

Editorial

Advanced Strategies in Thin Films Engineering by Magnetron Sputtering

Alberto Palmero ^{1,*}  and Nicolas Martin ^{2,*} 

¹ Instituto de Ciencia de Materiales de Sevilla (CSIC-Universidad de Sevilla), Americo Vespucio 49, 41092 Sevilla, Spain

² Institut FEMTO-ST, UMR 6174, CNRS, University Bourgogne Franche-comté, 15B, Avenue des Montboucons, 25030 Besançon, France

* Correspondence: alberto.palmero@csic.es (A.P.); nicolas.martin@femto-st.fr (N.M.)

Received: 27 March 2020; Accepted: 20 April 2020; Published: 23 April 2020



Abstract: This Special Issue contains a series of reviews and papers representing some recent results and some exciting perspectives focused on advanced strategies in thin films growth, thin films engineering by magnetron sputtering and related techniques. Innovative fundamental and applied research studies are then reported, emphasizing correlations between structuration process parameters, new ideas and approaches for thin films engineering and resulting properties of as-deposited coatings.

Keywords: magnetron sputtering; nanostructures; growth mechanism; functional properties; HiPIMS; oblique angle deposition

1. Introduction

Thin films are the workhorses of many of today's innovative technologies. Entire processes, from organic electronics to aerospace to packing industries, are strongly dependent on thin films. There are many cases where a given property of thin films gave rise to an entirely new field of technology. During these last decades, thin films engineering has been changed from a laboratory curiosity to become a multi-billion euros industry worldwide. New production technologies and advanced techniques are introduced every year to add new tools to the thin film toolbox [1–4]. One of the most exciting motivations is to generate innovative thin films and original nanostructured thin films. For this purpose, recent years have witnessed the flourishing of numerous novel strategies based on the magnetron sputtering technique, aimed at the advanced engineering of thin films, such as HiPIMS, combined vacuum processes, the implementation of complex precursor gases, or the inclusion of particle guns in the reactor, among others [5–8]. At the forefront of these approaches, investigations focused on nanostructured coatings appear today as one of the priorities in many scientific and technological communities: The science behind them appears in most of the cases as a "terra incognita", fascinating both the fundamentalist, who imagines new concepts, and the experimenter, who is able to create and study new films with, as of yet, unprecedented performances [9,10].

2. Thin Films Engineering: Where Do We Stand?

Scientific and technological challenges focused on thin films engineering, along with the existence of numerous scientific issues that have yet to be clarified in classical magnetron sputtering depositions (e.g., process control and stability, nanostructuration mechanisms, connection between film morphology and properties, or upscaling procedures from the laboratory to industrial scales) have motivated us to edit a specialized volume containing the state-of-the art that put together these innovative fundamental and applied research topics.

It is systematically observed that most of the scientific and technological developments are closely linked and often limited by the performance of materials and surfaces. As a result, this last decade has seen the development of original scientific fields related to the creation of intelligent materials, functional materials, biomaterials, etc. [11,12] Structured thin films, in particular, are thus moved from laboratory curiosity to objects of high added value. They are becoming a science in themselves and complete technologies may now depend on their properties and their integration [13–15]. Various fields, such as electronics, space vehicles, decorative, etc., are highly dependent on materials and their functionality. In many cases, the scientific observation of a characteristic of a material led to the creation of a new technology. New production systems and techniques are advanced and implemented each year to create new performances in the current rush to multifunctional surfaces and materials. As a result, it became a scientific requirement to provide new opportunities for the development of components and innovative structured materials.

At the forefront of many scientific strategies, investigations focused on the surfaces and structured materials appear today as one of the priorities of many laboratories. If some groups are devoting considerable efforts to the study of nano-scaled objects, or inversely, to systems of a few tens of micrometers, the components of intermediate sizes located between the nano- and micrometer remain a "gap" of knowledge to explore. This window size appears as a "terra incognita", fascinating both for the fundamentalist, who imagines new concepts, but also for the experimenter, who is able to create and study components with unprecedented performances. It is in this dimensional window spanning the nano- to micrometer that thin films engineering strategies become more than relevant and definitely provide an extra dimension in the current race to expand the range of thin film properties.

3. This Special Issue

This Special Issue, entitled "Advanced strategies in thin films engineering by magnetron sputtering", contains five reviews and six research articles covering fundamental investigations, as well as applied research studies devoted to nanostructuration and thin films engineering produced by magnetron sputtering and related deposition methods. Without going into detail, the individual work is briefed below:

The structure, stress state and phase composition of MeN/SiN_x (Me = Zr, Cr, Al) multilayered films are reviewed by Saladuhkin et al. [16] The stability of the coatings to oxidation is studied as a function of the thickness of sub-layers at the nanometric scale. The oxidation resistance of MeN/SiN_x multilayers is significantly improved compared to reference monolithic films, especially by increasing the fraction of SiN_x layer thickness. An optimized performance is obtained for CrN/SiN_x and AlN/SiN_x with nanometric periods, which remain stable up to 950 °C.

Liang et al. [17] report on the preparation of Mg nano-sculpted thin films by magnetron sputtering, implementing the glancing angle deposition technique. They demonstrate how the microstructure of the film can be tuned by adjusting deposition parameters such as the tilt angle or the sputtering pressure, which both largely influence the shadowing effect during the film deposition. They also model the growth of the material using kinetic Monte Carlo approaches, which prove the role of surface diffusion during the preparation of the film.

The paper "Gas Sensing with Nanoplasmonic Thin Films Composed of Nanoparticles (Au, Ag) dispersed in a CuO matrix" by Proença et al. presents original and interesting nano-plasmonic platforms capable of detecting the presence of gas molecules [18]. The authors show that the localized surface plasmon resonance phenomenon, LSPR, is produced by the morphological changes of the nanoparticles (size, shape, and distribution modified by thermal annealing of the films). Such an approach can be used to improve the sensitivity to the gas molecules, with the highest sensing performances for the bimetallic films.

Cougnon and Depla [19] develop thin film thermocouples as a potential way to embed sensors in composite systems, especially for their application in lightweight and smart structures. They experimentally investigate the influence of the discharge current and residual gas impurities on the

Seebeck coefficient for sputtered copper and constantan thin films. These deposition parameters both lead to changes in the ratio between the impurity flux to metal flux towards the growing film. Such a parameter is assumed to be a quantitative criterion for the background residual gas incorporation in the film, and acts as a grain refiner.

The angle-resolved composition evolution of Mo-B-C thin films deposited from a Mo₂BC compound target is experimentally and theoretically investigated by Achenbach et al. [20]. The authors use TRIDYN and SIMTRA to calculate the influence of the sputtering gas on the angular distribution function of the sputtered species from the target surface, transport through the gas phase, and film composition. They show that the mass ratio between sputtering gas and sputtered species defines the scattering angle within the collision cascades in the target, as well as for the collisions in the gas phase, which influences the angle- and pressure-dependent film compositions.

The electrical and structural properties of sputter-deposited p-Mg-In_xGa_{1-x}N/n-Si hetero-junction diodes and Al/SiO₂/p-GaN MOS Schottky diodes are studied by Tuan et al. [21,22] Electronic transport properties by means of Hall effect measurements are comprehensively performed. Holes concentration and mobility at room temperature are determined, as well as *I*-*V* and *C*-*V* measurements at different frequencies. Other characteristics for MOS diodes are performed and compared by Cheung's and Norde's methods.

Thao et al. [23] investigate Ge_{0.07}GaN films prepared by radio frequency reactive sputtering changing RF sputtering power and heating temperature conditions. Structure, optical and electrical characteristics of the films are significantly affected by both deposition parameters and with the best electronic transport properties and the lowest photoenergy produced for the deposited-150 W Ge_{0.07}GaN film.

The paper "Phase Selectivity in Cr and N Co-Doped TiO₂ Films by Modulated Sputter Growth and Post-Deposition Flash-Lamp-Annealing" by Gago et al. presents how the interface engineering strategy can vary the phase occurrence in Cr and N co-doped TiO₂ (TiO₂:Cr,N) sputter-deposited films [24]. A post-deposition flash-lamp-annealing (FLA) is also used to favor anatase phase, and to give rise to dopant activation and diffusion. The authors show that using interface engineering and millisecond-range-FLA allows tailoring the structure of TiO₂-based functional materials.

In order to investigate the lowering of the contact resistance in the NiSi/Si junction, Eadi et al. systematically change the RF power implemented for the sputter-deposition of Ni thin films [25]. A post-deposition rapid thermal annealing is applied for the nickel silicide fabrication and a circular transmission line model (CTLM) procedure is developed to obtain the contact resistance. They demonstrate that Ni film resistivity can be reduced for an optimized RF sputtering power and the formed NiSi phase shows a low contact resistance.

Achour et al. [26] report on VN thin films produced by DC reactive magnetron sputtering, followed by vacuum annealing. They apply different temperatures and study the effect on the electrochemical stability and surface chemistry of the films. They particularly focus on the oxide layer formed on the VN and prove that annealing of VN films makes them an attractive candidate for long-term use in electrochemical capacitors.

In summary, this Special Issue of Coatings gathers reviews and original articles illustrating the strong potential of thin films engineering for the creation of attractive and original functional coatings based on magnetron sputtering processes. This series of publications also demonstrate the fundamental role of thin films structuration at the micro- and nanoscale for understanding growth mechanisms and generating innovative behaviors of materials and surfaces.

Funding: This research received no external funding.

Acknowledgments: We would like to warmly thank all the authors, reviewers and editors for their valuable contribution in this Special Issue of Coatings.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gleiter, H. Nanostructured materials: Basic concepts and microstructure. *Acta Mater.* **2000**, *48*, 1–29. [\[CrossRef\]](#)
2. Lakhtakia, Y.; Messier, R. *Sculptured Thin Films*; SPIE Press: Bellingham, WA, USA, 2005. [\[CrossRef\]](#)
3. Fendler, J.H. Self-assembled nanostructured materials. *Chem. Mater.* **1996**, *8*, 1616–1624. [\[CrossRef\]](#)
4. Xi, J.Q.; Schubert, M.H.; Kim, J.K.; Schubert, E.F.; Chen, M.; Lin, S.Y.; Liu, W.; Smart, J.A. Optical thin-film materials with low refractive index for broadband elimination of Fresnel reflection. *Nat. Photonics* **2007**, *1*, 176–179. [\[CrossRef\]](#)
5. Schlom, D.G.; Chen, L.Q.; Pan, X.; Schmehl, A.; Zurbuchen, M.A. A thin film approach to engineering functionality into oxides. *J. Am. Ceram. Soc.* **2008**, *91*, 2429–2454. [\[CrossRef\]](#)
6. Bunker, B.B.; Rieke, P.C.; Tarasevich, B.J.; Campbell, A.A.; Fryxell, G.E.; Graff, G.L.; Song, L.; Liu, J.; Virden, J.W.; McVay, G.L. Ceramic thin-film formation on functionalized interfaces through biomimetic processing. *Science* **1994**, *264*, 48–55. [\[CrossRef\]](#)
7. Choy, K.L. Chemical vapour deposition of coatings. *Prog. Mater. Sci.* **2003**, *48*, 57–170. [\[CrossRef\]](#)
8. Hawkeye, M.M.; Brett, M.J. Glancing angle deposition: Fabrication, properties, and applications of micro- and nanostructured thin films. *J. Vac. Sci. Technol.* **2007**, *25*, 1317–1336. [\[CrossRef\]](#)
9. Valet, T.; Fert, A. Theory of the perpendicular magnetoresistance in magnetic multilayers. *Phys. Rev. B* **1993**, *48*, 7099–7113. [\[CrossRef\]](#)
10. Ohta, T.; Bostwick, A.A.; McChesney, J.L.; Seyller, T.; Horn, K.; Rotenberg, E. Interlayer interaction and electronic screening in multilayer graphene investigated with angle-resolved photoemission spectroscopy. *Phys. Rev. Lett.* **2007**, *98*, 206802–206804. [\[CrossRef\]](#)
11. Choi, K.; Park, S.H.; Song, Y.M.; Lee, Y.T.; Hwangbo, C.K.; Yang, H.; Lee, H.S. Nano-tailoring the surface structure for the monolithic high-performance antireflection polymer film. *Adv. Mater.* **2010**, *22*, 3713–3718. [\[CrossRef\]](#)
12. Spillman, W.B., Jr.; Sirkis, J.S.; Garnider, P.T. Smart materials and structures: What are they? *Smart Mater. Struct.* **1996**, *5*, 247–254. [\[CrossRef\]](#)
13. Arico, A.S.; Bruce, P.; Scrosati, B.; Tarascon, J.M.; van Schalkwijk, W. Nanostructured materials for advanced energy conversion and storage devices. *Nat. Mater.* **2005**, *4*, 366–377. [\[CrossRef\]](#)
14. Grier, D.G. A revolution in optical manipulation. *Nature* **2003**, *424*, 810–816. [\[CrossRef\]](#)
15. Brett, M.J.; Hawkeye, M.M. New materials at a glance. *Science* **2008**, *319*, 1192–1193. [\[CrossRef\]](#)
16. Saladuhkin, I.; Abadias, G.; Uglov, V.; Zlotski, S.; Janse van Vuuren, A.; Herman O’Connell, J. Structural properties and oxidation resistance of ZrN/SiN_x, CrN/SiN_x and AlN/SiN_x multilayered films deposited by magnetron sputtering technique. *Coatings* **2020**, *10*, 149. [\[CrossRef\]](#)
17. Liang, H.; Geng, X.; Li, W.; Panepinto, A.; Thiry, D.; Chen, M.; Snyders, R. Experimental and modeling study of the fabrication of Mg nano-sculptured films by magnetron sputtering combined with glancing angle deposition. *Coatings* **2019**, *9*, 361. [\[CrossRef\]](#)
18. Proença, M.; Rodrigues, M.S.; Borges, J.; Vaz, F. Gas sensing with nanoplasmonic thin films composed of nanoparticles (Au, Ag) dispersed in CuO matrix. *Coatings* **2019**, *9*, 337. [\[CrossRef\]](#)
19. Cougnon, F.; Depla, D. The Seebeck coefficients of sputter deposited metallic thin films: The role of process conditions. *Coatings* **2019**, *9*, 299. [\[CrossRef\]](#)
20. Achenbach, J.O.; Mraz, S.; Primetzhofer, D.; Schneider, J.M. Correlative experimental and theoretical investigation of the angle-resolved composition evolution of thin films sputtered from a compound Mo₂BC target. *Coatings* **2019**, *9*, 206. [\[CrossRef\]](#)
21. Tuan, T.T.A.; Kuo, D.H.; Cao, P.T.; Nguyen, V.S.; Pham, Q.P.; Nghi, V.K.; Tran, N.P.L. Electrical characterization of RF reactive sputtered p-Mg-In_xGa_{1-x}N/n-Si hetero-junction diodes without using buffer layer. *Coatings* **2019**, *9*, 699. [\[CrossRef\]](#)
22. Tuan, T.T.A.; Kuo, D.H.; Cao, P.T.; Pham, Q.P.; Nghi, V.K.; Tran, N.P.L. Electrical and structural properties of all-sputtered Al/SiO₂/p-GaN MOS Schottky diode. *Coatings* **2019**, *9*, 685. [\[CrossRef\]](#)
23. Thao, C.P.; Kuo, D.H.; Tuan, T.T.A.; Tuan, K.A.; Vu, N.H.; Na, T.T.V.S.; Nhut, K.V.; Sau, N.V. The effect of RF sputtering conditions on the physical characteristics of deposited GeGaN thin film. *Coatings* **2019**, *9*, 645. [\[CrossRef\]](#)

24. Gago, R.; Prucnal, S.; Hübner, R.; Munnik, F.; Esteban-Mendoza, D.; Jiménez, I.; Palomares, J. Phase selectivity in Cr and N co-doped TiO₂ films by modulated sputter growth and post-deposition flash-lamp-annealing. *Coatings* **2019**, *9*, 448. [[CrossRef](#)]
25. Eadi, S.B.; Song, H.S.; Song, H.D.; Oh, J.; Lee, H.D. Nickel film deposition with varying RF power for the reduction of contact resistance in NiSi. *Coatings* **2019**, *9*, 349. [[CrossRef](#)]
26. Achour, A.; Islam, M.; Ahmad, I.; Saeed, K.; Solaymani, S. Electrochemical stability enhancement in reactive magnetron sputtered VN films upon annealing treatment. *Coatings* **2019**, *9*, 72. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).