygen peak positions are also related to this pre-hydration effect.

Likewise, XPS results assure that the evaporated  $C_2S$  chemical material is very similar to the bulk material, with the peaks located at the same BE and with similar FWHM values (**Figure 2**), and the appearance of a new silicon peak, together with the slight shifts in the oxygen peaks energy, can also be attributed to the substrate as well as to pre-hydration. On the other hand, magnesium (a minor component in the original bulk material) is also detected in the thin film spectrum.

#### 2.2. Calcium aluminates

 $C_3A$  films exhibit better-defined GIXRD peaks (**Figure 3a**), less noise and higher intensity than the silicate samples. This is due to the larger sample used for the test, which provides larger area for analysis, since the detector aperture can be larger, allowing more signal to be collected. In this case, the film produced from the evaporation of  $C_3A$  was formed by other phases (including calcite, lime and portlandite; **Figure 4a**), but no phases with aluminum are identified.

The evaporated  $C_4AF$  has a similar behavior to  $C_3A$ . In this case, the GIXRD spectrum is not conclusive as it is extremely noisy and indicates the formation of amorphous materials (**Figure 3b**). For the bulk material, the peaks correspond to Brownmillerite, or  $C_4AF$ , except for one peak at 18.11°, which may be related to the presence of  $Fe_3O_4$ , which cannot be discarded, as discussed later in the XPS analysis.

Diffraction data are confirmed by the XPS analyses, which show that the calcium is deposited in similar chemical state as in the bulk material (shifts of 0.2–0.3 eV), but the aluminum peak does not appear in the thin film spectrum, meaning that it did not recondense on the substrate (**Figure 4**).

 $C_4AF$  bulk and thin film present Fe 2p peaks with two components, indicating the presence of two compounds (**Table 3**, **Figure 4**). The BE themselves are not conclusive of what compounds are present, as the observed BEs are similar to the ones of Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and FeO. While the Fe 2p components at lower BE present negligible changes from the bulk to the thin film, the second component at higher energies presents significant changes (about +0.7 eV); this indicates strong bonding changes in iron after the evaporation. Since differences in the O 1s BE are observed as well by shifts of +0.4 and +0.8 eV, differences between this two samples are clear. Finally, Ca

2p peaks shift to higher energies by +0.7 eV, indicating again differences in the thin film material.



**Figure 3.** (a)  $C_3A$  powder (top) and grazing incident angle (bottom) XRD from the bulk and thin lm samples, respectively. (b)  $C_4AF$  powder (top) and grazing incident angle (bottom) XRD from the bulk and thin lm samples, respectively.



**Figure 4.** XPS spectra of the  $C_3A$  (top) and  $C_4AF$  (bottom), for their respective bulk material and thin film. Thick lines are the spectra collected, while the thin lines are the background and the result of peak fitting. XPS spectra for Ca 2p, O 1s, Al 2p and Fe 2p (for  $C_4AF$  only) are shown.

Analysis of the material left in the crucible after the evaporation of  $C_3A$  shows the presence of tricalcium aluminate and mayenite ( $Ca_{12}Al_{14}O_{33}$  or  $C_{12}A_7$ ; **Figure 5a**).  $C_{12}A_7$  is formed from the phase that liquefied during the evaporation, indicating at least partially incongruent evaporation of  $C_3A$ , yielding to an evaporate/condensate that is substantially richer in Ca (note that the Ca/Al ratio of mayenite is 0.86, about 3.5 times lower than that of  $C_3A$ , and hence, the Ca enrichment of the evaporate can be inferred). The presence of portlandite and calcite in the thin films can therefore be interpreted as partial hydration and carbonation of a Ca-rich phase upon atmospheric exposure (although limited) of the thin films.



Figure 5. XRD of the residue left in the crucible after the evaporation of (a) C<sub>3</sub>A and (b) C<sub>4</sub>AF.



**Figure 6.** XPS spectra of the material left in the crucible after evaporation of  $C_3A$  (top) and  $C_4AF$  (bottom). Thick lines are the spectra collected, while the thin lines are the background and the result of peak fitting.

The absence of Al in the XPS spectra (**Figure 6**) could be due to some reaction scavenging from the silicon substrate, leading to aluminosilicates, similarly to what has been observed by Toda et al. [19] during production of  $C_{12}A_7$  thin films. However, XPS data do not show any evidence of silicon, while reaction at deeper regions cannot be excluded, as on XPS the X-rays only penetrate a few nanometers on the surface.

Before completion of  $C_3A$  evaporation, a liquid phase formed while, probably, the bulk material was being converted into a mix of solid CaO and liquid calcium aluminate, with higher aluminum content than the initial  $C_3A$ . Possibly, only the solid phase evaporated and became the precursor of the generated thin film, since no aluminum is observed there.

The BE of the calcium peaks does not present relevant shifts from those in the bulk material. However, oxygen and aluminum peaks in the melt residue in the crucible present significant changes in both BE and FWHM (**Table 3**, **Figure 6**), which indicates a different coordination state.

Electron beam bombardment of C<sub>4</sub>AF led, as in the case of C<sub>3</sub>A, to the formation of a liquid phase, with a higher concentration of aluminum than in the bulk material. The phase diagram of CaO-Fe<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> [20] shows that, when there is an incomplete fusion, the equilibrium is reached with a Ca<sub>2</sub>(Al,Fe<sup>+3</sup>)<sub>2</sub>O<sub>5</sub> phase with higher content of Fe (solid) and one liquid phase mix of CaO.Al<sub>2</sub>O<sub>3</sub>, without Fe. Analogous formation happens in the C<sub>3</sub>A at up to 1542°C, when the equilibrium is reached for CaO solid + liquid (~40% wt of Al<sub>2</sub>O<sub>3</sub> + CaO).

XRD patterns of the bulk material (**Figure 3a**) and the residue left in the crucible after the evaporation (**Figure 5a**) are remarkably similar. The main component in both materials is brownmillerite ( $Ca_2(Al,Fe^{+3})_2O_5$ ); however, the presence of  $Fe_3O_4$  or  $Ca_2Al_{1.38}Fe_{0.62}O_5$  cannot be discarded.

In fact, Taylor [20] stated that "iron-rich mixes tend to lose oxygen when heated in air above 1200–1300°C, with consequent replacement of hematite by magnetite ( $Fe_30_4$ )," which is in accordance with the observations here, even though it was not possible to verify the temperature in the crucible during the evaporation.

Likewise in the  $C_3A$  sample, during the evaporation of  $C_4AF$ , the material in the crucible melted and there were eruptions, as well as there was no aluminum in the film. That means the residue left in the crucible has to be richer in aluminum. Again, as observed for the  $C_3A$  sample, reaction with the substrate at deeper regions, as observed by Toda et al. [19], cannot be discarded. However, no XPS signal of silicon can be detected, suggesting that such a reaction does not occur.

In the same way, the XPS analyses for the material left in the crucible after the evaporation of the C<sub>4</sub>AF (**Figure 5b**) present a strong difference when compared to the initial bulk material: Fe 2p peak presents only one component at 709.8 eV (Fe 2p3/2) and 723.0 eV (Fe 2p1/2), meaning important changes happened in the chemical/electronic state of this element. O 1s presents BE shifts of +0.3 eV and Ca 2p of -0.5 eV, while BE of Al 2p is similar to the starting material (**Table 3**).

The XPS 2p spectra of Fe, as other transition metals, present complex lineshapes due to the electrons exchange interaction effects, as well as electron correlation effects [21]. Normally, Fe 2p peaks are broad, asymmetric and may contain satellites, which are observed here as well.

On the other hand, for iron oxides, the O 1s BE is expected to increase with a decrease in the oxidation number of the cation of the same metal; it is observed here an increase in O 1s BE by +0.3 eV from the bulk to the material left in the crucible. At the same time, Graat and Somers [22] describe an increase in BE for increase in oxidation state of iron; here, this is very much evident as with the existence of only one iron component, which still presents a BE lower by -0.4 eV than the Fe 2p peak with the lowest BE in the bulk material (709.8 vs 710.2 eV), suggesting a decreasing in the oxidation state for the material left in the crucible (**Table 3**).

This may explain the possible existence of  $Ca_2Al_{1.38}Fe_{0.62}O_5$ , besides the brownmillerite, in the material in the crucible, as XRD could suggest. This compound was also observed by Vázquez-Acosta et al. [23].

The phase diagram for the C<sub>4</sub>AF partial fusion relates to a solid phase C<sub>2</sub>F (2CaO.Fe<sub>2</sub>O<sub>3</sub>) and a liquid with composition similar to the Ca<sub>2</sub>(Al<sub>x</sub>Fe<sub>1-x</sub>)O<sub>5</sub>, in direction to phases with higher aluminum concentration than the C<sub>4</sub>AF itself. As underlined by Taylor [20] "for bulk compositions in the Ca<sub>2</sub>(Al<sub>x</sub>Fe<sub>1-x</sub>)O<sub>5</sub> series, the liquid is of higher Al/Fe ratio than the ferrite phase with which it is in equilibrium."

# 3. Hydration of calcium silicate thin films

Calcium silicates' hydration happens over a dissolution-precipitation process that may occur through the formation of etch pits, where the calcium silicate hydrate (C-S-H) preferentially precipitates, together with calcium hydroxide (portlandite or CH), the two hydration products. C-S-H is the main product formed by the hydration of the calcium silicates and responsible for the strength of the cement paste. It is mostly amorphous, and the dashes indicate a disordered structure. Its particle density was found by Gauffinet et al. [18] to be in the order of 2500 kg/m<sup>3</sup>.

At the molecular level, C-S-H has a structure similar to the tobermorite  $(Ca_5Si_6O_{16}(OH)_2 \cdot 8H_2O)$ and jennite  $(Ca_9Si_6O_{18}(OH)_6 \cdot 8H_2O)$ , rare minerals found in nature. Most of the models predicting the C-S-H nanostructure involve elements of jennite-like or even tobermorite-jennite structures [26].

After running the initial pattern presented previously (**Figures 2** and **3**),  $C_3S$  and  $C_2S$  dry thin film samples were hydrated separately in a reaction chamber that was located in the same vacuum line as the XPS, hence avoiding any hydration and/or carbonation from the contact with the atmosphere. Saturated water vapor with argon as a carrier was inserted at 20 mL/min. Prior to hydration, the system was purged for 5 min to avoid any contamination.

XPS analyses of the hydrated 110-nm-thick  $C_3S$  thin film are presented in detail in Ref. [3]. Results show, after 3 h of exposure to water vapor, a shift in the Si 2p peak of about 0.7 eV (from

101.9 to 102.6 eV) (**Table 4**), while the literature reports lower BE for this peak (100.57 eV in fresh  $C_3S$ , [6]). This indicates a progressive disordering of the silicate structure, which denotes the C-S-H formation.

Time (mins)	Peak positon (eV)			Ca/Si ratio	
	Si 2p	δCa 2p-Si 2p	Ca 2p 3/2	Ca 2p/Si 2p	
0	101.9 (2.5)	245.2	346.8 (2.7)	3.4	
2	101.9 (2.4)	245.3	347.0 (2.7)	3.4	
7	102.2 (2.4)	245.1	347.1 (2.6)	3.4	
12	102.4 (2.5)	245.0	347.3 (2.6)	3.4	
17	102.4 (2.5)	244.9	347.3 (2.6)	3.4	
27	102.6 (2.6)	245.0	347.4 (2.5)	3.8	
42	102.5 (2.5)	244.9	347.4 (2.5)	3.6	
62	102.6 (2.5)	244.9	347.4 (2.5)	3.6	
122	102.6 (2.5)	244.6	347.2 (2.5)	3.5	
182	102.6 (2.5)	244.6	347.2 (2.5)	3.6	

Table 4. Evolution of binding energies and peak width (FWHM) of Si and Ca, Ca-Si peak distance and Ca/Si ratio during vapor hydration of  $C_3S$ .

The measurement of the energy separation  $\delta$ Ca 2p-Si 2p between the Ca 2p 3/2 and Si 2p peaks minimizes errors due to the charge correction and provides reliable information on chemical changes [8, 24]: Shifts on Si peaks to higher BE due to the progressive hydration of C<sub>3</sub>S lead to reduction in the distance between the peaks of calcium and silicon, as there is a polymerization of the isolated silicate tetrahedra upon formation of C-S-H, and/or carbonation [9]. However, the formation of calcium carbonate is unlikely to occur here due to the nature of the experiments. Initial  $\delta$ Ca 2p-Si 2p values found here (245.3 eV) are lower than those from the literature [6, 24, 25]; however, the decrease in the Ca-Si distance after 3 h of hydration of C<sub>3</sub>S ( $\delta$ Ca 2p 3/2 - Si 2p = 0.6) is identical to that found by [24] after 4 h.

In the same way, the molar Ca/Si ratio of the newly formed hydrates Ca/Si ratio remains the same, as the expected isochemical conditions of the experiment. The excess Ca content (Ca/Si of about 3.5 vs. 3.0 of stoichiometric tricalcium silicate, **Table 4**) during the early hydration can be related to fast partial hydration and carbonation of the upper few nanometers of the sample during manipulation under atmospheric conditions prior to the experiments.

However, peak deconvolution of the Ca 2p 1/2 peaks shows contributions from carbonates and silicates: Calcium silicates have Ca 2p BE slightly higher than those of calcium carbonates. Considering only the calcium related to silicates in this equation, the Ca/Si ratio drops from the initial 1.6 to 0.5, as hydration progresses. Such low values indicate a progressive polymerization of silicate tetrahedra and subsequent increase in C-S-H chain

length, equivalent to an increase in  $SiO_2$  content [9, 26]. These results agree with Taylor [26], who suggests that the first precipitate is a jennite-like material, with a Ca/Si ratio of about 1.5, evolving to a tobermorite-like material as the hydration progresses. Detailed information on the tobermorite and jennite structure can be found elsewhere [20, 26].

The same experimental procedure was used for the hydration of a 200-nm-thick  $C_2S$  thin film (presented in detail in [4]), which, with exposure to water vapor, shows a similar drift of the main Si 2p peak, from 101.2 to 102.6 eV, denoting the disordering of the silicate structure related to progressive C-S-H formation (**Table 5**). This shift is accompanied by a peak broadening at higher ages, forming an additional peak at around 100.2 range, same as described by Black et al. [6], where a Si 2p 3/2 BE of 100.8 eV is observed for the fresh  $C_2S$  and followed by two peaks at 102.44 and 100.51 eV, which are seen for the aged sample. The peak at lower energies is related to unaltered  $\beta$ -C<sub>2</sub>S, while the peak at higher binding energy is assigned to a calcium-depleted C-S-H phase.

Age (min)	Binding energy (eV) and (FWHM)				Ca-Si distance (eV)	NBO-BO distance (eV)
	Si 2p	Ca 2p 3/2	O 1s NBO	O 1s BO	δCa 2p-Si 2p	δΝΒΟ-ΒΟ
0	101.2 (2.6)	347.0 (2.1)	530.1 (1.5)	531.4 (3.0)	245.8	1.3
2	101.4 (2.6)	347.1 (2.1)	530.3 (1.4)	531.5 (3.1)	245.7	1.2
7	101.7 (2.7)	347.3 (2.6)	530.4 (1.5)	531.7 (3.0)	245.7	1.3
12	101.6 (2.8)	347.3 (2.2)	530.3 (1.3)	531.7 (3.1)	245.7	1.3
17	101.8 (2.9)	347.5 (2.1)	530.3 (1.2)	531.9 (3.0)	245.8	1.5
27	101.9 (2.8)	347.4 (2.1)	530.3 (1.5)	531.9 (2.8)	245.5	1.5
42	102.0 (2.9)	347.4 (2.2)	530.2 (1.8)	531.9 (2.9)	245.5	1.7
62	100.2 (1.2)	347.5 (2.2)	530.4 (2.0)	532.1 (2.8)	245.5	1.7
	102.0 (2.9)					
122	100.1 (1.2)	347.5 (2.2)	530.2 (2.0)	532.1 (2.8)	245.4	1.8
	102.1 (2.8)					
182	100.2 (1.3)	347.7 (2.3)	530.4 (1.9)	532.2 (2.8)	245.3	1.9
	102.4 (2.9)					
272	100.2 (1.7)	347.6 (2.3)	530.2 (1.8)	532.2 (2.8)	245.1	1.9
	102.5 (2.8)					
632	100.4 (1.4)	347.7 (2.2)	530.4 (2.0)	532.3 (2.8)	245.1	1.9
	102.6 (2.8)					

Table 5. Evolution of binding energies of Si, Ca and O (peak width, FWHM), Ca-Si peak distance and NBO-BO peak distance during vapor hydration of C<sub>2</sub>S.

The Ca BE, on the other hand, shows a small progressive shift (0.7 eV) when hydration goes on. The Ca 2p3/2 peak is centered at around 347.0 eV (**Table 5**) for fresh C<sub>2</sub>S, a value slightly lower than the one previously reported by Black et al. [6] (347.23 eV).

The initial energy separation between Ca 2p 3/2 and Si 2p peaks found in this work (245.8 eV) is fairly lower than those reported by Black et al. [6], (246.72 eV). The progressive hydration of C<sub>2</sub>S results in shifting of the Si 2p peak to higher BE, therefore reducing the  $\delta$ Ca 2p-Si 2p, due to the polymerization of the isolated silicate tetrahedra upon formation of C-S-H.

The molar Ca/Si ratio of the newly formed hydrates in  $C_2S$  thin film starts with a lower value than expected from the bulk material (initial Ca/Si of about 1.6 vs. 2.0 of stoichiometric dicalcium silicate), indicating a partial hydration of the upper few nanometers of the sample during manipulation under atmospheric conditions, and decreases over time, reaching Ca/Si = 1.0. The same values are described by Regourd et al. [24], who found this value after 4 h of hydration. While small contributions from portandite and/or unhydrated  $C_2S$  cannot be excluded, such low Ca/Si values clearly evidence the formation of C-S-H. Here, different peaks related to the contributions from carbonates and silicates are not observed.

In this sample, it was possible to study the O 1s spectrum, which provides important information on the structure of minerals and glasses but is complex to be assessed. O 1s can be present in different components, which have different BE: non-bridging oxygen (530–530.5 eV), bridging oxygen (531.5–532.7 eV), hydroxide species (533–533.5 eV), bound water (534 eV) and portlandite at calcium-rich samples (531.6 eV), while amorphous silica does not add any extra component [27].

Changes in the peaks separation between bridging and non-bridging oxygen atoms ( $\delta$ NBO-BO) are related to silicon polymerization: Peak distance grows with the falling of the Ca/Si ratio that happens together with hydration by water vapor, since the contribution from non-bridging oxygen decreases as the hydration progresses (the number of Ca-O-Si units decreases and Si-O-Si units increases), as observed in **Table 5**.

# 4. Final remarks

The fact that the chemical and mineralogical composition of the calcium silicate thin films is in accordance with the respective bulk materials proves that the electron beam evaporation is a useful and powerful way for synthesizing thin films of calcium silicates. However, not the same was observed for the calcium aluminate phases: The electron beam evaporation conditions used in this work are not suitable for producing thin films of these materials. Chemical and mineralogical analysis of the residue left in the crucible after the evaporation shows that the aluminum present on these phases does not evaporate, and for this reason, there is no signal of this element in the thin films. Aluminum reacts abnormally when submitted to the extreme conditions during the sample preparation.

This behavior is clearly observed with the GIXRD and XPS data. Even as the electron beam evaporation fails to provide the expected results for the evaporation of phases containing

aluminum, other standard techniques for producing ceramic thin films can be applied. Presumably, sputtering may allow synthesizing thin films of these phases as in this technique the sample is not heated. Instead, atoms are ejected through the bombardment of the target material by energetic particles.

The difficulty on using sputtering techniques arises from the fact that it is challenging to have suitable targets as it demands unusual preparation and generally companies that manufacture them refuse to produce targets with special specifications. In this case, additional manufacturing effort is needed for producing targets so that this technique can be applied for the synthesis of thin films of clinker phases.

This type of sample has been proven to be useful in attaining information related to dissolution, hydration and carbonation in ways never before explored. Research using thin films of clinker phases for hydration analysis is found elsewhere [3, 4].

XPS provides information on the upper few nanometers of the sample only, being suitable for thin films studies, offering accurate chemical composition and coordination state data. Regarding the XPS data for all the  $C_3S$  and  $\beta$ - $C_2S$  samples, the peak positions, peak distances and peak widths are typically equivalent to the bulk material, proving that they have the same chemical composition. However, pre-hydration is observed due to the contact of the sample with the atmosphere.

Hydration of  $C_3S$  presented shifts on Si 2p peak to higher BE, related to silicon polymerization by the formation of C-S-H. The  $\delta$ Ca 2p-Si 2p distance decreased with time, indicating that the kinetics of early C-S-H formation is not significantly altered when vapor is used instead of liquid water.

The molar Ca/Si ratio in both  $C_2S$  and (from carbonate contribution)  $C_3S$  decreases as the hydration proceeds, due to the progressive polymerization with an increase in chain length of the silicate hydrates formed. Initial Ca/Si values in  $C_3S$  correspond to a jennite-like material and evolve to a tobermorite-like component after 3 h of exposure to water.

Some possible pre-hydration is observed in both calcium carbonates, by the contact with the atmosphere during the sample manipulation or due to the preferential deposition of the silicon on the sample's surface after the evaporation. Besides that, the peak positions of the bulk material are maintained and so the chemical state.

The  $C_2S$  samples provided clearly distinguished O 1s spectra, allowing to identify the  $\delta$ NBO-BO peak separation, which increases with the silicon polymerization, describing the C-S-H formation.

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#### References

- K. L. Scrivener and A. Nonat. Hydration of cementitious materials, present and future. Cem. Conc. Res. 2011;41(7):651–665.
- [2] E. Dubina, L. Black, J. Sieber, and R. Plank. Interactions of water vapour with unhydrous cement minerals. Adv. Appl. Ceram. 2010;109:260–268.
- [3] V. Rheinheimer and I. Casanova. Hydration of C3S thin films. Cem. Concr. Res. 2012;42:593–597.
- [4] V. Rheinheimer and I. Casanova. An X-ray photoelectron spectroscopy study of the hydration of C2S thin films. Cem. Concr. Res. 2014;60:83–90.
- [5] L. Black, A. Stumm, K. Garbev, P. Stemmermann, K. R. Hallam, and G. C. Allen. X-ray photoelectron spectroscopy of the cement clinker phases tricalcium silicate and βdicalcium silicate. Cem.Conc.Res. 2003;33(10):1561–1565.
- [6] L. Black, K. Garbev, P. Stemmermann, K. R. Hallam, and G. C. Allen. Characterisation of crystalline C-S-H phases by X-ray photoelectron spectroscopy. Cem. Concr. Res. 2003;33(6):899–911.
- [7] L. Black, K. Garbev, and I. Gee. Surface carbonation of synthetic C-S-H samples: A comparison between fresh and aged C-S-H using X-ray photoelectron spectroscopy. Cem. Concr. Res. 2008;38(6):745–750.
- [8] L. Black, K. Garbev, G. Beuchle, P. Stemmermann, and D. Schild. X-ray photoelectron spectroscopic investigation of nanocrystalline calcium silicate hydrates synthesised by reactive milling. Cem. Concr. Res. 2006;36(6):1023–1031.

- [9] M. Yousuf, A. Mollah, T. R. Hess, Y.-N. Tsai, and D. L. Cocke. An FTIR and XPS investigations of the effects of carbonation on the solidification/stabilization of cement based systems-Portland type V with zinc. Cem. Concr. Res. 1993;23(4):773–384.
- [10] L. Dubina, E. Sieber, R. Plank, and J. Black. Effects of pre-hydration on hydraulic properties of Portland cement and synthetic clinker phases. Cem. Conc. Sci. 2008; 64:49–67.
- [11] L. Nicoleau, E. Schreiner, and A. Nonat. Ion-specific effects influencing the dissolution of tricalcium silicate. Cem. Conc. Res. 2014;59:118–138.
- [12] P. Dutta. Grazing incidence X-ray diffraction. Curr. Sci. 2000;78(12):1478–1483.
- [13] M. Bouroushian. Characterization of thin films by low incidence X-ray diffraction. Cryst. Struct. Theory Appl. 2012;1(3):35–39.
- [14] S.-L. Chang. Thin-film characterization by grazing incidence X-ray diffraction and multiple beam interference. J. Phys. Chem. Solids. 2011;62(9–10):1765–1775.
- [15] V. R. Mastelaro, C. R. Foschini, and J. A. Varela. Grazing incidence X-ray diffraction and atomic force microscopy analysis of BaBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> thin films. Thin Solid Films. 2002;415(1– 2):57–63.
- [16] C.-H. Ma, J.-H. Huang, and H. Chen. Residual stress measurement in textured thin film by grazing-incidence X-ray diffraction. Thin Solid Films. 2002;418(2): 73–78.
- [17] R. Thomas, N. K. Karan, P. Ehrhart, R. Waser, and R. S. Katiyar. Dysprosium scandate thin films prepared by metal organic chemical vapor deposition on Pt/TiOx/SiO2/Si substrates for MIM capacitor applications. ECS Transactions. 2007;11(4):529–540.
- [18] S. Gaufinet, E. Finot, and A. Nonat. Experimental study and simulation of C-S-H nucleation and growth. Mater. Struct. 1997;38:435–442.
- [19] Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, and H. Hosono. Thin film fabrication of nano-porous 12CaO<sub>7</sub>Al<sub>2</sub>O<sub>3</sub> crystal and its conversion into transparent conductive films by light illumination. Thin Solid Films. 2003;445(2):309–312.
- [20] H. F. W. Taylor. Cement Chemistry. Thomas Telford Publishing ed.; London: 1997.
- [21] E. Paparazzo. On the quantitative XPS analysis of Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>1-x</sub>O oxides. J. Electron Spectros. Relat. Phenomena. 2006;154(1–2):38–40.
- [22] P. C. J. Graat and M. A. J. Somers. Simultaneous determination of composition and thickness of thin iron-oxide films from XPS Fe 2p spectra. 1996;36–40.
- [23] F. Vázquez-Acosta, L. M. Torres-Martínez, W. López-González, and J. Ibarra-Rodríguez. Influence of iron content on the color of the C3A–Fe2O3 system synthesized under different conditions of temperature, atmosphere and cooling. Ceram. Int. 2012;38(4):3261–3272.

- [24] M. Regourd, J. H. Thomassin, P. Baillif, and J. C. Touray. Study of the early hydration of Ca3SiO5 by X-ray photoelectron spectrometry. Cem. Concr. Res. 1980;10(2):223–230.
- [25] S. Long, C. Liu, and Y. Wu. ESCA study on the early C3S hydration in NaOH solution and pure water. Cem. Concr. Res. 1998;28(2):245–249.
- [26] H. F. W. Taylor. Proposed structure for calcium silicate hydrate gel. J. Am. Ceram. Soc. 1986;69(6):464–467.
- [27] M. Regourd, C. Defosse, S. A. Jefferis, and J. Bensted. Microanalytical studies (X-ray photoelectron spectrometry) of surface hydration reactions of cement compounds [and discussion]. Philos. Trans. R. Soc. London. Ser. A, Math. Phys. Sci.. 1983;310(1511): 85–92.

Application of Thin Films: A Synergistic Outlook

# Layer-by-Layer Thin Films and Coatings Containing Metal Nanoparticles in Catalysis

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Additional information is available at the end of the chapter

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#### Abstract

The layer-by-layer (LbL) technique is one of the most promising ways of fabricating multilayer thin films and coatings with precisely controlled composition, thickness, and architecture on a nanometer scale. This chapter considers the multilayer thin films and coatings containing metal nanoparticles. The main attention was paid to LbL films containing metal nanoparticles assembled by convenient methods based on the different intermolecular interactions, such as hydrogen bonding, charge transfer interaction, molecular recognition, coordination interactions, as driving force for the multilayer buildup. Much attention has paid to the LbL films containing metal nanocomposites for multifunctional catalytic applications, in particular, photocatalysis, thermal catalysis, and electrocatalysis. The preparation protocol of LbL-assembled multilayer thin films containing metal nanoparticles (such as Au, Ag, Pd, Pt), metal oxides (Fe<sub>2</sub>O<sub>4</sub>), and sulfides (CdS) that are supported on the various surfaces of nanotubes of TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> membranes, graphene nanosheets, graphene oxide and further applications as catalysts with respect to photocatalytic, electrocatalytic performances is discussed. The systematization and analysis of literature data on synthesis, characterization, and application of multilayer thin films and coatings containing metal nanoparticles on the diverse supports may open new directions and perspectives in this unique and exciting subject.

**Keywords:** layer-by-layer assembling, thin films and coatings, polyelectrolytes, metal nanoparticles, immobilization, semiconductors, catalysts

## 1. Introduction

One of the main purposes of nanotechnology is fabrication of highly functional low-dimensional materials and systems [1]. Most of such systems are produced by assembling of nano

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© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. objects in thin films or coatings [2]. The utilization of high functional materials is steadily growing and covers many areas of human activity such as fabrication of drug delivery systems [3], antibacterial coatings [4, 5], electronics [6], chemical sensors [7], and even in dentist applications. Some assembling procedures need to immobilize metal nanoparticles such as gold, silver, copper, palladium, and platinum to preserve them in origin state and to avoid the aggregation. Such immobilization can be proceeded by the incorporating of nanoclusters into polymer scaffold. The scaffold plays three main roles [8]:

- (1) It provides assistance to particle assembling.
- (2) It ministers like a matrix for ordering and homogeneous orientation of systems.
- (3) Due to its some properties, such electronic properties, it acts as a functional element.

Polymer science and technology that spreads polymer-based biomaterials, catalysts bounded by polymer, nanofibers fabricated by polymer assisted electrospun and attracts tremendous attention [9]. The interlacing of polymer technology with nanoscience allows expanding both of them and solving the existing challenges in the fabrication on a nanoscale. Because of plenty of binding region in polymer, it can effectively immobilize the nanoparticles and at the same time act as a mediator between the substrate and nano objects [2]. Wide exploitation of polymers as supporting agents during formation of the coating is applied in the LbL assembling technique. The LbL assembling approach can be qualified as a good alternative approach to the well-known deposition methods, because it is versatile, inexpensive, and comfortable for use. Moreover, the large advantage of LbL method is that, in contrast to widespread strategies of fabrication of nanoscale structures on top of planar substrate such as chemical vapor deposition [10], atomic layer deposition [11], molecular beam epitaxy [12], hydrothermal deposition [13] and so forth, it is suitable for the formation of a uniform coating on curved surfaces [14]. The whole process of multilayer structures buildup by LbL assembling, whose driving force, despite hydrogen bonding, covalent bonding, etc., is mainly electrostatic interaction between the oppositely charged species [14, 15], usually consists of four steps [16] (**Figure 1a**):

- (1) Immersing of a cleaned, positively charged solid substrate into the solution of an anionic polyelectrolyte. Electrostatic force, collectively with adsorption, builds the first layer of multilayer construction.
- (2) Removal of the excess and weak adsorbed polyelectrolyte from the surface is carried out by substrate rinsing with deionized water.
- (3) Bilayer structure is achieved by immersing of the substrate into the solution of the cationic polyelectrolyte. This step restores the original surface charge.
- (4) Final rinsing removes the excess of cationic polyelectrolyte.

By repetition of these cycles [17], a desired number of layers can be achieved on curved planes, as shown in **Figure 1b**, therefore the whole thickness of multilayer is easy controlled. Generally, to create a difference in surface charges, using the LbL procedure,

various polyelectrolytes are employed. The mostly applied positively charged polyelectrolytes are: poly(allylamine hydrochloride) (PAH), polyethyleneimine (PEI), or poly(diallyldimethylammonium chloride) (PDDA) and negatively charged polyelectrolytes are: poly(vinyl sulfate) (PVS), poly(acrylic acid) (PAA), or poly(styrene sulfonate) (PSS). It should be also mentioned that the LbL method expands the possibilities of obtaining organic/inorganic films with high accuracy just by changing the number of multilayers, concentration and pH of the solution. The application area of nanosystems obtained by LbL assembly is very wide. It includes fabrication of layers with magnetic, fluorescent, catalytic and various electronic properties. For example, the magnetic multilayers can be used in medicine as well as other technical applications. Fluorescent properties are widely benefited in optical devices. LbL-assembled catalysts can be applied for hydrogenation, oxidation of various substrates and water splitting. Nobel metal particles incorporated into the multilayer structures are adopted as coatings for light absorption enhancing by the surface plasmonic effect. In the following subsection we consider the LbL thin films and coatings containing metal nanoparticles, metal oxides, and sulfides together with their application of in catalysis.



**Figure 1.** Schematic illustration of the LbL assembling process by alternately dipping of a positively charged substrate into the solutions of a oppositely charged polyelectrolyte (a) and formation of shell structure on curved planes (b).

# 2. LbL thin films and coatings containing metal nanoparticles, metal oxides, and sulfides

#### 2.1. LbL thin film and coatings containing gold (AuNPs) and silver (AgNPs) nanoparticles

The metal nanoparticles with attractive optical, electronic, and catalytic properties are used in a broad range of applications ranging from physics to medicine [18]. For assembling such nanoscaled particles with controlled parameters, it is necessary for scientists to develop new methods which can allow to obtain constructions with required properties [19]. The charge transfer properties of metal particles incorporated in a thin layer depend on particle size and distance between them in vertical and space distributions [20]. At the same time, the dependence between the particle size reflects to a high reactivity/selectivity for the hydrogenation of unsaturated alcohols [21, 22]. Recently, noticeable research works were conducted with respect to immobilization of mono- and bimetallic nanoparticles into the matrices of ultrathin films to obtain the effective nanocatalysts [23]. Such, LbL-assembled layers of gold nanoparticles within interpolyelectrolyte complexes can be formed either by interaction of poly(ethyleneimine)-gold nanoparticles (PEI-AuNPs) with poly(acrylic acid) (PAA) or by interaction of poly(acrylic acid)-gold nanoparticles (PAA-AuNPs) with PEI [24]. It is also well known that the noble metal nanoparticles, in particular Au, Ag, and Pt possess strongly marked plasmonic properties, which can be controlled by changing fabrication parameters. Thus, changing of volume, dipolar coupling, or a type of solvent alters the wavelength of plasmonic resonance. For instance, dipolar coupling of Au can be controlled by changing the distance between the particles, such distance among the particles is easily adjusted by modification of dendrimers, highly branched monodisperse molecules. The dendrimers have the series of chemical modifications and cavities which act as templates for nanoparticle growth. For example, polyamidoamine (PAMAM) or carboxyl-terminated PAMAM [25] dendrimers are utilized as a matrix with effective nanoparticle stabilization [26]; therefore, Au, Cu, Pt, and Pd nanoparticles can be formed and stabilized therein [27]. The wavelength of surface plasmonic resonance of nanoscaled gold nano objects incorporated within PAMAM depends on the number of the layers. Increasing of the number of LbL-assembled PAMAM enlarges the distance between the Au nano objects, which leads to an ultraviolet shifting of plasmonic glow. Besides the tuning of plasmonic properties, it is also possible to adjust the fluorescent properties of gold nano objects only by magnification the thickness of multilayer or by the increasing the number of LbL cycles. For example, fluorescence of Au, covered in a core-shell manner by organic multilayers, can be easily tuned by varying the number of nonfluorescent layers [28].

Silver/gold coatings formed onto a commercial anion exchange resin via LbL [5] are very appropriate bimetallic composition for catalytic reduction of nitroaromatic compounds. Such core-shell heterostructures can be prepared by using of electrostatic force of the charged resin beads. Such resin beads support immobilization of anionic metal precursors of silver/gold nanoparticles onto the solid resin matrix and reduce 2-nitrobenzoic acid to obtain the corresponding amines through the effective catalysts.

**Figure 2** demonstrates a simple method of integrating the electroactive gold nanoparticles (AuNPs) with graphene oxide (GO) nanosheets. Such LbL structures composed of threedimensional electrocatalytic thin films are active toward methanol oxidation [9]. This approach involves the electrostatic interaction of negatively charged graphene oxide nanosheet with positively charged AuNPs. The distribution of gold nanoparticles on the surface of GO can be controlled using the LbL method, the latter enhances the stability keeping from aggregation during the electrocatalytic cycles. Due to high versatile and tunable properties of LBL-assembled thin films, a hybrid electrocatalyst can be easily designed for direct methanol fuel cell (DMFC). Such LbL assembly allows for the fabrication of the nanoparticle/graphene hybrid multilayer structure, which exhibits a wide range of functionalities. **Figure 3** shows a schematic representation of the LbL film made of poly-N-vinylpyrrolidone-stabilized AuNPs (PVP-AuNPs) and single-walled CNTs deposited on a fluorine-doped tin oxide (FTO) glass. Such structures may be used in the field of catalysis, fuel cells, and sensing.



Figure 2. LbL integration of gold nanoparticles (AuNPs) with graphene oxide (GO) nanosheet.



Figure 3. LbL films of PVP-AuNPs and single-walled CNTs supported on a fluorine-doped tin oxide (FTO) glass.

#### 2.2. Immobilization of Pd and Pt nanoparticles into the LbL matrix

One of the main important catalytic properties of Pt and Pd containing films is electrocatalytic oxidation of methanol [12, 29, 30]. Immobilization of Pd nanoparticles (PdNPs) usually proceeds on solid supports, such as carbon, graphene, metal oxides, and zeolites [26]. Assembling of PdNPs onto carbon allows for obtaining a nanocomposite possessing chemosensitive properties. The electrocatalytically active graphene-palladium composites can be utilized as hydrogen detectors [31]. The PdNPs are stabilized by capping with ligands, ranging from small organic molecules to large polymers [22]. Immobilization of PdNPs in the form of spherical aggregates takes place by using of dendritic molecules such as amine-terminated PAMAM dendrimers (G1.0 PAMAM) or POSS-NH<sub>3</sub><sup>+</sup> [32]. The process of self-organization of spherical templates is carried out in solution at room temperature, which allows for obtaining the dendrimers with an average size of about 70 nm.

The PdNPs synthesized by the reduction of Pd(II) to Pd(0) by using NaBH<sub>4</sub> can be incorporated onto magnetic nanoparticles (MNPs). Such incorporation is carried out by the LbL technique, which is suitable to poly(acrylic acid)-poly(ethyleneimine)/Pd(II) multilayers formation in a core-shell manner [33]. Such hybrid structures are considered to employ for the hydrogenation of various olefin alcohols. Besides using MNP as a substrate, it is also possible to assemble nanosized Pd-polyelectrolyte multilayer onto aluminum powder [34]. Diversity of PdNPs diameters, within multilayers onto aluminum powder, can be regulated by changing the ratio between poly(acrylic acid) and Pd(II). Such changing allows to obtain the ranging of particles with diameters from 2.2 to 3.4 nm. Consequently, by this way, it is easy to tune the catalytic selectivity of such a hybrid system.

The Pt nanoparticles (PtNPs) with good optical and catalytic properties can also be incorporated within PAMAM dendrimers. The simple way of PAMAM dendrimers with incorporated Pt nanoclusters deposition is LbL assembling them onto the solid substrates [28]. For instance, the Pt-PAMAM structures are obtained through the chemical reduction of  $H_2PtCl_6$ , in the presence of PAMAM, using formic acid as a reducing agent. Then, by alternating immersions of the substrate into the polyelectrolyte solutions consisting of poly(vinylsulfonic acid) and PAMAM dendrimers the multilayer structures are produced. Time duration for each layer formation is about 5 min [35].

Using PAMAM dendrimers/PtNPs allows to obtain the nonvolatile memory (NVM) devices [36]. However, the process of NVM assembling is slightly differ from the above-described process and involves the formation of PtNPs within a ultrathin film matrix, formed by covalent LbL assembly of pyromellitic dianhydride (PMDA) and second generation of PAMAM dendrimer in supercritical carbon dioxide (SCCO<sub>2</sub>). To design such a structure, nanoparticles' precursor is sequestered within a dendrimer matrix by using SCCO<sub>2</sub> as a processing medium. This technique of preparation nanostructured films, with assistance of SCCO<sub>2</sub>, at room temperature is a comparable clean process.

Aside from NVM, the metal-insulator semiconducting (MIS) devices can be formed using dendrimer-encapsulated nanoparticles. MIS installation proceeds by the covalent molecular assembly of dendrimers with incorporated agents. The MIS device configuration is shown in **Figure 4**.



Figure 4. MIS device configuration consisting of Au bottom electrode, dendrimer-encapsulated nanoparticle layer,  $Al_2O_3$  layer, and Au top electrode.

#### 2.3. Assembling of LbL films and coatings containing Fe<sub>3</sub>O<sub>4</sub> and CdS

In this section, we describe LbL immobilized  $Fe_3O_4$  and CdS nanoparticles that possess magnetic, semiconducting, optic, and other properties. Since metal oxides are widely used in gas sensing application [38], electrochemical capacitors [39], lithium-ion batteries [40], photocatalytic materials [41]; it is important to develop their installation direct on the electrodes. Therefore, the process of immobilization of metal oxides such as  $TiO_{\nu}$ ,  $Fe_{2}O_{\mu}$  and ZnO by using the LbL method, where the general assembling of metal oxides proceeds with assistance of polyelectrolytes [42], has been tremendously studied [43]. In the past two decades, a great attention has been paid to the synthesis of  $Fe_3O_4$  magnetic nanoparticles due to their cheapness, nontoxicity and readily producing. Direct deposition of Fe<sub>3</sub>O<sub>4</sub> onto an electron conductive material, such as indium tin oxide (ITO)-coated glass, allows using it in electrochemical capacitor application [44] and biomedicine. Combination of various fabrication methods of these particles with the LbL deposition technique allows to obtain high quality core-shell architectures. The Fe<sub>3</sub>O<sub>4</sub> preparation method in general involves the dissolution of the mixture of FeCl<sub>3</sub> and FeCl<sub>3</sub> in aqueous solution (chemical coprecipitation). The obtained particles of  $Fe_{a}O_{a}$ , modified by polymers, can be coated onto quantum dots (Qds), such as CdTe, in a core-shell manner via the LbL technique. Such strategy allows to fabricate the magnetic luminescence  $Fe_3O_4$  nanocomposites [44]. The medical application of magnetic structures, incorporated via LbL has also been developed. In particular, the Fe<sub>3</sub>O<sub>4</sub> and Pt nanoparticles, incorporated into hemoglobin, improves the biosensitivity of the protein [45]. Employment of  $Fe_3O_4$  for magnetic separations of protein is possible by coating it onto SiO<sub>2</sub> particles [46]. Another good example of  $Fe_3O_4$  particles involved in the high functional core-shell formation is Fe<sub>3</sub>O<sub>4</sub>/Au structure. Such composition is widely applied in biomedical and technological fields due to their unique optical, magnetic, and catalytic properties [47].

Since the  $Fe_3O_4$  particles possess magnetic properties, it is possible to assemble them with the help of magnetic field. Combination of the LbL technique and magnetic field leads to compaction of particle packing without increasing the total thickness of the obtained film [48].

CdS is one of the most interesting semiconducting materials due to its band structure, luminescent aptitude, etc. Nanoscaled CdS particles with a size range up to 10 nm can be considered as Qds and currently attract a large number of researchers due to their unique optical and electrical properties [49]. There are several CdS Qds preparation methods, but among them the LbL derivation, also known as successive ionic layer adsorption SILAR [50] deposition, is a very promising approach due to its versatility and simplicity to obtain high controlled objects. The method is as follows: in separate beakers, the dissolved ions of Cd<sup>+</sup> and S<sup>-</sup> are deposited onto a substrate, forming CdS structure. It is obvious that the structure-building force is Columbic attraction. This technique proceeds without participation of polymers, consequently it is not necessary to remove organics by the calcination of structure for increasing the attaching surface between the CdS layer and the active materials. The theoretical description of SILAR (LbL derivation) [50] can be described as following, the sequential immersion of the substrate into oppositely charged liquid solution results the reaction between the substrate and dissolved species. Heterogeneity of layer structure enriches by rinsing in water after each dipping into electrolyte solution. The principle of film growing can be explained by the following equation:

$$(p K_{aq}^{a+} + q X_{aq}^{b-}) + (b' Y_{aq}^{q'+} + a A^{p-}) \to KpA a_{s} \downarrow + q X_{aq}^{b-} + b' Y_{aq}^{q+}; ap = bq = b' q',$$
(1)

where,

K is cation ( $Cd^{2+}$ ,  $Fe^{3+}$ ,  $Cu^+$ , etc.)

A represents the anions (O, S, or Se)

p is the number of cations

*a* is the numerical value of charge on cation

Y is the ion which is attached to chalcogen ion

X represents an ion in cationic precursors

q represents the number of ions

*b* represents the charge value of ions

b' represents the number of ions attached to chalcogens

q' represents the charge value of ions attached to chalcogens

Schematic representation of the SILAR process is shown in **Figure 5**. The CdS Qds obtained by the LbL (SILAR) method can easily be used in the fabrication of Qds sensitized solar cells, which are very well suited for the creation of alternatives to silicon-based photovoltaic devices. A simple example of preparation of CdS-based Qds-sensitized solar energy converting construct is given by Chen and co. [51]. They sensitized ZnO nanosheets, obtained through the three-electrode electrodeposition method, with further coating them by CdS Qds. Such coating can be assembled through alternating dipping of ZnO nanosheets comprise a glass substrate into the liquid solutions. The whole process of LbL CdS assembling can be described as:

- (1) Immersing of negatively charged ZnO deposited glass substrate in a beaker containing 0.05 M Cd(NO<sub>3</sub>)<sub>2</sub> to adsorb Cd<sup>2+</sup>. Resulting charge of the glass surface becomes positive.
- (2) Rinsing surface with deionized water to remove excess of ions.
- (3) Dipping of a positively charged substrate into dissolved 0.05 M Na<sub>2</sub>S to deposit S<sup>2-</sup>.
- (4) Final cleaning of surface is carried out by rinsing with clean water.



Figure 5. General scheme of the SILAR method for the fabrication of Qds.

### 3. Application of NPs immobilized via the LbL assembly in catalysis

#### 3.1. LbL-assembled layers for water splitting application

Hydrogen production by solar driving water splitting is a promising energy generation way. The development of hydrogen production is based on the fact that it is an ideal fuel for the future [52]. Among the different approaches to release hydrogen gas, photoelectrochemical (PEC) water splitting is the most promising. Overall water splitting reaction can be written as:

$$H_{2}O(liquid) = H_{2}(gas) + \frac{1}{2}O_{2}(gas).$$
 (2)

A PEC cell consists of two electrodes: one is called anode/photoanode and another is cathode/ photocathode. On the surface of cathode,  $H_2O$  molecule is reduced:

$$2H + 2e^{-} = H_{2(gas),}$$
 (3)

whereas on the anodes, it oxidized.

$$H_{2}O_{\text{(liquid)}} + 2h^{+} = 2H + O_{2(\text{gas}),}$$
 (4)

where  $e^{-}$  is an electron and  $h^{+}$  is a hole.

This process must take place under solar irradiation. Efficiency of this process depends on the following factors:

- (1) The ability of photoelectrodes to adsorb a photon
- (2) The performance of creation charge carries
- (3) The efficacy of charge carriers in the water splitting process.

To overcome these affecting factors on the efficiency of the cell, scientists need to develop more ideal electrodes. It means the control of all technical parameters including thickness of semiconducting layer, morphology, and density of particles, which forms active layer and so on. A simple way to control the distance between the electroactive species inside of multilayer structure is offered by LbL assembling [53]. Absorption of light by semiconducting materials results in creation an exciton, electron-hole pair. To use an exciton in the water splitting process, it must be separated. The separated electron and hole act as reduction and oxidation centers. Coupling of two different types of active materials allows the faster separation of exciton. For example, a couple of anatase and rutile phases of TiO<sub>2</sub> improves the separation of exciton, created in the anatase structure [43]. In order to obtain a homogeneously distributed anatase/rutile, a heterostructure LbL approach is applied. The LbL assembling to building of anatase/rutile heterostructure is carried out in the presence of poly(sodium-4-styrenesulfonate) (PSS). This polymer serves as an adsorption layer. The rutile phase of TiO, coated by PSS adsorbs an anatase structure. To remove polymer interlayer and form good attachment between rutile and anatase the obtained material is heated up to 500°C (Figure 6).



Figure 6. Formation of rutile/anatase heterostructure by LbL assembling.

Improvement of solar energy conversion can be achieved using an aligned structure, such as ZnO nanorods, because of reducing the charge pathway (**Figure 7**). The ZnO is a broadly used as a wide band gap semiconductor [37], and it plays a great role in gas sensing, optical and electrical devices. In spite of similarity of band structures between ZnO and  $\text{TiO}_{2^{\prime}}$  electron mobility on ZnO is much higher. But negligible instability of ZnO in an aqueous solution makes it unfavorable for this material in the water splitting process. Recently, protection of ZnO was offered by building a core/shell structure, where a core is ZnO and a shell is represented by narrow band gap semiconductors. Covering of ZnO nanorods by narrow band gap CdS was studied a lot. The most attractive approach for it is using of SILAR technique [20, 54, 55]. The covering of free-standing ZnO nanorods by CeO<sub>2<sup>'</sup></sub>, CdS, and Ag nanoparticles proceeds, as shown in **Figure 8**. The negative charges on the ZnO surface are formed by immersing the substrate into PAH and PSS. Then, the oppositely charged ions (Ce<sup>3+</sup>, Cd<sup>2+</sup>, Ag<sup>+</sup>) are adsorbed on the surface of negatively charged ZnO nanorods due to strong electrostatic attraction. Reduction of metal ions is performed by NaBH<sub>4</sub>. To use such composition for PEC water splitting or in dye-sensitized solar cells they should have a good contact to the electrode.



Figure 7. Schematic representation of the electron transport process through nanoparticles (a) and nanorods (b).

The immersing of the conductive substrate coated by aligned ZnO nanorods in two different aqueous solutions of Cd<sup>2+</sup> cations and S<sup>2-</sup> anions for 20 second allows to obtain a ZnO/CdS core-shell structure, which is a suitable heteromaterial for water splitting application. Effectiveness of such PEC water splitting of the ZnO/CdS core-shell composition has been showed an increased open voltage of around –1.55 V vs. bare ZnO arrays whose open voltage is – 0.8 V [56].

# 3.2. Reduction and oxidation of organic substrates by metal nanoparticles immobilized within LbL films and membranes

In the past few years, LbL films and membranes are more commonly used in catalytic processes. Films with incorporated metal nanoparticles synthesized by the LbL technique are commonly used for multifunctional catalytic applications, including photocatalysis, thermal catalysis, and electrocatalysis, which means the reduction [57] and oxidation of various organic substrates [18, 58]. Authors [59] showed that LbL covalently stacked multilayer structure of immobilized metal nanoparticles ensure the stability of particles against aggregation. Such multilayer structure can be achieved by embedding the nanoparticles into a porous polymer membrane. The porous structure of polymer membrane is utility to creation of concentration gradient between the aqueous medium and reaction centers, which accelerate the reaction rate. The catalytic activity of immobilized metal nanoparticles within the polymer scaffold depends on the number of bilayers as well as the size of the particles. For instance, 10 bilayers show higher catalytic activity than the higher numbers of layers. While the high number of bilayers exhibits good stability. The optimization of such criteria is possible by modulating the number of layers in the LBL structure, which allows to prepare highly catalytic active and stable films using this simple and versatile approach.



Figure 8. Using the LbL technique for covering free-standing ZnO nanorods by CeO., CdS, and Ag nanoparticles.

The multilayered metal nanoparticles deposited onto  $TiO_2$  nanotubes demonstrate efficient thermal catalytic activities toward reduction of nitrophenol to nitroaniline under ambient conditions [60]. The catalytic properties of metal nanoparticles/ $TiO_2$  nanotubes (M/TNT) nanocomposites are

achieved mainly due to the distribution of monodispersed metal nanoparticles on TNT [61, 62]. It is evident that distribution of nano objects onto a substrate affects the catalytic performance of multilayer films. Therefore, surface modification of 1D semiconductors through the LbL assemble strategy can be used as an effective way to achieve a uniform deposition of metal nanoparticles for various catalytic applications. The electrocatalytic performances of LbL-assembled multilayers are also extensively exploit for selective hydrogenation of a series of unsaturated alcohols [34] and methanol oxidation. For example, a strong synergistic catalytic behavior exhibits polyaniline-Pt (PANI/Pt) nanocomposites fabricated by the modification of LbL assembly by electrodeposition [42]. Such synergic catalytic activity is used for methanol oxidation. But the catalytic activity of such composites depends not only on a number of layers (and hence the Pt loading) but mostly on nature of the outermost layer. The catalytic activity of such multilayers can be enhanced when they end by the PANI layer as the oxidation of methanol by Pt particles facilitated by the formation of hydrogen bonds with the outer PANI layer.

# 4. Concluding remarks

Immobilization of metal and semiconducting nanoparticles within the multilayer structure by the LbL self-assembling technique is an effective process to design drug delivery systems, capacitors, sensors, solar and fuel cells, quantum dots, catalysts with unique properties. Gold, silver, palladium, and platinum nanoparticles incorporated into the polymer thin films leads to enhancement of plasmonic and catalytic properties, which can be easily tuned by changing multilayer structure. Preparation of nanocatalysts using the LbL assembly technique represents a comparatively simple, robust, efficient, and highly versatile method and demonstrates significant advantages over routine methods. The multilayer thin films containing metal nanoparticles demonstrate efficient catalytic activities toward reduction of nitrophenol, oxidation of methanol, and selective hydrogenation of unsaturated alcohols under ambient conditions. One of the promising areas is to use the LbL technology for photocatalytic decomposition of water. Photoelectrochemical cells can be develop by alternately applying of organic and inorganic semiconducting materials and dyes on transparent conductive substrates such as indium tin oxide glass, aluminum-doped zinc oxide glass, and so forth. It is anticipated that the LbL methods and technologies will definitely expand its horizon toward practical applications in the commercial realm and to new discoveries in the fields of polymer and materials science and engineering.

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# References

- Mnyusiwalla A., Daar A. S., Singer P. A. 'Mind The Gap': Science and Ethics in Nanotechnology. Nanotechnology. 2003;14(3):R9–R13. DOI: 10.1088/0957-4484/14/3/201
- [2] Malynych S., Luzinov I., Chumanov G. Poly(Vinyl Pyridine) as a Universal Surface Modifier for Immobilization of Nanoparticles. Journal of Physical Chemistry B. 2002;106(6):1280–1285. DOI: 10.1021/Jp013236d
- [3] Farokhzad O. C., Langer, R. Impact of Nanotechnology on Drug Delivery. ACS Nano. 2009;**3**(1):16–20. DOI: 10.1021/Nn900002m
- [4] DubasS.T., KumlangdudsanaP., PotiyarajP. Layer-By-Layer Deposition of Antimicrobial Silver Nanoparticles on Textile Fibers Colloids and Surfaces a-Physicochemical and Engineering Aspects. 2006;289(1–3):105–109. DOI: 10.1016/J.Colsurfa.2006.04.012
- [5] Fu J. H., Ji J., Fan D. Z., Shen J. C. Construction of Antibacterial Multilayer Films Containing Nanosilver via Layer-by-Layer Assembly of Heparin and Chitosan-Silver Ions Complex. Journal of Biomedical Materials Research Part A. 2006;79A(3):665–674. DOI: 10.1002/Jbm.A.30819
- [6] Bohr M. T. Nanotechnology Goals and Challenges for Electronic Applications. IEEE Transactions on Nanotechnology. 2002;1(1):56–62. DOI: 10.1109/Tnano.2002.1005426
- [7] Xi Q., Chen X., Evans D. G., Yang W. S. Gold Nanoparticle-Embedded Porous Graphene Thin Films Fabricated via Layer-by-Layer Self-Assembly and Subsequent Thermal Annealing for Electrochemical Sensing. Langmuir. 2012;28(25):9885–9892. DOI: 10.1021/ La301440k
- [8] Ofir Y., Samanta, B., Rotello, V. M. Polymer and Biopolymer Mediated Self-Assembly of Gold Nanoparticles. Chemical Society Reviews. 2008;37(9):1814–1823. DOI: 10.1039/ B712689c
- [9] Paul D. R., Robeson L. M. Polymer Nanotechnology: Nanocomposites. Polymer. 2008;49(15):3187–3204. DOI: 10.1016/J.Polymer.2008.04.017
- [10] Zhang B. P., Binh N. T., Segawa Y., Wakatsuki K., Usami N. Optical Properties of Zno Rods formed By Metalorganic Chemical Vapor Deposition. Applied Physics Letters. 2003;83(8):1635–1637. DOI: 10.1063/1.1605803
- [11] Cao Y. Q., Meng X. B., Elam J. W. Atomic Layer Deposition of Lixalys Solid-State Electrolytes for Stabilizing Lithium-Metal Anodes. Chemelectrochem. 2016;3(6):858– 863. DOI: 10.1002/Celc.201600139
- [12] Marshall S. Molecular-Beam Epitaxy Solid State Technology. 1976;19(5):29–29.
- [13] Hsu Y. F., Xi Y. Y., Djurisic A. B., Chan, W. K. Zno Nanorods for Solar Cells: Hydrothermal Growth Versus Vapor Deposition. Applied Physics Letters. 2008;92(13)DOI: 10.1063/1.2906370

- [14] Ariga K., Lvov Y. M., Kawakami K., Ji Q. M., Hill J. P. Layer-by-Layer Self-Assembled Shells for Drug Delivery. Advanced Drug Delivery Reviews. 2011;63(9):762–771. DOI: 10.1016/J.Addr.2011.03.016
- [15] Caruso F., Lichtenfeld H., Giersig M., Mohwald H. Electrostatic Self-Assembly of Silica Nanoparticle - Polyelectrolyte Multilayers on Polystyrene Latex Particles. Journal of the American Chemical Society. 1998;120(33):8523–8524. DOI: 10.1021/Ja9815024
- [16] Decher G., Hong J. D., Schmitt J. Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: III. Consecutively Alternating Adsorption of Anionic and Cationic Polyelectrolytes on Charged Surfaces. Thin Solid Films. 1992;210(1–2):831–835. DOI: 10.1016/0040-6090(92)90417-A
- Srivastava S., Kotov N. A. Composite Layer-by-Layer (LBL) Assembly with Inorganic Nanoparticles and Nanowires. Accounts of Chemical Research. 2008;41(12):1831–1841. DOI: 10.1021/Ar8001377
- [18] Guo S. J., Dong S. J. Biomolecule-Nanoparticle Hybrids for Electrochemical Biosensors. Trac-Trends in Analytical Chemistry. 2009;28(1):96–109. DOI: 10.1016/J.Trac.2008.10.014
- [19] Liz-Marzan L. M. Tailoring Surface Plasmons through the Morphology and Assembly of Metal Nanoparticles. Langmuir. 2006;22(1):32–41. DOI: 10.1021/La0513353
- [20] Zhou Q., Li X. W., Fan Q., Zhang X. X., Zheng J. W. Charge Transfer Between Metal Nanoparticles Interconnected with a Functionalized Molecule Probed by Surface-Enhanced Raman Spectroscopy. Angewandte Chemie-International Edition. 2006;45(24):3970–3973. DOI: 10.1002/Anie.200504419
- [21] Lin Y. G., Hsu Y. K., Lin Y. C., Chang Y. H., Chen S. Y., Chen Y. C. Synthesis of Cu2O Nanoparticle Films at Room Temperature for Solar Water Splitting. Journal of Colloid and Interface Science. 2016;471:76–80. DOI: 10.1016/J.Jcis.2016.03.010
- [22] Bhattacharjee S., Bruening M. L. Selective Hydrogenation of Monosubstituted Alkenes by Pd Nanoparticles Embedded in Polyelectrolyte Films. Langmuir. 2008;24(6):2916– 2920. DOI: 10.1021/La703055d
- [23] Wu P., Zhang H., Du N., Ruan L. Y., Yang D. R. A Versatile Approach for the Synthesis of Zno Nanorod-Based Hybrid Nanomaterials via Layer-by-Layer Assembly. Journal of Physical Chemistry C. 2009;113(19):8147–8151. DOI: 10.1021/Jp901896u
- [24] Tatykhanova G., Bakranov N., Kudaibergenov S. Layer-by-Layer Thin Films of Interpolyelectrolyte Complexes Containing Gold Nanoparticles. In: Abstract Book of the 11th International Symposium of Polyelectrolytes; June 27–30, 2016; Moscow, Russia. 2016. 161 p.
- [25] Samadi M., Zirak M., Naseri A., Khorashadizade E., Moshfegh A. Z. Recent Progress on Doped Zno Nanostructures for Visible-Light Photocatalysis. Thin Solid Films. 2016;605:2–19. DOI: 10.1016/J.Tsf.2015.12.064

- [26] Islam M. S., Hossain M. F., Razzak S. M. A. Enhanced Photoelectrochemical Performance of Nanoparticle Zno Photoanodes for Water-Splitting Application. Journal of Photochemistry and Photobiology A-Chemistry. 2016;326:100–106. DOI: 10.1016/ J.Jphotochem.2016.04.002
- [27] Oh S. K., Kim Y. G., Ye H. C., Crooks R. M. Synthesis, Characterization, and Surface Immobilization of Metal Nanoparticles Encapsulated within Bifunctionalized Dendrimers. Langmuir. 2003;19(24):10420–10425. DOI: 10.1021/La0353778
- [28] Schneider G., Decher G., Nerambourg N., Praho R., Werts M. H. V., Blanchard-Desce M. Distance-Dependent Fluorescence Quenching on Gold Nanoparticles Ensheathed with Layer-by-Layer Assembled Polyelectrolytes. Nano Letters. 2006;6(3):530–536. DOI: 10.1021/NI052441s
- [29] Crespilho F. N., Huguenin F., Zucolotto V., Olivi P., Nart F. C., Oliveira O. N. Dendrimers as Nanoreactors to Produce Platinum Nanoparticles Embedded in Layer-by-Layer Films for Methanol-Tolerant Cathodes. Electrochemistry Communications. 2006;8(2):348–352. DOI: 10.1016/J.Elecom.2005.12.003
- [30] Liu H. S., Song C. J., Zhang L., Zhang J. J., Wang H. J., Wilkinson D. P. A Review of Anode Catalysis in the Direct Methanol Fuel Cell. Journal of Power Sources. 2006;155(2):95–110. DOI: 10.1016/J.Jpowsour.2006.01.030
- [31] Jin H., Choi S., Lim S. H., Rhee S. W., Lee H. J., Kim S. Layer-by-Layer-Assembled Quantum Dot Multilayer Sensitizers: How the Number of Layers Affects the Photovoltaic Properties of One-Dimensional Zno Nanowire Electrodes. Chemphyschem. 2014;15(1):69–75. DOI: 10.1002/Cphc.201300844
- [32] Naka K., Itoh H., Chujo Y. Self-Organization of Spherical Aggregates of Palladium Nanoparticles with a Cubic Silsesquioxane. Nano Letters. 2002;2(11):1183–1186. DOI: 10.1021/Nl025713p
- [33] Kulal P. M., Dubal D. P., Lokhande C. D., Fulari V. J. Chemical Synthesis of Fe<sub>2</sub>O<sub>3</sub> Thin Films for Supercapacitor Application. Journal of Alloys and Compounds. 2011;509(5):2567–2571. DOI: 10.1016/J.Jallcom.2010.11.091
- [34] Bhattacharjee S., Dotzauer D. M., Bruening M. L. Selectivity as a Function of Nanoparticle Size in the Catalytic Hydrogenation of Unsaturated Alcohols. Journal of the American Chemical Society. 2009;131(10):3601–3610. DOI: 10.1021/Ja807415k
- [35] Syrrokostas G., Govatsi K., Yannopoulos S. N. High-Quality, Reproducible Zno Nanowire Arrays Obtained by a Multiparameter Optimization of Chemical Bath Deposition Growth. Crystal Growth & Design. 2016;16(4):2140–2150. DOI: 10.1021/Acs.Cgd.5b01812
- [36] Warren Scott C., Thimsen E. Plasmonic Solar Water Splitting. Energy& Environmental Science. 2012;5(1):5133–5146. DOI: 10.1039/C1ee02875h
- [37] Ren X., Sangle A., Zhang S. Y., Yuan S., Zhao Y., Shi L. Y., Hoye R. L. Z., Cho S., Li D. D., Macmanus-Driscoll J. L. Photoelectrochemical Water Splitting Strongly Enhanced in Fast-Grown Zno Nanotree and Nanocluster Structures. Journal of Materials Chemistry A. 2016;4(26):10203–10211. DOI: 10.1039/C6ta02788a

- [38] Rossinyol E., Arbiol J., Peiro F., Cornet A., Morante J. R., Tian B., Bo T., Zhao D. Nanostructured Metal Oxides Synthesized by Hard Template Method for Gas Sensing Applications. Sensors and Actuators. B-Chemical. 2005;109(1):57–63. DOI: 10.1016/J.Snb.2005.03.016
- [39] Cottineau T., Toupin M., Delahaye T., Brousse T., Belanger D. Nanostructured Transition Metal Oxides for Aqueous Hybrid Electrochemical Supercapacitors. Applied Physics A-Materials Science & Processing. 2006;82(4):599–606. DOI: 10.1007/S00339-005-3401-3
- [40] Wu H. B., Chen J. S., Hng H. H.B Lou X. W. Nanostructured Metal Oxide-Based Materials as Advanced Anodes for Lithium-Ion Batteries. Nanoscale. 2012;4(8):2526–2542. DOI: 10.1039/C2nr11966h
- [41] Van De Krol R., Liang Y. Q., Schoonman J. Solar Hydrogen Production with Nanostructured Metal Oxides. Journal of Materials Chemistry. 2008;18(20):2311–2320. DOI: 10.1039/B718969a
- [42] Patrocinio A. O. T., Paterno L. G., Iha N. Y. M. Layer-By-Layer Tio<sub>2</sub> Films as Efficient Blocking Layers in Dye-Sensitized Solar Cells. Journal of Photochemistry and Photobiology A-Chemistry. 2009;205(1):23–27. DOI: 10.1016/J.Jphotochem.2009.04.008
- [43] Liu Z. Y., Zhang X. T., Nishimoto S., Jin M., Tryk D. A., Murakami T., Fujishima A. Anatase Tio<sub>2</sub> Nanoparticles on Rutile Tio<sub>2</sub> Nanorods: A Heterogeneous Nanostructure via Layerby-Layer Assembly. Langmuir. 2007;23(22):10916–10919. DOI: 10.1021/La7018023
- [44] Sun P., Zhang H. Y., Liu C., Fang J., Wang M., Chen J., Zhang J. P., Mao C. B., Xu S. K. Preparation and Characterization of Fe<sub>3</sub>O<sub>4</sub>/CdTe Magnetic/Fluorescent Nanocomposites and their Applications in Immuno-Labeling and Fluorescent Imaging of Cancer Cells. Langmuir. 2010;26(2):1278–1284. DOI: 10.1021/La9024553
- [45] Yu C. M., Wang Y. D., Wang L., Zhu Z. K., Bao N., Gu H. Y. Nanostructured Biosensors Built with Layer-by-Layer Electrostatic Assembly of Hemoglobin and Fe<sub>3</sub>O<sub>4</sub>@Pt Nanoparticles. Colloids and Surfaces B-Biointerfaces. 2013;103:231–237. DOI: 10.1016/J. Colsurfb.2012.10.005
- [46] Shao M. F., Ning F. Y., Zhao J. W., We, M., Evans D. G., Duan X. Preparation of Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>@Layered Double Hydroxide Core-Shell Microspheres for Magnetic Separation of Proteins. Journal of the American Chemical Society. 2012;134(2):1071–1077. DOI: 10.1021/Ja2086323
- [47] Ballesteros C. A. S., Cancino J., Marangoni V. S., Zucolotto V. Nanostructured Fe<sub>3</sub>O<sub>4</sub> Satellite Gold Nanoparticles to Improve Biomolecular Detection. Sensors and Actuators B-Chemical. 2014;198:377–383. DOI: 10.1016/J.Snb.2014.03.079
- [48] Dey S., Mohanta K., Pal A. J. Magnetic-Field-Assisted Layer-by-Layer Electrostatic Assembly of Ferromagnetic Nanoparticles. Langmuir. 2010;26(12):9627–9631. DOI: 10.1021/La101132z
- [49] Lin Y. W., Tseng W. L., Chang H. T. Using A Layer-By-Layer Assembly Technique to Fabricate Multicolored-Light-Emitting Films of Cdse@Cds and Cdte Quantum Dots. Advanced Materials. 2006;18(11):1381–1386. DOI: 10.1002/Adma.200502515

- [50] Pathan H. M., Lokhande C. D. Deposition of Metal Chalcogenide Thin Films by Successive Ionic Layer Adsorption and Reaction (SILAR) Method. Bulletin of Materials Science. 2004;27(2):85–111. DOI: 10.1007/Bf02708491
- [51] Chen H. N., Li W. P., Liu H. C., Zhu L. Q. Cds Quantum Dots Sensitized Single- and Multi-Layer Porous Zno Nanosheets for Quantum Dots-Sensitized Solar Cells. Electrochemistry Communications. 2011;13(4):331–334. DOI: 10.1016/J.Elecom.2011.01.017
- [52] Ni M., Leung M. K. H., Leung D. Y. C., Sumathy K. A Review and Recent Developments in Photocatalytic Water-Splitting using TiO<sub>2</sub> for Hydrogen Production. Renewable & Sustainable Energy Reviews. 2007;11(3):401–425. DOI: 10.1016/J.Rser.2005.01.009
- [53] Youngblood W. J., Lee S. H. A., Maeda K., Mallouk T. E. Visible Light Water Splitting Using Dye-Sensitized Oxide Semiconductors. Accounts of Chemical Research. 2009;42(12):1966–1973. DOI: 10.1021/Ar9002398
- [54] Wang D., Zhang X. T., Sun P. P., Lu S., Wang L. L., Wei Y. A., Liu Y. C. Enhanced Photoelectrochemical Water Splitting on Hematite Thin Film with Layer-by-Layer Deposited Ultrathin Tio<sub>2</sub> Underlayer. International Journal of Hydrogen Energy. 2014;**39**28):16212–16219. DOI: 10.1016/J.Ijhydene.2014.01.164
- [55] Beermann N., Vayssieres L., Lindquist S. E., Hagfeldt A. Photoelectrochemical Studies of Oriented Nanorod Thin Films of Hematite. Journal of the Electrochemical Society. 2000;147(7):2456–2461. DOI: 10.1149/1.1393553
- [56] Tak Y., Hong S. J., Lee J. S., Yong K. Fabrication of ZnO/CdS Core/Shell Nanowire Arrays for Efficient Solar Energy Conversion. Journal of Materials Chemistry. 2009;19(33):5945– 5951. DOI: 10.1039/B904993b
- [57] Zhao N., Shi F., Wang Z. Q., Zhang X. Combining Layer-by-Layer Assembly with Electrodeposition of Silver Aggregates for Fabricating Superhydrophobic Surfaces. Langmuir. 2005;21(10):4713–4716. DOI: 10.1021/La0469194
- [58] Jiang C. Y., Markutsya S., Tsukruk V. V. Collective and Individual Plasmon Resonances in Nanoparticle Films Obtained by Spin-Assisted Layer-by-Layer Assembly. Langmuir. 2004;20(3):882–890. DOI: 10.1021/La0355085
- [59] Qiu J. D., Peng H. Z., Liang R. P., Li J., Xia X. H. Synthesis, Characterization, and Immobilization of Prussian Blue-Modified Au Nanoparticles: Application to Electrocatalytic Reduction of H<sub>2</sub>O<sub>2</sub>. Langmuir. 2007;23(4):2133–2137. DOI: 10.1021/La062788q
- [60] Han J. H., Liu Z. F., Guo K. Y., Zhang X. Q., Hong T. T., Wang B. Agsbs2 Modified ZnO Nanotube Arrays for Photoelectrochemical Water Splitting. Applied Catalysis B-Environmental. 2015;179:61–68. DOI: 10.1016/J.Apcatb.2015.05.008
- [61] Kuang P. Y., Ran J. R., Liu Z. Q., Wang H. J., Li N., Su Y. Z., Jin Y. G., Qiao S. Z. Enhanced Photoelectrocatalytic Activity of BiOI Nanoplate-Zinc Oxide Nanorod P-N Heterojunction. Chemistry-A European Journal. 2015;21(43):15360–15368. DOI: 10.1002/Chem.201501183
- [62] Hsu Y. K., Chen Y. C., Lin Y. G. Novel Zno/Fe<sub>2</sub>O<sub>3</sub> Core-Shell Nanowires for Photoelectrochemical Water Splitting. ACS Applied Materials & Interfaces. 2015;7(25):14157–14162. DOI: 10.1021/Acsami.5b03921

# RRAM Memories with ALD High-K Dielectrics: Electrical Characterization and Analytical Modeling

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#### Abstract

Resistive switching phenomena with adequate repetitiveness on  $Ta_2O_5$ - $TiO_2$ - $Ta_2O_5$  and  $TiO_2$ - $Ta_2O_5$ - $TiO_2$  stacks are reported. In particular, 5–nm-thick  $TiO_2$  films embedding a monolayer of  $Ta_2O_5$  show the best behavior in terms of bipolar cycles loop width, with separate low and high resistive states up to two orders of magnitude. Tantalum oxide layer increases the defect density in titania that becomes less leaky, and thus, resistive switching effects appear. Small signal ac parameters measured at low and medium frequencies, namely capacitance and conductance, also show hysteretic behavior during a whole bipolar switching cycle. This means that the memory state can be read at 0 V, without any power consumption. High-frequency measurements provide information about dipole relaxation frequency values in the dielectric bulk, and this can be connected with resistive switching behavior. Finally, a double tunneling barrier model fits I-V curves at the low-resistance state even at the bias range where reset occurs and a sharp fall takes place.

**Keywords:** resistive switching, tantalum oxide, titanium oxide, RF impedance, modeling

## 1. Introduction

Nowadays, resistive random access memories (RRAMs) have been considered as adequate candidates to replace the current nonvolatile memories, because of their good characteristics



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. in terms of integration density, speed, power dissipation, and endurance [1, 2]. RRAMs modify the resistivity of metal-insulator-metal (MIM) or metal-insulator-semiconductor (MIS) structures. These devices exhibit a resistive switching (RS) behavior, due to the creation after an initial step (electroforming), of one or several nano-conductive filaments that can connect the two electrodes [3]. Filaments can be broken and formed again by means of an external bias; hence, there are two different resistive states, low resistance (LR) and high resistance (HR). The device can remain in one of the two resistive states for a long time. The RS behavior depends on the dielectric material. Also, top and bottom electrodes play an important role. It has been reported that atomic layer deposited (ALD) transition metal oxides, such as HfO2/ ZrO<sub>2</sub>, TiO<sub>2</sub>, and so on, exhibit RS behavior [4]. Usually, RS is classified into unipolar and bipolar: The first one depends only on the amplitude of the applied voltage, whereas the second one depends also on the polarity of the applied voltage. Three different mechanisms are considered as responsible for the RS phenomena [5, 6]: the conducting bridge random access memories (CBRAM), in which the conductive filament is formed from the atoms of one of the two metallic electrodes; the valence change mechanism that is attributed to the migration of oxygen anions and a subsequent redox reaction; and finally, the thermochemical mechanism that consists of a change of stoichiometry related to the temperature increment. Despite the great amount of work done, the physic mechanisms of RS are not fully understood; therefore, a great deal of research must be still carried out.

This chapter consists of three parts: In the first one, constituting the main body of this work, resistive switching phenomena on Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-based metal-insulator-metal (MIM) structures are reported. Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> films were grown to target thickness of 6 nm. The films were grown either as nanolaminate-like stacks consisting of Ta<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> constituent layers, each grown to nominal thickness of 2 nm, or 5- to 6–nm-thick TiO<sub>2</sub> films embedding a monolayer of  $Ta_2O_5$ grown using only 1–3 ALD cycles of  $Ta_2O_{e}$ . The stacks were grown in order to increase the defect densities in titania by inserting otherwise more insulating tantalum oxide and examine the possible effect of the controlled, artificial, layering of different metal oxides to the appearance of resistive switching effect. In the second part, some RF impedance measurement results in more standard metal-insulator-semiconductor (MIS) samples (Ni/HfO<sub>2</sub>/Si and W/ HfO,/Si) are shown. The response at frequencies up to 3 GHz is analyzed. The most remarkable fact is that both the relaxation frequency in capacitance curves and the conductance maximum position can vary with the bias voltage depending on the top electrode material. Finally, in the third part of this chapter, two analytical models that fit well the current values in the low-resistance state for Ni/HfO<sub>2</sub>/Si structures are described. The first one considers a single tunneling barrier, whereas the second one uses the double tunneling barrier model. A comparison between the two models is carried out.

#### 2. Resistive switching on Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-based MIM structures

MIM samples investigated were obtained by depositing the films on 15 nm-RuO<sub>2</sub>/10 nm-TiN/ Si substrates. Thin solid titanium tantalum oxide films were grown in an in-house built low-pressure flow-type ALD reactor [7] as stacks formed as  $TiO_2$ -Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> or Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-Ti

triple layers [8] at the substrate temperature of 350°C. Constituent TiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> layers were grown by using TiCl<sub>4</sub> [7] and TaCl<sub>5</sub> [9], respectively, as metal precursors. In both cases, ozone, O<sub>3</sub>, was applied as oxygen precursor. TiO<sub>2</sub> layers were grown using cycle times 2–2–5–5 s, denoting sequence of TiCl<sub>4</sub> pulse length—purge time—ozone pulse length—purge time, respectively. For Ta<sub>2</sub>O<sub>5</sub>, the corresponding cycle times were 3–2–5–5 s. In all cases studied, these process time parameters allowed reliable self-limited ALD-type growth of constituent layers in this reactor, as evaluated by quartz crystal microbalances in real time prior to the growth of stacked layers. For the growth of Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> stacks, 60 × Ta<sub>2</sub>O<sub>5</sub> + 50 × TiO<sub>2</sub> + 60 × Ta<sub>2</sub>O<sub>5</sub> ALD cycles were applied, denoting the consequent numbers of the constituent oxide growth cycles. Analogously, for the growth of TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> stacks, 50 × TiO<sub>2</sub> + 70 × Ta<sub>2</sub>O<sub>5</sub> + 50 × TiO<sub>2</sub> + 1 × Ta<sub>2</sub>O<sub>5</sub> + 75 × TiO<sub>2</sub> and 75 × TiO<sub>2</sub> + 3 × Ta<sub>2</sub>O<sub>5</sub> + 75 × TiO<sub>2</sub> ALD cycles. The abovementioned stacked films will hereafter be denoted as samples (60-50-60), (50-70-50), (75-1-75), and (75-3-75), respectively. Top electrodes were Pt dots with two different areas (0.52 × 10<sup>-3</sup> cm<sup>2</sup> and 2.04 × 10<sup>-3</sup> cm<sup>2</sup>).

TiCl<sub>4</sub> was kept at room temperature ( $22 \pm 3^{\circ}$ C). TaCl<sub>5</sub> was evaporated at 80-85°C from a fused silica boat inside the reactor. O<sub>3</sub> was generated from O<sub>2</sub> (99.999%) in a BMT Messtechnik 802N ozone generator. Ozone concentration measured with BMT Messtechnik 964 analyzer at the reactor inlet was 200–230 g/m<sup>3</sup> at the normal pressure. N<sub>2</sub> (99.999%) was used as the carrier and purging gas. No post-deposition heat treatment was applied on the samples.

The mass thickness and elemental composition of the films were measured by X-ray fluorescence (XRF) spectroscopy method using ZSX400 (Rigaku) spectrometer, recording  $K_{\alpha}$  lines for Ti, Cl, and O, and  $L_{\alpha}$  for Ta. For the calibration of the XRF measurement procedure, binary TiO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> films earlier grown to known thicknesses and densities determined by the X-ray reflection (XRR) method were used. Grazing incidence X-ray diffraction (GIXRD) was applied for the examination of the film structure using Smartlab (Rigaku) X-ray diffractometer with CuK $\alpha$  radiation. In accord with the XRF analysis, the (60-50-60) stacks contained 54.5 wt.% Ta, 12.1 wt.% Ti, 32.8 wt.% O, and 0.55 wt.% residual Cl, whereas the (50-70-50) ones contained 48.8 wt.% Ta, 21.0 wt.% Ti, 30.0 wt.% O, and 0.24 wt.% residual Cl. On the other hand, the (75-3-75) stacks contained 10.9 wt.% Ta, 48.7 wt.% Ti, 40.0 wt.% O, and 0.28 wt.% residual Cl, whereas the (75-1-75) ones contained 4.6 wt.% Ta, 53.8 wt.% Ti, 41.4 wt.% O, and 0.23 wt.% residual Cl.

Considering the results of the compositional analysis, the relative amounts of titanium and tantalum (oxides) in the films appreciably correlated with the amounts of cycles applied for either constituent oxide. Certain residual contamination with chlorine was expected due to the presence of chlorine as ligand atoms in both metal precursors and their incomplete removal during surface reactions with ozone. The films deposited to rather low thicknesses of 6 nm and below that were essentially amorphous as revealed by their featureless XRD patterns (**Figure 1**). Short-range order was recognized, however, in the TiO<sub>2</sub>-rich films deposited using the cycle sequence 75-1-75, that is, in the film containing markedly less than one monolayer of Ta<sub>2</sub>O<sub>5</sub> between two TiO<sub>2</sub> layers both grown using 75 ALD cycles. The amorphicity of the films can be explained taking into account that layers are too thin to become ordered



**Figure 1.** Grazing incidence X-ray diffraction (GIXRD) patterns from nanolaminate  $TiO_2-Ta_2O_5-TiO_2$  and  $Ta_2O_5-TiO_2-Ta_2O_5$  stacks. The numbers of both constituent oxide growth cycles in sequence is indicated by labels.



**Figure 2.** Raman spectra from bare ruthenium oxide electrode (bottom curve), and  $\text{TiO}_2$ -Ta<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> stacks grown applying one (middle curve) and three (top curve) ALD cycles of Ta<sub>2</sub>O<sub>5</sub> between TiO<sub>2</sub> layers. The total film thicknesses were 5.0 and 5.5 nm, respectively.

crystallographically. Moreover, the layers consist of mixed materials foreign to each other both chemically and structurally. This, as any other doping, essentially increases the disorder in the materials, both in terms of long-range and short-range periodicity. In the Raman spectra of the 75-1-75 sample (**Figure 2**), a peak typical for anatase phase was detected at 143–145 cm<sup>-1</sup> [10, 11] and also seen earlier in TiO<sub>2</sub> films grown by ALD from TiCl<sub>4</sub> to H<sub>2</sub>O [12]. In the 75-3-75 sample, three Ta<sub>2</sub>O<sub>5</sub> growth cycles were applied between the halves of the TiO<sub>2</sub> host layer, and the structural disorder was evidently increased. Consequently, anatase phase could not be recognized any more. Instead, broad Raman bands appeared at 300 and 800 cm<sup>-1</sup>, which could not be clearly attributed to any known TiO<sub>2</sub> phase. However, the bands follow those obtained from the bare reference RuO<sub>x</sub> electrode substrate. RuO<sub>2</sub> [13] is known as the material possessing rutile structure, and the bands in **Figure 2** are thus denoted with R, to guide the
readers eye. In this connection, these 5- to 7-nm-thick films studied are to be characterized as crystallographically very weakly ordered and highly defective.

Electrical measurements of MIM structures were carried out, putting the sample in a lighttight and electrically shielded box. I-V curves were measured using a HP-4155B semiconductor parameter analyzer. C-V and G-V measurement setup was based on a Keithley 4200SCS semiconductor analyzer. After the study of pristine samples, the filaments in MIM devices were electroformed by DC bias sweeping from 0 to 0.7 V with a current compliance of 10 mA. Then, successive I-V cycles showing low-resistance state (LRS) to high-resistance state (HRS) transitions were recorded with current compliance of 100 mA.

Current measurements were carried out by varying the applied voltage in two modes: DC sweep and pulse modes. It is mandatory to carry out measurements using bias pulses, because in the final high-end applications of RRAM, devices are operated in the pulse mode [14]. **Figure 3** shows filament electroforming and the first resistive switching cycles of a  $Pt/Ta_{2}O_{z}$ -TiO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub>/RuO<sub>2</sub> MIM sample at room temperature. Voltage bias applied was progressively varied as it is indicated by arrows. After the first forming cycle at 0.7 V, subsequent voltage ramps were applied showing the two different resistance states. Positive voltages produce the high-resistance state to the low-resistance state transition (set). On the back sweep, the lowresistance state is maintained. Using a negative polarity, when voltage reaches the values of about -1 V, the device is switched back to the high-resistance state (reset). Thus, this sample exhibits bipolar resistance switching at low-voltage values. RS parameters are independent on the electrode area; therefore, the switching mechanism is governed by filamentary conduction. The most likely hypothesis is the generation of oxygen vacancies under the applied electric field during positive forming sweep [15]. Oxygen vacancies tend to cluster and generally form filamentary shapes under an electric field. When such clusters are formed, the resistance of the local region becomes much lower than that of the surrounding oxide, and the low-resistance and high-resistance states will therefore be determined by the creation and



Figure 3. CF electroforming and the first bipolar switching cycles of  $Pt/Ta_2O_5$ -Ti $O_2$ -Ta $_2O_5/RuO_x$  MIM samples at room temperature.

rupture of the filaments, respectively, which percolate through the sample. In general, set and reset loops are asymmetrical, as it is seen in **Figure 3**. Electroforming in bipolar switching may be a process of introducing asymmetric interfaces in a two-terminal switching cell, which are beyond the asymmetry due to asymmetric electrodes, that is, different top and bottom electrodes. Thus, the electroforming may take one of the two interfaces as an active interface, depending on the polarity of the electroforming voltage, so that reactions taking place in the vicinity of the active interface are responsible for the subsequent bipolar switching [6].

Pulsed biasing comprises positive and negative pulses which lead the samples to the lowresistance and high-resistance states, respectively. To illustrate this technique, we have included the example for a  $Pt/Ta_2O_5$ - $TiO_2$ - $Ta_2O_5/RuO_x$  MIM capacitor in **Figure 4**. Using stairshaped voltage instead of a voltage ramp allows us to record current transients at different states. In this case, we can see that current transients appear when switching to negative voltages, that is, in the reset process (low-resistance to high-resistance transition). Interestingly, resistive switching affects not only the dc currents, but also the small signal ac parameters measured at low and medium frequencies. Indeed, capacitance and conductance also show hysteretic behavior during a whole bipolar switching cycle, as we can see in **Figure 5**. Both magnitudes varied in great extent when the sample was driven from the low-resistance state to the high-resistance state or *vice versa*, even at 0 V bias. This fact indicates that the memory state can be read at 0 V by sensing the admittance at 0 V, without any power consumption.

In order to study the influence of set voltage values on the RS cycles shape, the following experiment was carried out. After the initial electroforming step, some RS cycles under the same condition of current compliance were made in order to stabilize the process. Once repetitive RS curves were obtained, some cycles were recorded by varying the set voltage values regardless of the current compliance values (see **Figure 6**). By increasing the set voltage values, wider loops were obtained. It can be seen that current increases gradually in the



Figure 4. Bipolar switching response to stair-shaped voltage of Pt/Ta2O5-TiO2-Ta2O5/RuOx MIM samples.

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Figure 5. Capacitance (a) and conductance (b) hysteresis during a whole bipolar switching cycle of  $Pt/Ta_2O_5-TiO_2-Ta_2O_5/RuO_5$  MIM samples at room temperature.



**Figure 6.** Bipolar switching cycles of  $Pt/Ta_2O_5-TiO_2-Ta_2O_5/RuO_x$  and  $Pt/TiO_2-Ta_2O_5-TiO_2-/RuO_x$  MIM samples at room temperature, obtained by varying the SET voltage.

set processes, whereas it abruptly falls in the reset processes. From **Figure 6a** and **6b**, it seems apparent that RS cycles are wider in the  $TiO_2-Ta_2O_5-TiO_2$  stacks than in the  $Ta_2O_5-TiO_2-Ta_2O_5$  ones, indicating much more marked differences between high- and low-resistance states when the inner layer is  $Ta_2O_5$ . Making very much thinner the  $Ta_2O_5$  layer with respect to the two  $TiO_2$  surrounding layers (**Figure 6c** and **6d**), the RS cycles become wider, but in the (75-1-75) sample, the cycles are not enough stable, providing a mixed picture. On the contrary, the (75-3-75) sample maintains adequate repetitiveness conditions since the very first cycles, and therefore, the two resistive states are clearly distinguished.

In **Figure 7**, the linear correlation between set and reset voltages is depicted for the (75-3-75) sample (blue line). The rise of set voltage values induces a consequent increase in the absolute values of reset voltage. In the same figure, current difference values in the two resistance states measured at a fixed reset value (-0.5 V) for different set voltage values are shown (red line). It is clear that the current window of high- and low-resistance states opens as set voltage value increases. Both tendencies of **Figure 7**, although in minor extent, were also observed in all samples.



**Figure 7.** Variation of VReset with VSet of  $Pt/TiO_2$ -Ta2O<sub>5</sub>-TiO<sub>2</sub>-/RuOx MIM samples. The current variation values and VSET relationship are also shown.

#### 3. RF impedance measurements

A deep knowledge of dielectric properties could provide a wider insight of the RRAM behavior. In particular, RF impedance spectroscopy measurements allow detection of the dipolar relaxation of the dielectrics. In a dielectric material, the bound charges are polarized under the influence of an external electric field. Also, surfaces, grain boundaries, and interphase boundaries into the dielectric material contain dipoles that are oriented in an external field and thus contribute to the polarization of the material. When dipole relaxation occurs, the real part of the permittivity,  $\varepsilon'$ , shows an inflection point, whereas the imaginary part,  $\varepsilon''$ , has a maximum. In a capacitor,  $\varepsilon'$  and  $\varepsilon''$  are proportional to the capacitance and conductance signals, respectively. So, admittance measurements at high frequencies provide information about the permittivity relaxation [16].

This study was carried out by using a Keysight E4991B RF Impedance Analyzer, which allowed to carry out measurements in a frequency range of 1 MHz - 3 GHz. Capacitance and conductance of the samples were obtained by scanning the frequency of the ac signal while keeping the gate voltage at a given value. The gate voltage is applied by the voltage source that is built in the E4991B analyzer. A whole RF characterization is obtained by varying the voltage from accumulation to inversion regime. The influence of the gate voltage on the RF characteristics is obtained in this way. In Figure 8, we plot RF admittance curves of a W/HfO<sub>2</sub>/ Si MIS structure. The most noticeable point is the fact that the frequency of the inflection point of the capacitance signal and the maximum of the conductance signal depends on the bias voltage: More positive voltages yield to higher relaxation frequencies. In this case, MIS capacitors are in the inversion regime for positive bias and in accumulation for negative ones. The main conclusion is that the inversion layer at the interface channel affects to the dipole relaxation in such a way that it occurs at higher frequencies. In accumulation, the voltage drop in the oxide is equal to the applied gate voltage, whereas in depletion or inversion regime, part of the applied voltage drops in the semiconductor layer close to the interface. Hence, higher electric field exists on the accumulation regime, dipole orientation is more effective in this regime, and dipoles could not respond to so high frequencies as in the inversion regime. Figure 9 shows this effect from a three-dimensional point of view.

In order to check the influence of top electrode material on this effect, the same measurements were carried out on similar samples with nickel instead tungsten as top electrode (**Figure 10**). In this case, relaxation occurs at lower frequencies (15 MHz) and no influence of voltage bias on the dipole relaxation frequency values was observed. This can be due to some Fermi level pinning effect in the nickel samples. Also, it can be related to the fact that nickel ions diffuse inside the insulator. These charged ions create local electric fields that interact with insulator dipoles in such a way that relaxation occurs at lower frequencies. Local electric field



Figure 8. Frequency variations of capacitance (a) and conductance (b) for a  $W/HfO_2(10 \text{ nm})/Si$  MIS capacitor at different voltage values.



Figure 9. Three-dimensional plots showing frequency and voltage variations of capacitance (a) and conductance (b) for a W/HfO<sub>2</sub>(20 nm)/Si MIS capacitor.



**Figure 10.** Three-dimensional plots showing frequency and voltage variations of capacitance (a) and conductance (b) for a Ni/HfO<sub>2</sub>(20 nm)/Si MIS capacitor.

dominates over the external applied field, and the resonance frequency results independent of the externally applied voltage.

From the resistive switching point of view, it can be worth to point out here that  $W/HfO_2/Si$  MIS samples do not show any RS behavior, whereas Ni/HfO<sub>2</sub>/Si MIS samples exhibit unipolar RS due to the CBRAM mechanism [8, 17]. The set mechanism is controlled by the thermally

enhanced diffusion of Ni ions induced by local Joule heating, forming a connected nanofilament path. In the reset process, the previously formed filament is partially broken, limiting the current flow. These results agree well with the RF results described before. When no local electric field is detected, there is not resistive switching, as in the W top electrode case. However, in the Ni top electrode case, a local electrical field is detected as a consequence of the diffusion of Ni ions that, in the end, form the conductive filaments thus provoking the RS phenomena.

More detailed studies in this matter should be done in order to connect in more extent the resistive switching behavior with the dielectric properties.

# 4. Resistive switching modeling

A better knowledge of the nature of the switching behavior requires extending the previous experiments in a wide range of temperatures [18]. We reported an analytical model which fit well with the experimental results for temperatures ranging from 77 to 400 K [17]. This model assumes that the conductive filament does not entirely extend from the top to bottom electrode, and it is interrupted in a region close to one of the electrodes, as is drawn in the inset of **Figure 11**. This gap region behaves as a barrier for the conduction. When the barrier is narrow enough, a current can flow through it by tunneling, and the device is at the low-resistance state. On the contrary, when part of the filament closer to the gap is dissolved, the barrier



Figure 11. Fitting of a unipolar LRS cycle with the single tunneling barrier analytical model for a Ni/HfO<sub>2</sub>/Si MIS capacitor.

becomes thicker and tunneling can-not take place, so producing the low-resistance to high-resistance switching. Very good fitting is obtained with this model as is plotted in **Figure 11**, where the red line is the experimental I-V curves, and the blue line is the best fitting obtained with the following transcendental equation, which is the basis of this model:

$$V_1 = V - \frac{R_{\infty}}{R_0} \cdot V_1 \cdot e^{\alpha \cdot V_1}$$
(1)

where  $V_1$  is the voltage drop in the barrier, V is the applied bias voltage, and  $R_0$  and  $R_{\infty}$  are the resistance of the conductive filament at 0 V, and when reset occurs, respectively,  $\alpha$  is a parameter very closely related to the barrier tunneling probability, that is, with the filament gap thickness.

An improvement in the previous model assumes a double barrier instead of a single one, as it is illustrated in **Figure 12**. In this model, the current through the barriers is described by a Fowler-Nordheim law as follows:

$$I = \frac{1}{R} \cdot E^2 \cdot e^{-\alpha/E} \tag{2}$$

and the barrier thickness is related to the voltage according a potential law:

$$t(V) = V^{\lambda} \tag{3}$$





# 5. Conclusions

Resistive switching behavior in  $Ta_2O_5$ -TiO\_2-Ta\_2O\_5 and TiO\_2-Ta\_2O\_5-TiO\_2 stacks-based MIM structures was reported. Dielectric layers were grown by ALD. The best results were obtained for  $75 \times TiO_2 + 3 \times Ta_2O_5 + 75 \times TiO_2$  ALD cycles, yielding around 1 monolayer of  $Ta_2O_5$  in a structure with the total thickness of 5 nm. In this sample, wide RS loops were obtained. Moreover, current window of high- and low-resistance states opens as set voltage value increases, with very adequate repetitiveness. In order to try to connect the dielectric properties with the RS behavior, some high-frequency impedance measurements were carried out in W/HfO<sub>2</sub>/Si and Ni/HfO<sub>2</sub>/Si MIS samples. The detection of a local electric field in the last ones can be related to the diffusion of ions from the top electrode that creates the conductive filament and provoke the resistive switching effect. Finally, an analytical model based on double tunneling barrier was applied to low-resistance cycles of Ni/HfO<sub>2</sub>/Si MIS structures, with very good fitting. With respect to the single tunneling barrier, the sharp fall of current at the reset transition (low to high resistance) is also fitted.

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### References

- [1] Beck A, Bednorz J G, Gerber C, Rossel C, and Widmer D (2000), Appl. Phys. Lett., 77(1): 139.
- [2] Waser R and Aono M (2007), Nat. Mater., 6(11): 833.

- [3] Kim D C, Seo S, Ahn S E, Suh D S, Lee M J, Park B H, Yoo I K, Baek I G, Kim H J, Yim E K, Lee J E, Park S O, Kim H S, Chung U I, Moon J T, and Ryu B I (2006), Appl. Phys. Lett., 88(20): 202102.
- [4] Jeong D S, Thomas R, Katiyar R S, Scott J F, Kohlstedt H, Petraru A, and Hwang C S (2012), Rep. Prog. Phys., 75(7): 076502.
- [5] Waser R, Dittmann R, Staikov G, and Szot K (2009) Adv. Mater., 21: 2632.
- [6] Lee J S, Lee S, and Noh T W (2015) Appl. Phys. Rev., 2: 031303.
- [7] Arroval T, Aarik L, Rammula R, Kruusla V, and Aarik J (2016) Thin Solid Films, 600: 119.
- [8] Duenas S, Castán H, García H, Arroval T, Tamm A, Kukli K, and Aarik J (2016) ECS Transact., 72: 153.
- [9] Aarik J, Kukli K, Aidla A, and Pung L (1996) Appl. Surf. Sci., 103: 331.
- [10] Karunagaran B, Kim K, Mangalaraj D, Yi J, and Velumani S (2005) Solar Energy Mater. Solar Cells, 88: 199, and references therein.
- [11] Frank O, Zukalova M, Laskova B, Kürti J, Koltai J, and Kavan L (2012) Phys. Chem. Chem. Phys., 14: 14567.
- [12] Tamm A, Acik I O, Arroval T, Kasikov A, Seemen H, Marandi M, Krunks M, Mere A, Kukli K, and Aarik J (2016) Thin Solid Films, 616; 449.
- [13] Bhaskar S, Dobal P S, Majumder S B, and Katiyar R S (2001) J. Appl. Phys., 89: 2987.
- [14] Niu G, P. Calka P, Maur M A, Santoni F, Guha S, Fraschke M, Hamoumou P, Gautier B, Perez E, Walczyk C, Wenger C, Carlo A D, Alff L, and Schroeder T (2016) Sci. Rep., 6: 25757, doi:10.1038/srep25757.
- [15] Hudec B, Paskaleva A, Jancovic P, Dérer J, Fedor J, Rosová A, Dobrocka E, and Fröhlich K (2014) Thin Solid Films, 563:10–14.
- [16] Debye P (1929). Polar molecules. Chemical Catalog Company, NY, USA.
- [17] Vaca C, González M B, Castán H, García H, Dueñas S, Campabadal F, Miranda E, and Bailón L (2016) IEEE Trans. Electron Dev., 63: 1877.
- [18] Fang R, Chen W, Gao L, Yu W, and Yu S (2015) IEEE Electron Dev. Lett., 36: 567.

# Advanced Multifunctional Corrosion Protective Coating Systems for Light-Weight Aircraft Alloys— Actual Trends and Challenges

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Additional information is available at the end of the chapter

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#### Abstract

The present chapter is devoted to the recent trends in the field of the advanced corrosion protective layers elaboration. The chapter begins with brief classification of the standard aluminum alloys, remarking their importance for the transport sector, as well as the basic corrosion forms, typical for these alloys. It continues with the basic requirements regarding the elaboration of durable and reliable coating systems and the factors of detrimental effect during the service life time. The concept for passive and active corrosion protection capabilities is remarked as well. After description of the need for multi-layered coating systems elaboration, the function of each layer is described beginning from (i) UV light–absorbing exterior layers, (ii) self-repairing reinforced intermediate barrier layers, and (iii) cerium oxide primer layers (CeOPL). The importance and the basic approaches for metallic alloy preliminary treatment are remarked, as well. Finally, the basic concepts and the function of each layer in advanced multilayered coating system are summarized in a special section. The chapter finishes with brief conceptual description of two advanced versatile technological synthesis methods, which enable elaboration of organic/inorganic hybrid polymers and reinforcing nanoparticles.

**Keywords:** aircraft alloys, corrosion protection, cerium conversion coatings, technological aspects, hybrid and nanocomposite materials, corrosion inhibitors, multifunctionality

# **1.** Aluminum alloys as basic constructional material for the aircraft and transport industry

Aluminum (Al) is a lightweight relatively easily treatable metal that possesses an aptitude for passivation by formation of a natural oxide layer. Nevertheless, the pure Al is inapplicable in the industrial practice, since it does not present satisfying mechanical properties. The Al-based and



© 2017 The Author(s). Licensee InTech. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. (cc) BY magnesium (Mg)-based materials used for construction of various transport devices and vehicles must correspond to industrial standards, to construct transport equipment with reliable and predictable properties and performance. Recently, besides in the aircraft industry [1–3], the aluminum alloys have found continuously increasing applications for car body panels [4] and even in the modern shipbuilding [5, 6]. Besides, it is a common practice to apply multilayered coating systems for corrosion protection of metallic details, assemblies, and entire vehicle constrictions [7] (**Figure 1**).

According to the worldwide nomenclature, the Al alloys are denominated as "AA" with four digit numbers that reveal their chemical compositions as follows: AA1XXX—almost pure Al; AA2XXX with 1.9%–6.8% of copper (Cu); AA3XXX with 0.3%–1.5% of manganese; AA4XXX with silicon (Si) addition between 3.6% and 13.5%, AA5XXX with Mg content between 0.5% and 5.5%; AA6XXX prepared by both Mg 0.4%–1.5% and Si 0.2%–1.7%; AA7XXX with zinc (1%–8.2%); and finally, AA8XXX with other additives [14]. The rest three digits reveal the lower content elements and the acceptable contaminant concentrations. The compositions of the most widely used Al–Cu alloys, according to ISO 3522-2007, are summarized in **Table 1** [14].

The aluminum alloys are ranked second following the steels for industrial and household applications. Their mechanical properties—strength, stiffness, and durability—combined with their low weight and relatively low price make them preferable constructive materials. For instance, about 70% of all metal details in the nowadays airplanes are composed of aluminum alloys [3]. Irrespective of their excellent mechanical properties, these alloys exhibit a serious disadvantage—they are susceptible to corrosion. It is attributed to the additive components (Cu, Fe, Mn, Mg, Si, and so forth), which form intermetallics of a various composition dispersed throughout the aluminum matrix during the alloys hot rolling. In aggressive media, such as chloride ions containing ones, these inclusions become centers of initiation and further proliferation of localized corrosion [15].



**Figure 1.** Various kinds of vehicles composed by aluminum alloys. (a) Airbus A380 [8], (b) Boeing 747 [9], (c) Antonov 225 [10], (d, e) aluminum car bodies [11], (f) aluminum ship type Littoral Combat Ships [12], (g) aluminum sport boat [13].

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Designation	Si%	Cu%	Mn%	Mg%	Ni%	Ti%	Others%
AA2011	0.4 max	5.0-6.0	_	_	_	_	Pb0.4, Bi0.4
AA2014	0.5–1.2	3.9–5.0	0.4–1.2	0.2–0.8	_	0.15 max	_
AA2017	0.2–0.8	3.5-4.5	0.4–1.0	0.4–0.8	_	0.15 max	_
AA2018	0.9 max	3.5-4.5	_	0.4–0.9	1.7–2.3	_	-
AA2024	0.5 max	3.8-4.9	0.3–0.9	1.2–1.8	_	0.15 max	_
AA2025	0.5–1.2	3.9–5.0	0.4–1.2	_	—	0.15 max	-
AA2036	0.5 max	2.2–3.0	0.1–0.4	0.3–0.6	_	0.15 max	_
AA2117	0.8 max	2.2–3.0	0.2–0.5	_	—	-	-
AA2124	0.2 max	3.8-4.9	0.3–0.9	1.2–1.8	_	0.15 max	_
AA2218	0.9 max	3.5-4.5	_	1.2–1.9	1.7–2.3	-	-
AA2219	0.2 max	5.6-6.8	0.2–0.4	_	_	0.02–0.10	V-0.10 Zr-0.18
AA2319	0.2 max	5.6-6.8	0.2–0.4	_	_	0.10-0.20	V-0.10 Zr-0.18

 Table 1. Nominal standard compositions of copper-containing aluminum alloys.

### 2. Corrosion processes nature and impact

According to the exact definition, the corrosion, according to IUPAC, is a physical-chemical interaction between a metal and its environment, which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part [16].

Nowadays, the term "corrosion of the materials" comprises a large variety of detrimental processes which lead to lose of material integrity and mechanical properties of the corresponding details. Thus, recently, concepts for "corrosion of the plastics," formulated by Hojo et al. [17], as "degradation of polymeric materials with chemical reaction in which the molecular chains is cut" or "glass materials corrosion" [18], described as "fast and structure-dependent proton/cation(s) exchange and associated volume contraction which mechanically ruin the parts." In addition, the term "corrosion" already includes "microbially induced corrosion (MIC)" [19–21] caused by the metabolism of various acidogenic microorganisms or alcaligenes. The anaerobic microorganisms, such as iron-reducing bacteria (IRB) and sulfate reduction bacteria (SRB), also cause considerable corrosion damages [19]. The former reduces the insoluble ferric corrosion products to the soluble ferrous ones, whereas the latter reduces sulfate to sulfide compounds, contributing for additional cathodic activity enhancement. In general terms, all the corrosion processes result in partial or complete destruction of the metallic details.

Particularly, the metal corrosion processes possess electrochemical nature, and their appearance, rate, and impact are strongly dependent on the metal part features (i.e., structure and composition) and the environmental conditions (i.e., temperatures, pH, oxidant concentrations, and so forth).

Davis [22] has summarized all the basic corrosion impact forms, classifying them in uniform and localized corrosion phenomena (Figure 2).



Figure 2. Basic types of corrosion phenomena, according to Davis [22].

Finally, it is worth to remark that the corrosion process can alter its form pitting to intergranular [23]. The occurrence of especially cyclic mechanical loading enhances the corrosion impact, resulting in complete assembly or equipment failure. In general terms, the corrosion processes, related to the industrial alloys, usually begins as galvanic corrosion on the alloys' surface and continue subsequently as complete selective dissolution of the more active composing metals. Afterward, the complete dissolution of these alloy's components, resulting in pitting corrosion, continues in depth on the grain boundaries inside the metallic alloy, converting to intergranular corrosion. This already severe form of corrosion can lead to large domains exfoliation, due to thermal expansion of the heaped corrosion products and the entrapped moisture freezing. All these localized corrosion forms decrease the efficient cross-section of the metallic details, composing whatever assembly or construction. Finally, all these processes together lead to complete constructional failure, being sometimes even potential danger for the human life. One of the most famous cases is the accident with flight no. 243 at 1988 [24] (Figure 3).

After this accident, all the worldwide aircraft industry has accepted regular inspections, and the exploitation lifetime of the used commercial airplanes has been strongly restricted, in terms of maximal permitted flight hours, before decommission.

Thus, from all statements mentioned above, it can be considered that the term "corrosion" relays to whatever physical, chemical, or biological process which causes gradual geometrical shape altering and mechanical properties deterioration of given solid state object of industrial origin, due to interactions with its surrounding environment.

To prevent all these phenomena, the metallic surfaces should be insulated from the surrounding environment by coating. However, it should be mentioned that even the protective coatings

suffer destructive ageing processes and consequently should be created advanced coating systems with extended durability and capabilities for active protection even after any damage of their integrity.



Figure 3. Photography of the flight accident happened at 28th of April 1988 due to corrosion fatigue [24].

### 3. Protective coatings and layers: basic requirements

The efficient corrosion protection is only achievable when dense, uniform, and adherent layers are deposited. These protective layers should serve as efficient barriers against corrosive species ingress toward the protected metallic surface. However, these protective layers suffer the surrounding environment impact, as well. Consequently, the protective layers are susceptible to deterioration until barrier layer failure. Such failure can appear due to various reasons, like:

- Mechanical impact-caused by scratching, friction, and so forth
- Thermal expansion coefficient noncompliance—between the metallic surface and the protective layer itself.
- Chemical impact—when organic solvents or strong oxidants occur in the surrounding environment.
- Sunlight radiation—The UV spectrum of the sunlight radiation causes polymer chain disruption by direct scission or by photoinduced oxidation with the presence of oxidants [25].

Undoubtedly, the real exploitation conditions usually include combinations of the above mentioned detrimental factors. Thus, the coating systems should form durable adhesive barrier layers to execute efficiently their function of passive corrosion protection. Hence, in the industrial practice, the deposition of multilayered coating systems is commonly accepted practice (**Figure 4**). This



**Figure 4.** Schematic presentation of multilayer coating system according [7]. (1, 2) finishing double layer of polyurethane, (3) intermediate adhesive layer; (4) primer hybrid coating; (5) metal substrate.

approach enables deposition of advanced barrier coatings, where each composing layer has its own function.

However, recently new requirements arisen, related to further extension of the corrosion protective capabilities after barrier layer integrity disruption. Consequently, nowadays, coating systems should be capable for active corrosion protection, after damaging of their integrity. There are three basic roads to achieve active corrosion protective abilities:

- Incorporation of corrosion inhibitors
- Encapsulation of polymerizable compounds
- Introduction of hydrophobic compounds
- Addition of UV absorbers

According to the application of the coating system, other more specific requirements should appear. Montemor [26] proposes more complete classification of the beneficial properties and the respective requirements, related to the coating system application (**Figure 5**).

Other actual aspects related to the elaboration of advanced corrosion protective layers are rather related to the technological approaches used for their synthesis and deposition and the respective coating ingredients. In other words, every new coating system elaboration should comply the environmental restrictions, related to the use of volatile organic compounds (VOCs), [27, 28] and toxic metals, such as Pb, Cr, As, and so forth [29, 30].

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Figure 5. Overview of surface properties that can be developed or enhanced through functionalization by organic, inorganic or hybrid coatings, according to Montemor [26].

This considerable variety of requirements, related to the elaboration of durable and reliable, environmentally compliant coating systems with active corrosion protective capability impose the need for multilayered systems, where each layer has its own function. Thus, the coatings have at least exterior films, intermediate layers, and coating primers. Hence, the large number of requirements can be distributed to each one of the coating layers to obtain advanced multilayered coating system.

### 4. Exterior protective coatings and layers: basic requirements

The main function of the exterior layers is to protect the coating intermediate and primer layers against the impact of the surrounding environment. These exterior layers should possess mechanical strength against abrasion with high-speed solid particles, like dust or ice fogs, which spoil the fuselage metallic surface with the same speed as of the flight (i.e., up to 850–900 km/h). Other properties necessary for extension of the coating service lifetime are UV light absorption ability and hydrophobicity. The former property can be rendered by addition of UV absorbers into the external layers' composition. In this sense, Guillet [25] proposes several biphenyl, carbonyl-based compounds (**Table 2**).

Because the direct inclusion of these compounds to polymeric chain matrix is related to considerable difficulties, their preliminary incorporation in porous nanoparticles looks more appropriate approach. In this sense, ZnO, TiO<sub>2</sub>, and titanates-based porous nanoparticles are

much appropriated, since these oxides possess photochemical properties, as well. Besides, the photosensitizing of  $TiO_2$  particles is well-known method used for other applications such as photocatalysis [31], UV-spectrum photosensors [32, 33], elaboration of alternative energy sources [34, 35], and so forth.

Nevertheless, the approach of involvement of TiO<sub>2</sub> with incorporated photoabsorbers should be applied very attentively because the TiO<sub>2</sub> particles possess photodecomposition activity [36–39], and the organic UV light absorbers can terminate the polymerization processes of the basic coating layer matrix synthesis. Consequently, the elaboration of such coating compositions by addition of TiO<sub>2</sub> particles loaded by photoabsorbers should be combined by systematic comparative investigations with long-term UV-illumination, to detect whatever incompatibility effects on the basic polymer matrix. On the other hand, the successful introduction of preliminary impregnated titania nanoparticles into the basic polymer matrix converts the final coating as a composite material, where the TiO<sub>2</sub> particles serve as reinforcing phase, enhancing the mechanical strength, whereas the organic UV absorbers protect the polymer matrix against photochemical degradation. On the other hand, since ZrO<sub>2</sub> occupies the second place of the Mohs hardness scale after the diamond. That is why, zirconia-based composite protective coatings are already proposed for epoxide [40] and hybrid [41] polymer matrix.

Another aspect for barrier properties enhancement and service lifetime extension is to render hydrophobicity of the coating surface. Undoubtedly, one of the most efficient manners to avoid any corrosion phenomena is to render hydrophobic properties to the metallic surface. The surface hydrophobicity remarkably decreases the contact area with water condense. Another,

Name	Structural formula	Wavelength of maximal absorbance	Specific absorptivity
2-Hydroxy-4-methoxy benzophenone	CH10	326 nm	42.4
2,2'-Dihydroxy-4- methoxybenzophenone	CH <sub>1</sub> O	327 nm	41.2
2,2'-Dihydroxy-4,4'- dimethoxybenzophenone	CH,O CH	343 nm	50.2
Phenyl salicylate	CH <sub>1</sub> O	310 nm	23.6
2-(2'-Hydroxy-5'-methylphenyl)- benzophenone	OH HO N H,C	340 nm	73.0

Table 2. UV light-absorbing compounds proposed by Guillet [25].

much more important benefit is that the water drops have low cohesion to the metallic surface and can be leached from it by the spoiling air streams during flight. The hydrophobic surfaces do not allow water film formation on the metallic surface, preventing continuous contact between the metallic surface and any corrosive electrolyte.

The actual trends for hydrophobic and super-hydrophobic coating layers development are based on the formation of highly textured cerium oxide primers with micro and nanoflower [42], Gecko footprint [43] morphologies. This approach enables to avoid also the snow and ice heaping on the wings, which was the suspected reason for the aircraft crash at 7th of February 1958 in Munich, which was appeared to be a great disaster for the "Manchester United" football team during large years [44].

Nowadays, the de-icing procedures accepted as a common practice for the winter time exploitation in the commercial aircraft services appears the main reason for inconveniences, often related to schedule delays. In addition, these operations increase the economical spends, related to the needs for deicing solutions, staff, and equipment. In this sense, the hybrid polyfluorinated hybrid coatings [45] appear to be rather attractive alternative, since these coating materials combine the hydrophobicity with the beneficial features of the hybrid materials, discussed in the previous sections.

An interesting approach appears to be the proposed one by Arellanes-Lozada et al. [46]. This author's work-team proposes poly(1-vinyl-3-alkyl-imidazolium hexafluorophosphate, as corrosion inhibitor for aluminum corrosion in acidic media. This polymer seems really interesting, since it is able to be used as an alternative hydrophobic coating system, because it combines the beneficial effects of the presence of phosphate groups, long aliphatic chains, and hydrophobic fluorine moieties (**Figure 6**).



Figure 6. Schematic model of the corrosion protective action of poly(1-vinyl-3-alkyl-imidazolium Hexafluorophosphate toward AA 6061, proposed in [46].

Finally, it is important to mention that the exterior finishing coating layers should possess good adhesion to the intermediate layers. This indispensable property can be achieved easily when the basic polymer matrix is based on the same ingredients. Thus, some recent trends for development of the basic matrix of the exterior layers are described in the next paragraph.

# 5. Intermediate coating layers: barrier properties and self-reparation abilities

The polymer matrixes can possess organic nature, like polyepoxides, polyurethanes, polymethylmethacrilates, and so forth, or to have inorganic composition, being in form of glasses (i.e. silicates). Recently, various intermediate classes of materials have been introduced in the industrial practice. Hence, the use of organically modified inorganic polymers or hybrid materials opens entire new directions for advanced polymer matrix development. Haas and Rose [47] have done a versatile classification, including namely these intermediate classes of materials (**Figure 7**).



Figure 7. Classification of the basic types of polymer materials, according to Haas and Rose [47].

These intermediate groups of materials enable specific combination of the beneficial features of both the organic and inorganic composing moieties as follows [48, 49]:

- Organic part: (i) improved adhesion to the finishing organic paint layers; (ii) elasticity for compensation of the higher dilation coefficient, possessed by the metallic substrate; and (iii) hydrophobicity.
- Inorganic part: (i) improved adhesion to the coating primer layers; (ii) thermal resistivity; and (iii) mechanical strength.

In this sense, Frignani and coauthors have done [50] comparative assessment of primer coatings, obtained from alkoxides with different aliphatic chains, as follows: c n-propyl



Figure 8. Schematic view of self-assembled barrier protective film on aluminum surface according to Frignani et al. [50].

trimethoxysilane- $C_3H_7$ -Si-(OCH<sub>3</sub>)<sub>3</sub>; n-octyl trimetoxisilane- $C_8H_{17}$ -Si-(OCH<sub>3</sub>)<sub>3</sub>; n-octadecyl trimethoxysilane- $C_{18}H_{37}$ -Si-(OCH<sub>3</sub>)<sub>3</sub> and bis-trioximethyl-silyl-ethane – (CH<sub>3</sub>O)<sub>3</sub>-Si- $C_2H_7$ -Si-(OCH<sub>3</sub>)<sub>3</sub>. As conclusion, the authors have established that the larger aliphatic chains enhance the obtaining of thicker layers. The aptitude for self-healing provided by the hydrophobic intermolecular attraction (**Figure 8**), with simultaneous repulsion of entrapped water drops appear additional beneficial properties

These layers reveal aptitude for self-assembling, and this kind of hybrid materials is also known as (SAM—self-assembled monolayers). They have significantly lower number and size of defects in their structures and thus enable more efficient protection via formation of dense barrier layers [51, 52].

Another strategy is to encapsulate polymerizable substances. In this case, polymerizable compounds are enclosed inside polymer or glass capsules to polymerase when are exposed to air, by mixing each other or by toughing ingredients of the basic matrix. Following this concept, several authors [53, 54] have characterized an epoxy resin loaded by urea-formaldehyde submicrometer-sized capsules, filled with dicyclopentadiene as an active healing agent. Recently, three review works have been done over the variety of possible self-healing organic coatings [55–57] (**Table 3**).

The protective properties of the intermediate layers can be further improved, by addition of ceramic micro-sized and nanosized particles as reinforcing phase. In this sense,  $CeO_2$  [58, 59] and titanium dioxide (TiO<sub>2</sub>) [60, 61] have been recently obtained by precipitation from colloidal systems. Both these oxides possess significant mechanical and thermal strength and can be successfully used as reinforcing phase of advanced nanocomposite coating systems with

No	Self-reparation mechanism	Examples for self-reparation agents
1.	Molecular interdiffusion	Poly(methyl methacrylate) (PMMA) and PMMA-poly(methoxyethyl acrylate) (PMEA) copolymers
2.	Photo-induced self- healing	1,1,1-Tris-(cinnamoyloxymethyl) ethane (TCE) with urethane dimethacrylate (UDME), triethyleneglycol dimethylacrylate (TEGDMA)–based monomers
3.	Recombination of chain ends	Reactions such as polycarbonate (PC), polybutylene terephthalate (PBT), polyetherketone (PEK), and PEEK, polyphenylene ether (PPE)
4.	Reversible bond formation	Organosiloxanes, ionomers
5.	Living polymer approach	Living ring-opening metathesis polymerization (ROMP)
6.	Self-healing by nanoparticles	Described above
7.	Hollow fiber approach	Described above
8.	Microencapsulation approach	Diglycidyl ether of bisphenol-A (DGEBA), nadic methyl anhydride (NMA), benzyl dimethylamine (BDMA)

Table 3. Possible self-healing mechanism and active reparation agents according to Wu et al. [55].

extended durability. In addition, when these particles are preliminary filled by corrosion inhibitors, the final nanocomposite coatings obtain additional capability for active corrosion protection by gradual inhibitor release in the damaged zones, as it is already proposed by Zheludkevich et al. [48, 62] (**Figure 9**).

A promising alternative to the use of ceramic nanoparticles as inhibitor containers reinforcing the basic polymer matrix is the involvement of carbon nanoparticles (CNP) [63, 64]. Especially, the hollow carbon nanotubes (CNT) allow to be filled by inhibitors via intercalation. Indeed, the remarkable adsorption capability of the carbon-based materials was demonstrated by Lavrova [65] and Jumayeva et al. [66].

Various corrosion inhibitors are recently tested to substitute the already banned Cr(VI) compounds. Hence, the corrosion inhibition capability of benzotriazole and tolyltriazole [67–70] was examined, evincing the possibility for the use of these compounds as corrosion inhibitors. The inhibition mechanism of these compounds is based on film formation via adsorption on the metallic surface or by precipitation of derivative complex compounds. In this sense, the UV light absorbers, proposed by Guillet [25] (**Table 2**), should also possess potential corrosion inhibitive effect, protecting simultaneously both the coating polymer matrix against UV radiation, metallic surface against corrosion.

Alternatively, Cotting and Aoki [71] have proposed to encapsulate cerium-based corrosion inhibitor inside polystyrene capsules before their inclusion in an epoxide matrix. Indeed, the lanthanides have also shown high inhibition efficiency, due to their aptitude to form insoluble



Figure 9. Schematic view of self-healing effect by inhibitor gradual release from reinforcing nanoparticles.

hydroxides with the free OH<sup>-</sup> ions in the corrosive medium. The compounds of these elements are particularly efficient for corrosion prevention of Al corrosion, since this metal and its alloys are very susceptible to corrosion even in weakly alkaline media. Among the lanthanides, the cerium compounds have shown the highest inhibition efficiency [72]. In this sense, various comparative investigations have been performed, to determine the influence of Ce(III) or Ce (IV) compounds [73–75], the optimal Ce-inhibitor concentration [73, 75, 76], as well as the impact of the anionic moiety of the respective Ce-salt [76]. As general results of these research activities, it was evinced that the Ce(III) compounds are much more efficient inhibitors for AA2024-T3, whereas the Ce(IV) ones can even enhance the corrosion attack at higher concentrations. Furthermore, for each Ce(III) compound, an optimal concentration threshold exists, depending on the alloy to be protected, the corrosive medium properties, and so forth. Thus, at higher concentrations, the Ce-compounds enhance the corrosion instead to inhibit it. Here, the term "catalyst" is not appropriate, because the Ce-compounds also suffer chemical conversions, being activators of the corrosion processes. As was already mentioned above, the Cecompounds and the organic inhibitors follow different mechanisms of inhibition. Besides the former decelerate the cathodic reactions, affecting predominantly the cathodic zones, whereas the latter form protective films on the entire metallic surface. Consequently, a question has appeared about whether a synergistic effect could occur between these distinguishable kinds of inhibitors. Hence, recently, the potential synergism between both kinds of inhibitors was examined by various authors on Al/Cu couples [77], AA5052 alloy [78], and even carbon steel [79]. Finally, the Ce-compounds have shown capabilities to form uniform adherent primer layers at defined conditions.

### 6. Cerium oxide primer layers deposition: basic concepts and requirements

The basic function of the primer coating layers (i.e., the coating primers) is to improve the adhesion between the native Al-oxide layer of the metallic substrate and the upper (i.e., intermediate and finishing) layers, commented in the previous sections. Some authors even report for self-healing properties, possessed by these films [80].

Undoubtedly, among the basic advantages of this group of coatings is the possibility to deposit them by physical [81, 82], electrochemical [83–87], or chemical methods [88–94]. Regardless the method applied for cerium oxide primer layer (CeOPL) deposition, the respective technological regime includes three basic stages: (i) preliminary treatment of the metallic substrate, (ii) the CeOPL deposition itself, and (iii) final sealing of the already deposited CeOPL film [94, 95]. In this sense, a large field of possible combinations among the conditions for execution of each technological procedure exists.

As was mentioned in the previous sections, the inhibitor effect of the cerium compounds is based on the precipitation of  $Ce(OH)_3$  and/or  $Ce(OH)_4$ , predominantly on the cathodic areas of the Al alloys (composed by nobler metals), due to the cathodic reduction of the dissolved oxygen. However, the real mechanism is much more complicated and includes participation of intermediate peroxo-complexes [93, 94].

Scholes et al. [93] have made a simplified scheme (**Figure 10**) of the processes proceeding during the CeOPL deposition, after addition of  $H_2O_2$  as deposition activator.

The deposition of uniform, dense, and adherent CeOPL films instead of obtaining of discrete Ce precipitates appears a great challenge namely because of the complicated chemical mechanism. Besides the influence of the Ce-compound type and concentration, and, of course, the  $H_2O_2$  activator content, the deposition mechanism and rate can be driven by regulation of various factors, like pH, temperature, occurrence of additives, and so forth. In this sense, the beneficial effect of various additives has been evinced, like black cuprous oxide "smut" [94],  $AI^{3+}$ , and  $CI^-$  ions [96], pH-buffers [90, 97], and so forth. The recent work of Jiang et al. [98] has proposed combined Ce-V conversion layers for protection of magnesium alloys, discovering entire new direction for elaboration of combined conversion coatings. Finally, it should be mentioned that the metallic surface roughness and composition are of key importance for the quality and performance of the CeOPL, predetermining its adherence, structure, and density. The metallic surface characteristics can be easily modified by suitable preliminary surface treatment.



Figure 10. Schematic summarizing of the proposed mechanism of the cerium oxide layer deposition by Scholes [93].

### 7. Preliminary treatment procedures: basic concepts

The purpose of the preliminary treatment procedure is to modify the metallic substrate surface to be suitable for deposition of uniform and adherent primer layers. The impact of the preliminary surface treatment procedures comprises both the metallic surface roughness (by mechanical grinding in laboratory's conditions, or sand blasting in industrial scale) and the superficial chemical composition (by selective dissolution of the intermetallic inclusions, or affecting the surface oxide layer [92]).

The commonly accepted preliminary treatment procedures include four basic steps:

- Degreasing—by organic solvents, for removal of the temporal anticorrosion protective layer, deposited by the corresponding Al-producer, for protection during the alloy storage and transportation before its use for production of Al-details and tools.
- Mechanical grinding—This procedure is being performed by emery papers in laboratory's conditions and sand blasting, in real industrial scale. The basic purpose of this procedure is to smooth the metallic surface and to remove the thicker oxide layer, formed during the finishing metallurgical thermal posttreatment. Of course, immediately after this procedure, a new oxide layer is being formed on the bare metallic surface (even underwater film) because the exceptional passivation aptitude of this metal.
- Alkaline etching—This procedure results in dissolution of the surface aluminum layer, penetrating through the thin oxide layer, due to its defective structure and nonuniform composition. Usually, this film consists of boehmite γ-AlO(OH) domains with about 5 nm of thickness [99]. Even the corundum Al<sub>2</sub>O<sub>3</sub> fraction has strongly defective surface, due to the incompleteness of the superficial crystalline lattice cells. That is why, the surface oxide layer cannot protect the underlying metal against the aggressive OH<sup>-</sup> attack.

In addition, the surface oxide layers of the highly doped Al alloys are always interrupted by the intermetallic inclusions on the alloy's surface.

Acidic desmutting—The purpose of this procedure is to remove the black smut of the oxides of the intermetallic inclusions (like Cu<sub>2</sub>O, CuO, MnO<sub>2</sub>, and so forth). Usually, this process is being performed by dissolution in diluted HNO<sub>3</sub>.

Each one of these operations should be performed very attentively to obtain desirable surface conditioning. Besides, the optimal technological prescription for given aluminum alloy is not always appropriate for other alloys.

In this aspect, a comparative systematical investigation [100] was recently performed to evaluate the impact of each one of the above mentioned procedures. The authors have compared four groups of AA2024-T3 plates:

• Group G1: degreasing with an equal ratio of ethanol/ether mixture at room temperature for 10 minutes subjected to continuous stirring and subsequent abundant washing with distilled water;

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**Figure 11.** AFM images of samples underwent different approaches of superficial treatment; (a) degreasing (G1), (b) grinding (G2), (c) grinding and etching with a weak alkaline solution (G3) and (d) grinding and etching with a strong alkaline solution at high temperature (G4).

- Group G2: consecutive grinding with finer graded emery papers of 200, 360, 500 and 800 grit, followed by degreasing procedure with the same conditions as G1;
- Group G3: grinding as for G2 group, followed by etching with weak alkaline solution of (0.18 M) Na<sub>3</sub>PO<sub>4</sub> and (0.19 M) Na<sub>2</sub>CO<sub>3</sub> for 10 minutes at 30°C and subsequent abundant washing with distilled water;
- Group G4: grinding as for G2, followed by etching with a strong alkaline solution of (1.0 M) NaOH, (0.18 M) Na<sub>3</sub>PO<sub>4</sub>, and (0.19 M) Na<sub>2</sub>CO<sub>3</sub> for 3 minutes at 60°C, followed by abundant washing with distilled water, desmutting in (6.0 M) HNO<sub>3</sub> solution for 2 minutes at room temperature and a final copious washing with distilled water.

As main conclusion, the authors have established that the highest rate of reproducibility belongs to the mechanically polished (G2) and the softly etched (G3) groups, whereas the only degreased (G1) and the hard etched (G4) samples are more distinguishable among themselves. Besides, the different preliminary treatment procedures have rather distinguishable impacts on the resulting morphology (**Figure 11**).

The surface morphology of given Al alloy after any preliminary surface treatment procedure depends on both its chemical composition and the thermal treatment regime, applied for its metallurgical production. Thus, although the same chemical composition, the obtained alloys could possess completely different mechanical properties, predetermined by the finishing metallurgical thermal treatment. Indeed, in another comparative investigation, involving CeOPL



Figure 12. SEM (a, b) and EDX (c, d) images of the boundary between the bare and the coated areas of AA2024-T3 (a, c) and D16 AM (b, d) [100].

deposition at the same regime on AA2024-T3, and its Russian analogue—D16 AM tempered clad alloy [101], it was established that the CeOPL is much more uniform and fine grained in the former case, whereas in the latter case, the film is less uniform, because of the tempered shielding layers (**Figure 12**).

### 8. Conceptual summary

Following all the statements and the concepts, described in the present chapter, it can be inferred that a continuous need exists for elaboration of reinforced multilayered durable coating systems capable to provide active corrosion protection even after already appeared mechanical damages. Namely, the providing of durable and reliable corrosion protection enables extension of the service life time of the engineering construction and equipment and particularly—transport vehicles and aircraft. Thus, the reliable corrosion protection is the right way to save economical spends related to the shortening of the service life time before decommission of the used transport and especially aircraft equipment. In this sense, the UV light–protected, hydrophobic-reinforced self-reparable coating systems form reliable barrier against access of corrosive species to the constructive element metallic surfaces.

In this sense, the recent trends related to the elaboration of durable and reliable corrosion protective systems include several basic directions:

- Introduction of UV-radiation absorbers—to extend the service lifetime of the external coating layers polymeric matrixes.
- Involvement of reinforcing phases—to enhance the mechanical strength of the coating exterior finishes and the intermediate interlayers. This phase can serve even for UV-absorbent and/or corrosion inhibitor carriers.
- Use of hydrophobic and super hydrophobic finishes—to repel the water drops, preventing water film formation. Besides the hydrophobic intermolecular attraction forces among the coating ingredients enable additional repulsion of the already penetrated humidity in the coating bulk, achieving active corrosion protection.
- Encapsulation of active polymerizable agents—to achieve self-healing effect via coating self-recuperation.
- Addition of environmentally friendly synergistic corrosion inhibitor mixtures—to protect the metal surface even after coating damage.
- Deposition of reliable environmentally friendly coating primers—to substitute the widely used but already banned chromium conversion coatings (CCC).

As a result, advanced, environmentally compliant multilayered systems are under elaboration. Such system is well illustrated by Figueira et al. [102] (**Figure 13**).

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**Figure 13.** Schematic view of advanced multilayered coating system capable for active corrosion protection, according to Figueira et al. [102].

### 9. Advanced technological approaches

Besides the VOC-emission removal, the rest general trend in the technological aspect regarding the elaboration of advanced corrosion protective coating systems is to decrease the number of the intermediate technological states and the related energetic and material spends.

### 9.1. Sol-gel road

The literature analysis shows that recently the sol-gel approach enlarges its application, being more attractive for ease synthesis of hybrid polymer matrixes, able to combine the benefits of the organic and inorganic moieties (discussed above). As a result, a miscellaneous organic/ inorganic polymer matrix is being obtained, as is illustrated by Wang and Bierwagen [103] (**Figure 14**).

The sol-gel method, with hybrid precursors, like the proposed by Frignani and coauthors [50], is based on hydrolysis of the metal alkoxides, with coincident polymerization of the hydrolyzed radicals. By this manner, the initial precursor mixture (sol) gradually converts to gel.



Figure 14. Simplified schematic of bonding mechanism between silane molecules and metal surface hydroxide layer (a) before condensation: hydrogen-bonded interface; (b) after condensation: covalent-bonded interface [103].

After deposition and posterior appropriated thermal treatment, the already deposited gel film converts to solid state protective coating layer.

According to Kozhukharov [104], there are seven basic important conditions, which have to be driven, to obtain desirable gel product (i.e., dense, uniform film):

- Chemical composition of the liquid medium
- Chemical composition of the precursors (alkoxides)
- Molar factor (ratio between the alcohol as medium and the alkoxides as precursors)
- pH of the medium
- Presence of additives
- Temperature
- Pressure and chemical composition of the gaseous medium over the gelling system during the drying (annealing) process

The basic technological stages of the sol-gel synthesis process are illustrated in Figure 15.

As was mentioned in the present chapter, the basic manner for further improvement of the solgel-derived hybrid polymer matrices is to add micro-/or nanosized solid state fine dispersed phase directly into the sol-gel liquid system at intensive stirring, to obtain equally distribution. Among the most efficient methods for production nanoparticle production is the so-called

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**Figure 15.** Schematic presentation of the basic stages of the sol-gel synthesis process [104]: (1) initial gel formation, (2) gel drying, (3) finishing high temperature treatment.

spray pyrolysis synthesis (SPS). Besides, thin ceramic protective films able to work at very high temperatures can be produced by so-called spray pyrolysis deposition (SPD). This method is applicable for protective layer deposition for turbine blades in jet turbines, compressors, and so forth

### 9.2. Spray pyrolysis

According to [105], when a liquid drop of solution is already sprayed, it undergoes several processes in the high temperature space, until its conversion to a solid particle. These processes are illustrated in **Figure 16** and described, in brief, below.

Initially, each drop suffers heating, and evaporation of the solvent (1), until it achieves the stage A. It could be described as a liquid particle, represented by saturated solution, surrounded by vapors of the solvent. Afterward, due to the evaporation, an additive solid shell forms (2), leading to intermediated three phases system (B). It is represented by vapors, solid porous shell, and still liquid core. That process passes simultaneously with initiation of chemical conversion of the precursors to the desired product. During this stage, an additive interaction between components of the vapors and the solid shell are possible, as well. After completion of the evaporation,



Figure 16. Thermal processes related to SPS [105].

because of expense of the entire liquid, a spherical solid particle of the product appears (C). The process could be finished until this stage. That approach is also known as "one drop–one particle." It enables production of powder materials with one fraction size of particles. If these particles are submitted to further calcinations, then they could split up to form even smaller particles (E). That approach permits production of ultra dispersive nanoparticles. The transition from stage C to E passes through intermediate stage D. This stage could be reached because of appearance of cracks and ruptures (4). Their appearance is consequence of mechanical tensions, due to difference of the temperatures, and the volume expansions between the core and the surface of the respective particle. Another reason for the crumbling of the particles is that the processes described above could pass accompanied by polymorphic transitions in the solid phase.

Among the basic advantages of this method is that it enables large scale production of fine dispersion solid particles by use of rather simple equipment [106].



**Figure 17.** Basic constructions of spray pyrolysis installations [106, 107] a- vertical chambers; b- horizontal chambers; cchambers for film deposition; 1- vessel for precursor solution; 2- gas bottle for carrier gas; 3- spray nozzle; 4- spray burner; 5- gas bottle for combustible; 6- gas bottle for oxidizer; 7- vertical chamber; 8- horizontal chamber; 9- chamber for spray deposition; 10- electric heaters; 11- powder collectors; 12- substrates for film deposition; 13- filters.

In general, all the possible modifications of the spray pyrolysis installations are consisted on several basic operation units, which function is assisted by additional devices. The main equipment components for synthesis via spray pyrolysis method are: 1—spraying nozzle, 2—High temperature work space (i.e., furnace), 3—product collector for the fine dispersed powder-like products or film deposition substrate. To insure the regular function of these basic operation units, additional units are necessary, such as: initial precursor solution containers, nozzle feeding pumps, carrier gas compressors, thermal energy sources, powder fraction separators, and so forth. The basic types of SPS/SPD installations are illustrated in **Figure 17** [107].

Of course, the spray drops and the respective obtained particles size formation are almost entirely predetermined by the nozzle construction. There are specially designed nebulizers and atomizers, which enable nanosized drops formation. Alternatively, nozzle-less spray pyrolysis equipment is also proposed in the literature [108].

### 10. General conclusions

Aluminum (Al) is a lightweight, relatively easily treatable metal that possesses an aptitude for passivation by formation of a natural oxide layer. Nevertheless, the pure Al is inapplicable in the industrial practice, since it does not present satisfying mechanical properties. Irrespective of their excellent mechanical properties, these alloys are very susceptible to corrosion, due to occurrence of alloying phases, which become centers of initiation and further proliferation of localized corrosion

Nowadays, the term "corrosion of the materials" comprises a large variety of detrimental processes which lead to lose of material integrity and mechanical properties of the corresponding details. In addition, the term "corrosion," already includes "microbially induced corrosion (MIC)". Particularly, the metal corrosion processes possess electrochemical nature, and their appearance, rate and impact are strongly dependent on the metal part features (i.e. structure and composition) and the environmental conditions (i.e. temperatures, pH, oxidant concentrations, and so forth).

Thus, the term corrosion relays to whatever physical, chemical or biological process which causes gradual geometrical shape altering and mechanical properties deterioration of given solid state object of industrial origin, due to interactions with its surrounding environment.

To prevent all these phenomena, the metallic surfaces should be insulated from the surrounding environment by coating. However, it should be mentioned that even the protective coatings suffer destructive ageing processes and consequently, should be created advanced coating systems with extended durability and capabilities for active protection even after any damage of their integrity.

Other actual aspects, related to the elaboration of advanced corrosion protective layers, are rather related to the technological approaches used for their synthesis and deposition and the respective coating ingredients. In other words, every new coating system elaboration should comply the environmental restrictions, related to the use of volatile organic compounds (VOCs), and toxic metals, such as Pb, Cr, As, and so forth.

This considerable variety of requirements, related to the elaboration of durable and reliable, environmentally compliant coating systems with active corrosion protective capability imposes the need for multilayered systems, where each layer has its own function. The main function of the exterior layers is to protect the coating underlayers against the impact of the surrounding environment, like UV light absorption ability and hydrophobicity. The intermediate coating layers should possess extended barrier properties and self-repairing ability. The actual trend in this sense is to use hybrid matrix-based polymeric materials, able to combine the benefits of the organic and inorganic materials. Besides, this approach enables to deposit self-assembled monolayers (SAM), composed by siloxanes with large aliphatic chains. They have significantly lower number and size of defects in their structures, and thus enable more efficient protection via formation of dense barrier layers. Another strategy is to encapsulate polymerizable substances. In this case, polymerizable compounds are enclosed inside polymer or glass capsules to polymerase when are exposed to air, by mixing each other or by toughing ingredients of the basic matrix. A promising alternative to the use of ceramic nanoparticles as inhibitor containers reinforcing the basic polymer matrix is the involvement of carbon nanoparticles (CNP). Especially, the hollow carbon nanotubes (CNTs) allow to be filled by inhibitors via intercalation.

The basic function of the primer coating layers (i.e., the coating primers) is to improve the adhesion between the native Al-oxide layer of the metallic substrate and the upper (i.e., intermediate and finishing) layers, commented in the previous sections. Some authors even report for self-healing properties, possessed by these films. Undoubtedly, among the basic advantages of this group of coatings is the possibility to deposit them by physical, electrochemical, or chemical methods. Regardless the method applied for cerium oxide primer layer (CeOPL) deposition, the respective technological regime includes three basic stages: (i) preliminary treatment of the metallic substrate, (ii) the CeOPL deposition itself, and (iii) final sealing of the already deposited CeOPL film.

The purpose of the preliminary treatment procedure is to modify the metallic substrate surface, to be suitable for deposition of uniform and adherent primer layers. The impact of the preliminary surface treatment procedures comprises both the metallic surface roughness (by mechanical grinding in laboratory's conditions, or sand blasting in industrial scale) and the superficial chemical composition (by selective dissolution of the intermetallic inclusions or affecting the surface oxide layer). The commonly accepted preliminary treatment procedures include four basic steps: degreasing, mechanical grinding, alkaline etching, and acidic desmutting.

Finally, it should be remarked that among the various technological approaches, the sol-gel route and the spray-based techniques have shown to provide the synthesis of various nanosized materials and thin layer deposition.

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### References

- [1] Wildey, J. F.: Aging aircraft. Mater. Perform. 1990;29:80-85
- [2] Komorowski, J. P., Bellinger, N. C., Gould, R. W., Marincak, A., Reynolds R.: Quantification of corrosion in aircraft structures with double pass retroreflection. Can. Aeronaut. Space J. 1996;42:76–82
- [3] Starke E. A., Jr., Staley J. T.: Application of modern aluminum alloys to aircraft, Prog. Aerosp. Sci. 1996;32:131–172
- [4] Davies G.: Materials for Automobile Bodies. Linacre House, Jordan Hill, Oxford OX2, Burlington, 2nd. ed. (2003), ISBN 0 7506 5692 1, pp. 146–156.
- [5] Eyres D.: Ship construction, Linacre House, Jordan Hill, Oxford OX2, Burlington, 2007, 6th ed. pp. 50–52, ISBN 10:0-75-068070-913.
- [6] Aluminium in shipbuilding, accessible via INTERNET, access via: http://www. aluminiumleader.com/en/around/transport/ship 7.
- [7] Tsaneva G., Kozhukharov V., Kozhukharov S., Ivanova M., Gerwann J., Schem M., Schmidt T.: Functional nanocomposite coatings for corrosion protection of aluminum alloy and steel. J. Univ. Chem. Technol. Metall. 2008;43:231–238
- [8] Accessible via INTERNET via Internet: http://www.airbus.com/aircraftfamilies/passengeraircraft/a380family/
- [9] Accessible via INTERNET via Internet: http://www.google.com/imgres-boeing 747
- [10] Accessible via INTERNET via Internet: http://www.youtube.com/watch?v=SO-YLIj\_xwo&feature=related
- [11] Accessible via INTERNET via Internet: http://www.google.com/imgres?imgurl=http:// globalwarming-arclein.blogspot.com
- [12] http://nation.time.com/2011/07/05/u-s-navys-brand-new-aluminum-ship-foiled-by-seawater/
- [13] Accessible via INTERNET via Internet: http://www.advancedrobotic.com/blog/cnc-routers/cost-savings-in-the-manufacture-of-aluminium-ships

- [14] Mazzolani F. M.: Aluminium alloy structures. E& FN SPON: London ed. 2nd. ed. 1985:5-25
- [15] Yasakau K., Zheludkevich M., Lamaka S., Ferreira M. G. S.: Mechanism of corrosion inhibition of AA2024 by rare-earth compounds. J. Phys. Chem. B. 2006;110: 5515–5528
- [16] ISO 8044:1986, Corrosion of metals and alloys—terms and definitions, *Document published on:* 1986-12-22, access via: http://www.iso.org/iso/iso\_catalogue/catalogue\_ics/catalogue\_detail\_ics.htm?csnumber=15056
- [17] Hojo H., Tsuda K., Kubouchi M., Kim D-S.: Corrosion of plastics and composites in chemical environments. Metals Mater. 1998;4:1191–1197
- [18] Tournié A., Ricciardi P., Colomban Ph.: Glass corrosion mechanisms: a multiscale analysis. Solid State Ion. 2008;179:2142–2154
- [19] Javaherdashti R.: Microbiologically Influenced Corrosion An Engineering Insight. Springer-Verlag London Limited: London, 2008:54–57. ISBN-13: 9781848000735
- [20] Rosliza R., Senin H.B., Wan Nik W.B.: Electrochemical properties and corrosion inhibition of AA6061 in tropical seawater. Colloids and Surfaces A. 2008;312:185–189
- [21] Rosales B. Iannuzzi M.: Aluminium AA2024 T351 aeronautical alloy. Part 1. Microbial influenced corrosion analysis. Mater. Sci. Eng. 2008;472:15–25
- [22] Davis J.: Corrosion: Understanding the Basics. American Technical Publishers Ltd: Materials Park, Ohio, 2000:6–10
- [23] Zhang W., Frankel G. S.: Transitions between pitting and intergranular corrosion in AA2024. Electrochim. Acta 2003;48:1193–1210
- [24] Accessible via Internet: http://4.bp.blogspot.com/April28\_1988\_flightfailure.jpg
- [25] Guillet J. E.: Fundamental Processes in the UV Degradation and Stabilization of Polymers, Internet access via: http://old.iupac.org/publications/pac/1972/pdf/3001x 0135.pdf
- [26] Montemor M. F.: Functional and smart coatings for corrosion protection: a review of recent advances. Surf. Coat. Technol. 2014;258:17–37
- [27] Directive 2001/81/EC on National emission ceilings for certain atmospheric pollutants, Off. J. Eur. Communities, L 1309/22, 27-11-2001
- [28] Council Directive on the limitation of emissions of VOC due to the use of organic solvents in certain activities and installations, Off. J. Eur. Communities 2001; 44: pp. L 309
- [29] Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Off. J. Eur. Communities L 23, 26.1.2005, pp. 3–16, Special edition in Bulgarian: Chapter 15 Volume 21 P. 124–137.
- [30] EU Directive 2002/95/EC: Restriction of Hazardous Substances in Electrical and Electronic Equipment. (RoHS directive 2002), http://ec.europa.eu/environment/waste/ rohs\_eee/legis\_en.htm (accessed at 30. G.
- [31] Haneda D., Li H., Hishita S., Ohashi N., Labhsetwar N. K.: Fluorine-doped TiO powders prepared by spray pyrolysis and their improved photocatalytic activity for decomposition of gas-phase acetaldehyde. J. Fluorin. Chem. 2005;**126**:69-77
- [32] Teleki A., Bjelobrk N., Pratsinis S. E., Gouma P. I.: Flame-made Nb- and Cu-doped TiO<sub>2</sub> sensors for CO and ethanol. Sens. Actuators B 2008;130:449–457
- [33] Okuya M., Shiozaki K., Horikawa N., Kosugi T., Kumara G. R., Madarasz J., Kaneko S., Pokol G.: Porous TiO<sub>2</sub> thin films prepared by spray pyrolysis deposition (SPD) technique and their application to UV sensors. Solid State Ion. 2004;172:527–531
- [34] O'Regan B., Grätzel M.: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO<sub>2</sub> films. Nature 1991:353;737–740
- [35] Bozhilov V., Kozhukharov S., Bubev E., Machkova M., Kozhukharov V., Application of TiO<sub>2</sub> and its derivatives for alternative energetic sources, Ann. Proc. Univ. Rousse (Bulgaria) 2012;51:36–40
- [36] Jwo C., Chang H., Kao M., Lin C.: Photodecomposition of volatile organic compounds using TiO2 nanoparticles. J. Nanosci. Nanotechnol. 2007;7:1947–1952
- [37] Rezaee A., Pourtaghi Gh. H., Khavanin A., Mamoory R. S., Ghaniean M. T., Godini H.: Photocatalytic decomposition of gaseous toluene by TiO<sub>2</sub> nanoparticles coated on active carbon. Iran. J. Environ. Sci. Eng. 2008;5:305–310
- [38] Duan X., Sun D., Zhu Z., Chen X., Shi P.: Photocatalytic decomposition of toluene by TiO<sub>2</sub> film as photocatalyst. J. Environ. Sci. Health 2002;A-37:679-692
- [39] Ku Y., Chen J-S., Chen H-W.: Decomposition of benzene and toluene in air streams in fixedfilm photoreactors coated with TiO<sub>2</sub> catalyst, J. Air Waste Manag. Assoc. 2007;57:279–285
- [40] Xavier, J. R., Nallaiyan, R.: Application of EIS and SECM studies for investigation of anticorrosion properties of epoxy coatings containing ZrO<sub>2</sub> nanoparticles on mild steel in 3.5% NaCl solution. J. Fail. Anal. Preven. 2016:1–10
- [41] Balaji J., Sethuraman M. G.: Studies on the effects of thiourea and its derivatives doped — Hybrid/zirconium nanocomposite based sol-gel coating for the corrosion behaviour of aluminum metal. Prog. Org. Coat. 2016;99:463–473
- [42] Liu, F. Su, J. Liang, Huang P.: Facile fabrication of superhydrophobic cerium coating with micro-nano flower like structure and excellent corrosion resistance. Surf. Coat. Technol. 2014;258:580–586
- [43] Pedraza F., Mahadik S. A., Bouchaud B., Synthesis of ceria based supehydrophobic coating on Ni20Cr substrate via cathodic electrodeposition. Phys. Chem. Chem. Phys. 2015;17:31750–31757
- [44] Accessible via: http://www.theguardian.com/media/from-the-archive-blog/2011/may/ 28/munich-manchester-united-busby-1958
- [45] Suriano R., Oldani V., Bianci C. L.: AFM. Nanomechanical properties and durability of new hybrid polyfluorinated sol-gel coatings. Surf. Coat. Technol. 2015;264:87–96

- [46] Arellanes-Lozada P., Olivares-Xometl O., Guzmán-Lucero D., Likhanova N. V., Domínguez-Aguilar M. A., Lijanova I. V., Arce-Estrada E.: The inhibition of aluminum corrosion in sulfuric acid by poly(1-vinyl-3-alkyl-imidazolium hexafluorophosphate). Materials 2014;7(8):5711–5734
- [47] Haas K-H., Rose K.: Hybrid inorganic/organic polymers with nanoscale building blocks: precursors, processing. Rev. Adv. Mater. Sci. 2003;5:47–52
- [48] Zheludkevich M. L., Salvado I. M., Ferreira M. G.: Sol-gel coatings for corrosion protection of metals. J. Mater. Chem. 2005;15:5099–5111
- [49] Salve A. A., Kozhukharov S., Pernas J. E., Matter E., Machkova M.: Comparative research on hybrid nano-composite protective primary coatings for AA2024 aircraft alloy. J. Univ. Chem. Technol. Met. 2012;47:319–326
- [50] Frignani A., Zucchi F., Trabanelly G., Grassi V.: Protective action towards aluminium corrosion by silanes with long aliphatic chain. Corros. Sci. 2006;48:2258–2273
- [51] Laibinis P., Whitesides G., Allara D., Tao Y-T., Parkin A., Nuzzo R.: Comparison of the structures and wetting properties of self-assembled monolayers of n-alkanethiols on the coinage metal surfaces, copper, silver, and gold. J. Am. Chem. Soc. 1991;113:7152– 7167
- [52] Malzbender J., de With G.: Measuring mechanical properties of coatings: a methodology applied to nano-particle-filled sol–gel coatings on glass. Adv. Eng. Mater. 2002;4:296– 302
- [53] Kessler M. R., Sottos N. R., White S. R.: Self-healing structural composite materials. Composites Part A 2003;34:743–753
- [54] Kirkby E. L., Michaud V. J., M°anson J-A. E., Sottos N. R., White S. R.: Performance of self-healing epoxy with microencapsulated healing agent and shape memory alloy wires. Polymer 2009;50:5533–5538
- [55] Wu D. Y., Meure S., Solomon D.: Self-healing polymeric materials: a review of recent developments. Prog. Polym. Sci. 2008;33: 479–522.
- [56] Blaiszik B. J., Sottos N. R., and White S. R.. Nanocapsules for self-healing materials. Composites Sci. Technol. 2008;68:978–986
- [57] Abdolah Z. M., van der Zwaag S., Garcia S. J.: Self-healing corrosion-protective sol-gel coatings based on extrinsic and intrinsic healing approaches. Adv Polym. Mater. 2016;273:185–218.
- [58] Ketzal J. J., Nesaraj A. S.: Synthesis of CeO<sub>2</sub> nanoparticles by chemical precipitation and the effect of a surfactant on the distribution of particles sizes. J. Ceram. Process. Res. 2011;12:74–79
- [59] Chen H-I., Chang H-Y.: Homogeneous precipitation of cerium dioxide nanoparticles in alcohol/water mixed solvents. Colloids Surf. 2004;242:61–69

- [60] Nam H-D., Byung H. L., Kim S. J., Jung C-H., Ju-Hyeon Lee J-H. Park S.: Preparation of ultrafine crystalline TiO<sub>2</sub> powders from aqueous TiCl<sub>4</sub> solution by precipitation. Jpn. J. Appl. Phys. 1998;37:4603–4608
- [61] Coronado D., Rodriquez- Gattorno G., Espinosa-Pezqueira M. E., Oskam G.: Phase-pure TiO<sub>2</sub> nanoparticles: anatase brookite and rutile. Nanotechnology 2008;19:145605– 145613.
- [62] Zheludkevich M., Serra R., Montemor M. Ferreira M.: Oxide nanoparticle reservoirs for storage and prolonged release of the corrosion inhibitors. Electrochem. Commun. 2005;7:836–840
- [63] Hammer P., dos Santos F. C., Cerrutti B. M., Cerrutti B. M., Pulcinelli S. H., Santilli C. V.: Carbon nanotube-reinforced siloxane-PMMA hybrid coatings with high corrosion resistance. Prog. Org. Coat. 2013;76:601–608
- [64] Ghasemi-Kahrizsangi A., Shariatpanahi H., Neshati J., Akbarinezhad E.: Corrosion behavior of modified nano carbon black/epoxy coating in accelerated conditions, Appl. Surf. Sci. 2015;331:115–126.
- [65] Lavrova S.: Treatment of landfill leachate in two stage vertical-flow wetland system with/without addition of carbon source. J. Chem. Technol. Metall. 2016;**51**:223–228
- [66] Jumayeva D., Eshmatov I., Jumabaev B., Agzamkhodjayev A..: Carbon adsorbents on the basis of brown coal of angren for cleaning industrial wastewater. J. Chem. Technol. Metall. 2016;51:210–214.
- [67] Önal A. N. Aksüt A. A.: Corrosion inhibition of aluminium alloys by tolyltriazole in chloride solutions. Anti-Corros. Methods Mater. 2000;47:339–349
- [68] Kumari P., Nayak J., Shetty A.: 3-Methyl-4-amino-5-mercapto-1,2,4-triazole as corrosion inhibitor for 6061 Al alloy in 0.5 M sodium hydroxide solution. J. Coat. Technol. Res. 2011;8:685–695
- [69] Zheludkevich M. L., Yasakau K. A., Poznyak S. K., Ferreira M. G. S.: Triazole and thiazole derivatives as corrosion inhibitors for AA2024 aluminium alloy. Corros. Sci. 2005;47:3368–3383
- [70] Yasakau K. A., Zheludkevich M. L., Karavai O. V., Ferreira M. G. S.: Influence of inhibitor addition on the corrosion protection performance of sol–gel coatings on AA2024. Prog. Org. Coat. 2008;63:352–361
- [71] Cotting F.. Aoki I.. Smart protection provided by epoxy clear coating doped with polystyrene microcapsules containing silanol and Ce(III) ions as corrosion inhibitors. Surf. Coat. Technol. 2015;1:1–7
- [72] Bethencourt M., Botana F. J., Calvino J. J., Marcos M., Rodriguez-Chacon M. A.: Lanthanide compounds as environmentally-friendly corrosion inhibitors of aluminium alloys: a review. Corros. Sci. 1998;40:1803–1819

- [73] Matter E. A., Kozhukharov S., Machkova M., Kozhukharov V., Electrochemical studies on the corrosion inhibition of AA2024 aluminium alloy by rare earth ammonium nitrates in 3.5% NaCl solutions, Mater. Corrosion 2013;64: 408–414
- [74] Rodič P., Milošev I.: Corrosion inhibition of pure aluminium and alloys AA2024-T3 and AA7075-T6 by cerium(III) and cerium(IV) salts. J. Electrochem. Soc. 2016:163;C85–C93
- [75] Matter E. A., Kozhukharov S., Machkova M., Kozhukharov V., Comparison between the inhibition efficiencies of Ce(III) and Ce(IV) ammonium nitrates against corrosion of AA2024 aluminum alloy in solutions of low chloride concentration. Corros. Sci. 2012;62:22–33
- [76] Machkova M., Matter E. A., Kozhukharov S., Kozhukharov V.: Effect of the anionic part of various Ce(III) salts on the corrosion inhibition efficiency of AA2024 aluminium alloy. Corros. Sci. 2013;69;396–405
- [77] Coelho L. B., Mouanga M., Druart M.-E., Recloux I., Cossement D., Olivier M.-G.: A SVET study of the inhibitive effects of benzotriazole and cerium chloride solely and combined on an aluminium/copper galvanic coupling model, Corros. Sci. 2016;110: 143–156
- [78] Liu J., Wang D., Gao L., Zhang D., Synergism between cerium nitrate and sodium dodecylbenzenesulfonate on corrosion of AA5052 aluminium alloy in 3 wt.% NaCl solution. Appl. Surf. Sci. 2016;389:369–377
- [79] Liu X., Jianshu Y., Liu Y., Ji X., Lu Y., Yuan Y.: Synergism of rare earth Ce(III) ion with cysteine against corrosion of p110 carbon steel in 3% NaCl solutions. Surf. Rev. Lett. 2016. doi: 10.1142/S0218625X1750024X
- [80] Girčienė O., Gudavičiūtė L., Selskis A., Jasulaitienė V., Šakirzanovas S., Ramanauskas R.: The self-healing ability of cerium oxide films on carbon steel. Chemija 2015;26:175– 183
- [81] Ershov S., Druart M. E., Poelman M., Cossement D., Snyders R., Olivier M.-G.: Deposition of cerium oxide thin films by reactive magnetron sputtering for the development of corrosion protective coatings. Corros. Sci. 2013;75:158–168
- [82] Liu Y., Huang J., Claypool J. B., O'Keefe M. J.: Structure and corrosion behavior of sputter deposited Ce-Al-O coating on Al 2024-T3 alloy substrates. J. Electrochem. Soc. 2016;163:C198–C204
- [83] Jegdic B., Zivkovic L., Popic J., Bajat J., Miškovic-Stankovic V.: Electrochemical methods for corrosion testing of Ce-based coatings prepared on AA6060 alloy by the dip immersion method. J. Serb. Chem. Soc. 2013;78:997–1011
- [84] Ayuso J. A., Kozhukharov S., Machkova M., Kozhukharov V.: Electrodeposition of cerium conversion coatings for corrosion protection of D16 AM clad alloy. Bulg. Chem. Commun. 2013;45:33–40

- [85] Kozhukharov S., Ayuso J. A. P., Rodriguez D. S., Acuña O. F., Machkova M., Kozhukharov V.: Optimization of the basic parameters of cathodic deposition of Ceconversion coatings on D16 AM clad alloy. J. Chem. Technol. Metall. 2013;48:296–307.
- [86] Creus J., Brezault F., Rebere C., Gadouleau M.: Synthesis and characterisation of thin cerium oxide coatings elaborated by cathodic electrolytic deposition on steel substrate. Surf. Coat. Technol. 2006;200:4636–4645
- [87] Zivkovic Lj. S., Popic J. S., Jegdic B. V., Dohcevic-Mitrovuic Z., Bajat J. B., Miskovic-Stankovic V. B.: Corrosion study of ceria coatings on AA6060 aluminium alloy obtained by cathoduic electrodeposition: effect of deposition potential. Surf. Coat. Technol. 2014;240:327–335.
- [88] Dongre V. C.: Spontaneous Spray Deposition of Cerium Oxide Conversion Coatings on 7075-T6 Aluminum Alloy, Ed.: University of Missouri-Rolla, USA, 2004.
- [89] Rivera B. F., Johnson B. Y., O'Keefe M., Farenholz W. G.: Deposition and characterization of cerium oxide conversion coatings on aluminum alloy 7075-T6. Surf. Coat. Technol. 2004;176:349–356
- [90] Kozhukharov S., Acuña O. F., Machkova M. S., Kozhukharov V.: Influence of buffering on the spontaneous deposition of cerium conversion coatings for corrosion protection of AA2024-T3 aluminum alloy. J. Appl. Electrochem. 2014;44:1093–1105
- [91] Rodrìguez D. S., Kozhukharov S., Machkova M., Kozhukharov V.: Influence of the deposition conditions on the properties of D16 AM clad alloy, dip-coated in Cecontaining baths, Bulg. Chem. Commun. 2013;45:24–32
- [92] Lau D., Glenn A. M., Hughes A. E., Scholes F. H., Muster T. H., Hardin S. G.: Factors influencing the deposition of Ce-based conversion coatings, Part II: the role of localised reactions. Surf. Coat. Technol. 2009:203;2937–2945
- [93] Scholes F. H., Soste C., Huges A. E., Hardin S. G., Curtis P. R.: The role of hydrogen peroxide in the deposition of cerium-based conversion coatings. Appl. Surf. Sci. 2006;253:1770–1780
- [94] Palomino L. E. M., Aoki I. V., de Melo H. G.: Microstructural and electrochemical characterization of Ce conversion layers formed on Al alloy 2024-T3 covered with Curich smut. Electrochim. Acta 2006;51:5943–5953
- [95] Harvey T. G.: Cerium-based conversion coatings on aluminium alloys: a process review. Corros. Eng. Sci. Technol. 2013;48:248–269
- [96] Hughes A. E., Scholes F. H., Glenn A. M., Lau D., Muster T. H., Hardin S. G.: Factors influencing the deposition of Ce-based conversion coatings. Part I. The role of Al<sup>3+</sup> ions. Surf. Coat. Technol. 2009;203:2927–2936
- [97] Decroly A., Petitjean J. P.: Study of the deposition of cerium oxide by conversion on to aluminium alloys. Surf. Coat. Technol. 2005;**194**:1–9

- [98] Jiang X., Guo R., Jiang S.: Evaluation of self-healing ability of Ce–V conversion coating on AZ31 magnesium alloy. J. Magnes. Alloys 2016;4:230–241
- [99] van den Brand J., Sloof W. G., Terryn H., deWit J. H. W.: Correlation between hydroxyl fraction and O/Al atomic ratio as determined from XPS spectra of aluminium oxide layers. Surf. Interface Anal. 2004;36:81–88
- [100] Kozhukharov S. M., Machkova, Kozhukharov V.: Reproducibility of the corrosion parameters for aa2024-t3 aluminium alloy in chloride solution after different preliminary treatment procedures. J. Chem. Technol. Metall. 2015;50:52–64
- [101] Kozhukharov S., Milanes M., Girginov C., Machkova M.: Comparative evaluation of cerium oxide primers electrodeposited on AA2024-T3 and D16 AM aircraft alloys. Mater. Corros. 2016;67:710–720
- [102] Figueira R. B., Fontinha I. R., Silva C. J. R., Pereira E. V.: Hybrid sol-gel coatings: smart and green materials for corrosion mitigation. Coatings 2016;6: doi:10.3390/coatings6010012
- [103] Wang D., Bierwagen G.P., Sol-gel coatings on metals for corrosion protection. Prog. Org. Coat. 2009;64:327–338
- [104] Kozhukharov S.: Relationship between the conditions of preparation by the sol-gel route and the properties of the obtained products. J. Univ. Chem. Technol. Met. 2009;44:143– 150
- [105] Kozhukharov S., Tchaoushev S., Perspectives for development and industrial application of spray pyrolysis method" Ann. Proceed. Univ. Rousse, (Bulgaria) 2011;50:46–50
- [106] Kozhukharov, S. V.: High temperature methods for the synthesis and industrial production of nanomaterials. Nanofabrication using Nanomaterials, (eds. Jean E, Waqar A), One Central Press (OCP): Manchester (UK); 2016. ISBN (eBook): 978-1-910086-15-5
- [107] Kozhukharov S., Tchaoushev S., Spray pyrolysis equipment for various applications, J. Chem. Technol. Metall. 2013;48: 111–118
- [108] Acuautla M., Bernardini S., Pietri E., Bendahan M.: Nozzle-less ultrasonic spray deposition for flexible ammonia and ozone gas. Sens. Transducers 2016;201:59–64

## Edited by Jagannathan Thirumalai

The book Thin Film Processes - Artifacts on Surface Phenomena and Technological Facets presents topics on global advancements in theoretical and experimental facts, instrumentation and practical applications of thin-film material perspectives and its applications. The aspect of this book is associated with the thin-film physics, the methods of deposition, optimization parameters and its wide technological applications. This book is divided into three main sections: Thin Film Deposition Methods: A Synthesis Perspective; Optimization Parameters in the Thin Film Science and Application of Thin Films: A Synergistic Outlook. Collected chapters provide applicable knowledge for a wide range of readers: common men, students and researchers. It was constructed by experts in diverse fields of thin-film science and technology from over 15 research institutes across the globe.





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