RSD 2022

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About

The RSD conference

The International Conference on Reactive Sputter Deposition was established in Ghent in the year 2000. It provides a platform among leading international scientists, engineers and students to discuss recent achievements in reactive sputter deposition and thin films. The Conference has developed to an annual tradition, steadily growing without loosing its focus on reactive sputtering and its fundamental aspects. The symposium covers the production and use of coatings, from basic research to devices and new applications.

DRAFT

RSD2022 is organized by the research group DRAFT. Our mission statement of the research group DRAFT (Dedicated Research on Advanced Films and Targets) reads "At DRAFT we want to become the recognized leader in the understanding of thin film growth by reactive magnetron sputtering and to enjoy research by experiments and simulations." More information on this research group can be found on `www.draft.ugent.be`

Timetable

CT: Contributed Talk, IT: Invited Talk.

Wednesday, December 7th

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14:40–14:55	CT	**V. Popok** Aalborg University, Denmark	Optimizing the growth of thin AlN films by reactive DC magnetron sputtering
14:55–15:10	CT	**L. Kölbl** Montanuniversität Leoben, Austria	Influence of substrate temperature on formation of silver niobate during reactive d.c. magnetron sputtering
15:10–15:25	CT	**G. F. Regodón** Institute of Materials Science of Seville, Spain	Magnetron sputtering deposition on piezoelectric substrates subjected to electroacoustic excitation
15:25–15:40	CT	**R. Oliveira** Instituto Tecnológico de Aeronáutica, Brazil	Properties of gallium nitride thin films deposited by reactive magnetron sputtering onto Si and glass substrates kept at different temperatures
15:40–15:55	**Break: Bring your own coffee**		
15:55–16:10	CT	**J.C. Sagás** Universidade do Estado de Santa Catarina, Brazil	Grid-assisted magnetron sputtering: a versatile tool for reactive sputter deposition
16:10–16:25	CT	**J. Van Bever** Ghent University, Belgium	History Dependence of Feedback Control and Double hysteresis during reactive magnetron sputtering
16:25–16:40	CT	**N. Mahne** Jožef Stefan Institute, Slovenia Slovakia	Sputtering yields for a range of target materials calculated by SRIM simulations
16:40–16:55	CT	**N.F. Azevedo-Neto** São Paulo State University, Brazil	Effect of oxygen pressure on the structure and optical properties of cobalt oxide films prepared by dc magnetron sputtering
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CT: Contributed Talk, IT: Invited Talk.

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14:55–15:10	CT	**M. Fahland** Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology, Germany	Roll-to-roll deposition of thermochromic coatings on flexible glass
15:10–15:25	CT	**A. W. Oniszczuk** TRUMPF Huettinger, Poland	Study of $Ar/N_2/CH_4$ plasma composition in mixed HIPIMS/DCMS discharge and its effect on TiAlCN/VCN films
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16:10–16:25	CT	**A.L. Thomann** GREMI, UMR7344 CNRS/Université d'Orléans, France	Sputter deposition in He gas: gas/solid nano-composite or highly porous films synthesis
16:25–16:40	CT	**C. Poltronieri** Université Sorbonne Paris Nord, France	Synthesis, structural and mechanical characterization of ZnZr and ZnMg thin films
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CT: Contributed Talk, IT: Invited Talk.

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11:10–11:25	CT	**A. Wójcicka** Inst. of Microelectronics and Photonics, Poland	Complex studies of room temperature magnetron sputtering growth of ZnO:Al thin films
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List of Abstracts – Talks

December 7th

A kinetic model of residual stress in thin films: effect of processing conditions and microstructural evolution

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IS

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Stress in thin films is a critical issue that affects the performance and reliability of coatings. Multiple parameters have been shown to affect the stress evolution, including the growth rate, temperature, grain size and gas pressure. In addition, the deposition method (e.g., evaporation, electrodeposition, sputtering) is known to have an influence. To obtain a unified picture of the processes controlling stress, we have developed a kinetic model that includes the role of the deposition parameters and the microstructural evolution. The model is based on physical mechanisms for stress generation related to film growth kinetics, grain growth and energetic particle bombardment. Examples will be shown of applying the model to evaporated and sputter-deposited transition metals and sputtered metal nitrides. Trends in the fitting parameters for different materials are shown to be consistent with the results expected from the physical mechanisms in the model.

Optimizing the growth of thin AlN films by reactive DC magnetron sputtering

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With a wide bandgap of 6.2 eV, high thermal conductivity and excellent piezoelectric properties, AlN is an attractive material for the fabrication of many types of devices [1]. Applications include micro- and nano-electromechanical systems, surface acoustic wave devices and energy harvesting devices. AlN is also crucial as a buffer for achieving high quality GaN and AlGaN which are used in the power electronic industry for high electron mobility transistors [2].

In this study the growth process of high-quality AlN is optimized, prioritizing the industrial requirements, where high deposition rates, low residual stress and uniform substrate coverage are crucial. AlN thin films are deposited on 100 mm Si(111) substrates by reactive DC magnetron sputtering carried out using the Flextura system designed by Polyteknik AS [3].

The sputtering conditions during film growth greatly influence the structure of the resulting film, and thus, knowledge of the influence of different sputtering parameters is necessary for achieving the desired film properties. To investigate this, a number of AlN thin films have been produced under different sputtering conditions, where processing pressure, substrate temperature, magnetron power and ratio of supplied Ar/N gas have been systematically varied. The resulting films have been examined using a wide range of characterization methods including atomic force microscopy, scanning electron microscopy, ellipsometry, profilometry, and x-ray diffraction. This has allowed for a detailed analysis on the role of individual sputtering parameters affecting surface topography, film thickness, residual film stress and crystalline quality of the AlN films. The grown AlN films were found to exhibit a columnar structure with a highly c-axis oriented crystallinity. High crystalline quality and low surface roughness was achieved by keeping a low processing pressure, high N/Ar ratio and a substrate temperature above 450 °C.

References

[1] J.Y. Tsao et al., Ultrawide-bandgap semiconductors: Research opportunities and challenges, Adv. Electron. Mat. 4 (2018) 1600501

[2] H. Amano et al., The 2018 GaN power electronics roadmap, J. Phys. D Appl. Phys. 51 (2018) 163001

[3] M.K. Sandager, C. Kjelde, V. Popok, Growth of Thin AlN Films on Si wafers by Reactive Magnetron Sputtering: Role of Processing Pressure, Magntron Power and Nitrogen/Argon Flow Ratio, Crystals 12 (2022) 1279

Influence of substrate temperature on formation of silver niobate during reactive d.c. magnetron sputtering

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CT

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Due to its high energy storage density at room temperature, silver niobate ($AgNbO_3$) is one of the most promising lead-free dielectric perovskites for energy storage applications. In this work, $AgNbO_3$ thin films were deposited on Si(100) substrates at different substrate temperatures by direct current reactive magnetron co-sputtering from Nb and Ag targets in Ar-O_2 atmosphere. X-ray diffraction indicated the formation of crystalline silver oxide (Ag_2O) and metallic silver at substrate temperatures up to 500°C, whereas at 550°C the $AgNbO_3$ phase was formed. With further increasing substrate temperature, $AgNbO_3$ becomes the predominant phase, while fractions of metallic silver are still clearly observable. Raman spectroscopy confirmed the existence of the $AgNbO_3$ phase, while characteristic Raman bands for silver oxide could not be verified. In films deposited at substrate temperatures below 500°C, the $AgNbO_3$ phase was formed after annealing in ambient air at temperatures above 525°C. Microstructural inhomogeneities in the form of metallic silver are detectable in all samples using scanning electron microscopy. In conclusion, this study reports for the first time on the synthesis of lead-free crystalline perovskite thin films based on $AgNbO_3$ by reactive d.c. magnetron sputter deposition, opening paths for future process scalability.

Magnetron sputtering deposition on piezoelectric substrates subjected to electroacoustic excitation

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In this presentation we show a novel and potentially disruptive technology to control the thin film nanostructuring and patterning by magnetron sputtering techniques on acoustically-excited piezoelectric substrates. Despite the extensive research during the last decades in magnetron sputtering deposition, very little attention has been paid to the control of thin film deposition over a substrate in which an electroacoustic wave is excited. The electric field of the electroacoustic wave interacts with the plasma modifying the plasma volume closer to the substrate, while the acoustic part of the electroacoustic wave may affect nucleation and growth processes. The dual electrical-acoustic nature of this electroacoustic wave highlights the complexity that arises in this kind of thin film deposition. In order to shed light into this novel technique, a series of experiments were performed, and the thin films deposited were characterized. Titanium oxide and silicon oxide thin films were deposited on a lithium niobate piezoelectric substrate under electroacoustic excitation in the MHz range [1, 2].

Piezoelectric materials are characterized by the coupling between the polarization vector and the mechanical deformation. In the direct piezoelectric effect, an electric field appears in the material when a mechanical deformation is applied, while in the reverse piezoelectric effect, a mechanical deformation is forced when an external electric field is applied. In our experiments, electrical excitation is applied to the $LiNbO_3$ substrate to create an electroacoustic standing wave with a wavelength below the millimeters scale [1,2]. Patterning has been observed in the same spatial scale in experiments of magnetron sputtering deposition of TiO_2 and SiO_x which suggests that the deposition has been strongly modified by the presence of the electroacoustic wave [1,2].

The present work is aimed to establish a set of concepts that allows the control of the phenomenon. In this work we develop a fundamental study of the plasma-piezoelectric substrate interaction to account for the patterning that is produced in the experiments. The electroacoustic wave produces a heterogeneous polarization of the substrate that focuses the plasma ion bombardment on the regions that are more negatively charged. Monte Carlo simulations were performed to study the trajectories of the ions that enter the plasma sheath. The plasma ion bombardment is intensified in some regions of the substrate leaving others free from ion bombardment, explaining the differences observed between the different domains of the pattern in the experiments. This work lets us establish a road map to enhance the control of thin film nanostructures using this novel technique.

References

[1] A. García-Valenzuela et al. Patterning and control of the nanostructure in plasma thin films with acoustic waves: mechanical vs. electrical polarization effects Mater. Horiz., 2021, 8, 515

[2] V. Rico et al. When Plasmas and Piezoelectric Acoustic Waves come Together to Pattern the Nanostructure and Chemistry of thin films Submitted

Properties of gallium nitride thin films deposited by reactive magnetron sputtering onto Si and glass substrates kept at different temperatures

R.S. Oliveira*, *I.M. Horta*, *B.S. Damasceno*, *J.H.C. Augstroze*, *W. Miyakawa*, *A.S.S. Sobrinho*, *D.M.G. Leite

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Gallium nitride (GaN) thin films have become the target of state-of-the-art applications in optoelectronic devices, with frequent advances in their growth techniques [1,2]. This study evaluates the effect of substrate temperature and materials (Si and glass) onto the morphological, structural, and optical properties of GaN thin films deposited by reactive magnetron sputtering. The films were grown in an Ar + N_2 plasma atmosphere, at 3 mTorr and 60 W RF power applied to the Ga liquid target. In order to reduce the target poisoning effect, the nitrogen gas inlet was directed to the substrate holder while the argon is inserted through an injection ring around the gallium target. This separated gas inlet system also helped to reach such low working pressure (3 mTorr) even using a N_2 rich plasma as discussed elsewhere [3]. The substrates were kept facing the target surface 90 mm distance far, being heated by IR lamps up to 250, 400 and 550 °C in different experiments. The characteristics of the films were then analyzed by X-ray diffraction (XRD), Raman spectroscopy, UV-Vis spectrophotometry and atomic force microscopy (AFM). The results showed a tendency to obtain films with higher crystalline quality and c-axis texture, as well as more irregular surface topographies with increasing substrate temperature. All the results are discussed in terms of the balance between thermal and non-thermal energies involved in the growth of GaN by the reactive sputtering technique.

References

[1] H. Jia, L. Guo, W. Wang, and H. Chen, Adv. Mater., vol. 21, pp. 4641-4646, (2009).
[2] Y. Chen et. al., Mater. Sci. Eng. R Reports, vol. 138, pp. 60-84, (2019).
[3] R.S. Oliveira et al. Materials Research, v. 25, p. 9, (2022).

Grid-assisted magnetron sputtering: a versatile tool for reactive sputter deposition

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The grid-assisted magnetron sputtering (GAMS) was developed at the end of the 1990s by Fontana and Muzart [1,2] to eliminate the hysteresis in reactive sputter deposition. At the time, the system was called triode magnetron sputtering, once it has a third electrode (grid) between the target and the substrate. Besides the elimination of hysteresis for TiN deposition, the authors also showed an increase in plasma confinement when the grid is grounded or positively biased, i.e. when is the main anode.
Further studies, including simulations with the Berg model [3] and the RSD software (figure 1a), show that the reduction (and eventual elimination) of hysteresis is due to a decrease in the effective gettering area, which shifts the first critical point to lower reactive gas flow rates. On the other hand, the bias and position of the grid can tune the plasma potential distribution [4], affecting particle and energy flux (figure 1b) to the growing film and the substrate floating potential [5]. Other geometries like ring anodes can be used, avoiding the reduction in deposition rate with the grid [5]. The higher plasma confinement and lower energy flux make GAMS a suitable tool for deposition onto thermally sensitive substrate [6].

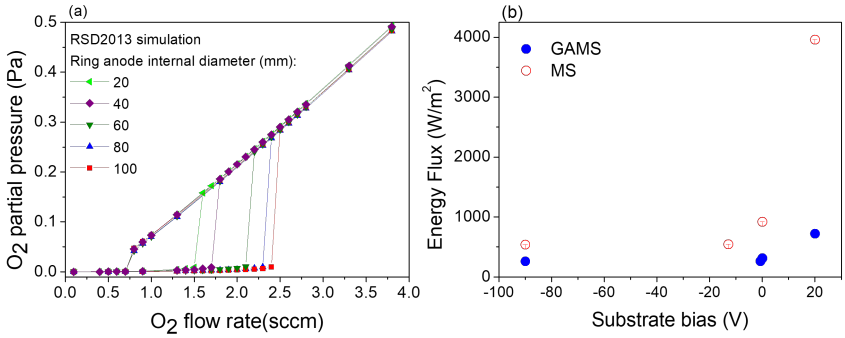

Figure 1: Simulated hysteresis curves during Al_2O_3 deposition using ring anodes (a). Energy flux to the substrate as a function of bias voltage for magnetron sputtering (MS) and grid-assisted magnetron sputtering (GAMS) (b).

In this presentation, we will discuss the main features of grid-assisted magnetron sputtering.

References

[1] L.C. Fontana, J.L.R. Muzart, Characteristics of triode magnetron sputtering: The morphology of deposited titanium films, Surf. Coatings Technol. 107 (1998) 24.

[2] L.C. Fontana, J.L.R. Muzart, Triode magnetron sputtering TiN film deposition, Surf. Coatings Technol. 114 (1999) 7.

[3] J.C. Sagás et al., Modeling reactive sputter deposition of titanium nitride in a triode magnetron sputtering system, Surf. Coatings Technol. 206 (2011) 1765.

[4] J.C. Sagás, R.S. Pessoa, H.S. Maciel, Langmuir Probe Measurements in a Grid-Assisted Magnetron Sputtering System, Brazilian J. Phys. 48 (2018) 61.

[5] K.A. Petroski, J.C. Sagás, Alternative anode geometry for magnetron sputtering, Vacuum. 182 (2020) 109703.

[6] D.A. Duarte et al., Control of the substrate temperature using a triode magnetron sputtering system, EPJ Appl. Phys. 52 (2010) 31001.

History Dependence of Feedback Control and Double hysteresis During Reactive Magnetron Sputtering

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Feedback process control [1] of reactive sputtering is often required to achieve specific thin film properties. Although conceptually simple, it is far from trivial to make it reliable and reproducible. Two major problems can be identified.

First, depending on the initial state of the process two S-shaped process curves can be obtained under certain conditions [1]. Many suggestions have been made for the observation of this “double hysteresis phenomenon" such as target erosion, chamber heating, or anode effects. But even when these effects are excluded, the phenomenon can still be observed [2]. Hence it seems to be of a fundamental nature. Independently of the experimental observations, the simulation of the processes at the cathode facing the gas discharge led to the prediction of a double hysteresis [3].

Secondly, the convergence of the feedback process strongly depends on the history of the target processes. A better understanding of the transient states therefore also assists to improve this convergence.

In the first part of the presentation we present high-throughput simulations for double hysteresis behavior as a function of different process and material parameters [4, 5]. New measures are introduced that characterize the hysteresis with a single number and that vary in a continuous way as a function of these parameters. This allows us to elucidate the nature of the double valued state during feedback control and to explain for which materials and under which conditions this behavior is expected to occur (Figure 1) [4].

In the second part we discuss the application of this analysis to feedback measurements of aluminum. A correct preparation of the sputter system is required to obtain a well defined and converged feedback process. A first direct proof of double hysteresis during feedback control is delivered.

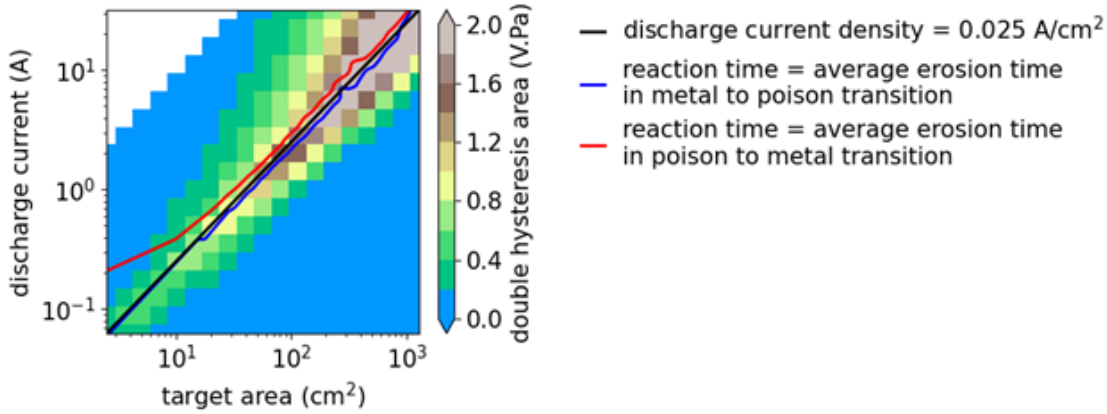

Figure 2: The difference between the two paths in feedback control is maximized at a certain constant discharge current density. This trend can be linked with the relation between the reaction and erosion of implanted oxygen ions. Data is taken from reference [4].

References

[1] W.D. Sproul et al. , Control of reactive sputtering processes, Thin Solid Films 491 (2005) 1

[2] R. Schelfhout et al., The existence of a double S-shaped process curve during reactive magnetron sputtering, Applied Physics Letters 109 (2016) 11605

[3] K. Strijckmans et al. ,Tutorial: Hysteresis during the reactive magnetron sputtering process, Journal of Applied Physics, 124 (2018) 241101

[4] J. Van Bever et al., A computational study of the double hysteresis phenomenon during reactive sputtering, Journal of Physics D: Applied Physics, 55 (2022) 355302

[5] J. Van Bever et al., Influence of chemisorption on the double hysteresis phenomenon during reactive sputtering, Applied Surface Science, accepted (2022).

Sputtering yields for a range of target materials calculated by SRIM simulations

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Sputtering yield is defined as the number of sputtered atoms per impinging ion. It depends on many parameters such as the energy, mass, and impact angle of the incident ions and also on the properties of the target material. Accurate sputtering yields are required for process control in thin film deposition, modeling of discharges, and in techniques where ion etching plays a central role. In this work, we used the SRIM (Stopping and Range of Ions in Matter) simulation software to calculate the total and differential sputtering yields. Sputtering yields were explored for perpendicular and non-perpendicular ion incidence in the 200-1200 eV energy range. We studied commonly sputtered target materials, including transition metals in groups 4-6 (Ti, V, Cr; Zr, Nb, Mo; Hf, Ta, and W) and group 11 (Cu, Ag, and Au), and selected lighter elements (B, C; Al, Si). SRIM program has several free input parameters. One of them is the surface binding energy whose experimental values are not well established. SRIM program, therefore, uses the heat of sublimation as an approximate estimation for this parameter. We modified the surface binding energy to obtain the best agreement between the simulated and experimental sputtering yield data for the studied energy range. The influence of the target atom mass, surface binding energy, mass and energy of incident ions on simulated sputtering yield will be presented. A relatively good correlation was observed between the simulated values and Sigmund's expression for the total sputtering yield using modified surface binding energy. When comparing the dependence of the target-to-ion mass ratio, a reasonable trend was also observed. Simulated and experimental total sputtering yields show a parabolic dependence on the ion energy. Therefore, we fitted a power factor to the ratio of the ion energy and the modified surface binding energy. A linear correlation between the power fitting coefficient and the atomic number was found for the transition metals. SRIM simulation results show that the angular distribution of sputtered transition metals is cosine. However, for the lighter elements (B, C, and Al) we observed a highly directional sputtering in the region near the surface normal. Such sputtering is highly unrealistic since there is no experimental evidence or physical reason for atoms to be predominantly directed towards the surface normal. For this reason, we presume that the spatial distribution for the light elements is not simulated correctly by SRIM software.

Effect of oxygen pressure on the structure and optical properties of cobalt oxide films prepared by dc magnetron sputtering

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The aim of this study was to tailor the deposition parameters of magnetron sputtering to synthesize cobalt oxide (Co_xO_y) films onto fused silica (a-SiO_2) substrates. The structural, optical properties and computer simulations were assessed. The impact of oxygen pressure on plasma reactivity was investigated. Co_xO_y films with estimated thickness of 260-570 nm and different phases (Co_3O_4 and CoO) were produced depending on the various oxygen flow rates. X-ray diffraction analysis revealed that low oxygen flow ($<$2.0 sccm) favors the formation of the CoO phase while higher oxygen flows ($>$2.5 sccm) favor the spinel Co_3O_4 phase formation. Effects of strain related to the partial pressure were also observed and discussed. Optical transmission spectra showed electronic transitions between the Co^{2+} and Co^{3+} cations in Co_3O_4 spinel structure for films deposited with higher oxygen flow and an attenuation of these transitions at low oxygen flow. Cobalt optical emission (CoI=340.5 nm) from the plasma showed an abrupt decrease at 2.5 sccm while the line oxygen emission (OI=777.3 nm) showed an expressive increase[1]. Computer simulations of the reactive sputtering supported the analysis of the film characterization and its correlation to the oxygen partial pressure.

References

[1] N.F. Azevedo Neto, C. Stegemann, L.J. Affonço, D.M.G. Leite and J.H.D. da Silva, *Role of oxygen flow rate on the structure and stoichiometry of cobalt oxide films deposited by reactive sputtering*, J. Vac. Sci. Technol. A 40 (2022) 013405. 10.1116/6.0001418

December 8th

Large area reactive magnetron sputtering using rotatable targets

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Sputter deposition with rotatable targets is industrial standard for large- area high-productivity coating. However, there is only very little research on rotatable targets compared to planar magnetron sputtering. Some important differences to planar magnetron sputtering are the material reservoir and material utilization one the one hand (economic aspects) but also emission characteristics of particles, the redeposition on the target, and the dynamic sputter erosion due to the rotating target tube on the other hand (process aspects). The latter properties are very important for reactive sputtering of such a rotating tube target.

The contribution will shortly address the history of magnetron development at VON ARDENNE leading from small planar sputter sources to large-size rotatable magnetron lids. Then the talk gives an overview on important aspects of the difference between planar and rotatable target sputtering in general and will give some examples which magnetron types are available for industrial large area sputter deposition. The importance of the tube rotation in reactive magnetron sputtering will be addressed and the consequences will be shown, and which actions can be taken to optimize the deposited film. Examples for the reactive sputtering with rotatable targets of several materials will be given.

HIPIMS reactive magnetron sputtering in resistive random-access memory application

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Reactive magnetron sputtering using HIPIMS discharge was used to fabricate metal oxide thin films. Such metal oxides, like zirconium oxide (ZrO_x), titanium oxide (TiO_x), hafnium oxide (HfO_x) or aluminum oxide (AlO_x) play important functions in various structures for novel electronic and photonic devices. The ultimate goal of this work is the examination of mutual dependences between the input parameters of the fabrication process (technological parameters) and the output parameters (properties of the obtained materials) to get ultrathin layers for the application of the MIM (Metal-Insulator-Metal) structures. Those structures are the basis of resistive random-access memory (RRAM) devices.

In the first part of this work, the optical properties of layer deposited by HIPIMS will be examined and compared to the layers deposited using a typical pulsed-DC processes. Several oxide materials will be characterized in terms of thickness, refractive indices, transmittance, and reflectance in the UV-VIS range. The resistive switching properties of the MIM structures with the employed oxide materials depend on the presence of oxygen vacancies in the layer bulk. In order to monitor the stoichiometry of the oxide layers, MIS (Metal-Insulator-Semiconductor) structures will be fabricated. The analysis of the obtained electrical characteristics will be performed. In the last part of this work, selected processes will be used to fabricate MIM devices. The results of the electrical characterization of the fabricated test structures will be described indicating concluding remarks on the feasibility of applying the studied structures in RRAM devices.

Roll-to-roll deposition of thermochromic coatings on flexible glass

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Vanadium oxide is the best investigated solid state thermochromic material. It undergoes a phase transition between a low temperature semiconducting and a high temperature metal state. This is accompanied by a sharp change in the electrical conductivity as well as in the reflectivity for infrared radiation. This makes the material interesting for intelligent windows. However, it is very challenging to deposit this material in the correct structure on a large area with sufficient reliability. The authors present results achieved in a roll-to-roll deposition process of vanadium oxide on flexible glass of 0.1 mm thickness. The thermochromic material was embedded in zirconium oxide top and bottom layers which served as an antireflection layer and a crystalline template, respectively. A reactive high power impulse magnetron sputtering (HIPIMS) process was implemented. It was applied to a metallic rotatable vanadium target of 650 mm length. A closed loop control stabilized the oxygen partial pressure during the sputtering process. The tungsten doping (1.2 at%) of the target resulted in reduction in the phase transition temperature of the deposited layers from 68°C for pure vanadium oxide to a temperature below 30°C. This is well suited for intelligent glazing solutions. The exact control of the sputtering process is essential for achieving the correct crystalline structure of the layer. The authors present results which reveal that the necessary oxygen partial pressure depends on the peak power realized in the HIPIMS sputtering process. The samples were characterized by X-ray diffraction measurements as well as by optical measurements in the UV-VIS-NIR spectral region.

Study of $Ar/N_2/CH_4$ plasma composition in mixed HIPIMS/DCMS discharge and its effect on TiAlCN/VCN films

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The effect of the working pressure of a reactive gas mixture of N2 and CH4 on the plasma chemistry in a mixed HIPIMS/DCMS discharge was studied. At a constant Ar flow of 200 sccm, the flow of a reactive gas mixture of N2+CH4 with a ratio of 2:1 was increased from 0 to 175 sccm resulting in a pressure increase from 0.25 to 0.28 Pa. Selected masses of metal and radical ions were measured using quadrupole mass spectrometry. It is shown that the plasma composition is initially dominated by the metal ions sputtered from targets (V^+, Ti^+, and Al^+). as reactive gases are added, initially metal and Ar ion density drops and N_2^+, N+ and CH_4^+ ions are detected. With further pressure increase, two stages of rapid change in plasma chemistry are observed, the first of which is related to the decomposition of the primary gases, and the second to formation of new radicals such as $C_3H_4^+$, HCN^+, $C_2H_2^+$, NH_3^+. At pressure above 0.272 Pa the plasma is dominated by NH_3^+ ions.

TiAlCN/VCN films were deposited at five different reactive gas flows selected using optical emission signal of V^* (V I). Resulting chemical makeup, phase composition, structure, physical and mechanical characteristics were analyzed. Semi-quantitative EDX analysis of the coatings showed a linear increase in nitrogen content with reactive gas flow. In contrast, no correlation between reactive gas flow and carbon content in the coatings was confirmed. Raman analyses indicated that the intensity ratio of carbon D/G peaks increased continuously with the increase of reactive gas flow. Furthermore, higher reactive gas flows increased the hardness of the coating up to 4.8 times. The structural characteristics show that for low reactive gas flows the microstructure is dense, with a glossy amorphous morphology with a metal-rich phase. As the reactive gas flow increases, the coating converts to a NaCl-type cubic crystalline phase with a dense microstructure and randomly oriented grains. Highest reactive gas flow leads to large diameter well defined columns.

Ag particle size distribution in amorphous carbon coating produced by magnetron sputtering

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The antimicrobial and aging properties of Ag-, Ag/Cu- and Ag cluster-doped amorphous carbon coatings produced by magnetron sputtering, have been studied for space applications [1]. Inside a spacecraft, the temperature and humidity, suitable for the human crew onboard, also creates an ideal breeding environment for the proliferation of bacteria and fungi; this can present a hazard to human health, and create issues for the safe running of equipment. To address this issue, wear-resistant antimicrobial thin films prepared by magnetron sputtering were developed, with the aim to coat key internal components within spacecrafts. Antibacterial tests, performed under both terrestrial gravity and microgravity conditions, have shown that although silver doped coatings possess extremely high levels of antimicrobial activity, silver cluster doped coatings are equally effective, whilst being more long-lived, despite containing a lower absolute silver concentration. It has been found that the longevity of these antimicrobial coatings is heavily influenced by metal diffusion within the coating. A higher diffusion rate tends to lead to a short lifetime. It seems there is a close link between the diffusion rate and the metal particle size in the matrix of carbon coating. In this short presentation, I'm going to report the influence of Ag concentration on Ag particle size distribution in the amorphous carbon coatings, prepared by conventional co-sputtering technique. To better control the particle size distribution, a magnetron-sputtering cluster-source was integrated into the main PVD system, so that Ag clusters can be preformed in a separate vacuum chamber then transported and embedded into carbon matrix. The particle size distribution of Ag clusters produced in this way was also measured and will be reported.

References

[1] G. Sanzone et al.,*Antimicrobial and aging properties of Ag-, Ag/Cu- and Ag cluster-doped amorphous carbon coatings produced by magnetron sputtering for space applications*, ACS Appl. Mater. Interfaces 14 (2022) 10154-10166 10.1021/acsami.2c00263

Magnetron sputtering onto liquids: the effect of liquid viscosity on the formation of nanoparticles and thin films

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Low-pressure plasma-based magnetron Sputtering onto Liquids (SoL) that withstand vacuum conditions is an efficient way to synthesize nanoparticles (NPs) and thin films (see review paper [1] and references therein). Despite the SoL process has been studied since 1996 there is still no clear answer what does provoke the film formation on the liquid surface.

To unravel the mechanism of NP and film growth we have performed magnetron sputtering onto a line of liquids having similar surface tension but different viscosities and while keeping all sputtering conditions identical. Most of SoL experiments have been done for a gold target sputtered onto a line of polymerized rapeseed oils (surface tension: 32.6-33.1 $mJ \cdot m^{-2}$ at RT) [2]. Well-dispersed individual Au NPs were formed into low viscosity oils (below 630 cP at 25 °C) while a thin gold films grew onto a surface of high viscosity oils (more than 1000 cP at 25 °C). According to transmission electron microscopy and small-angle X-ray scattering the mean diameter of Au NPs slightly increases with liquid viscosity and stays in range of 2.1-2.8 nm. The grain size in gold thin films is equal to (10±1) nm at 1000 cP and (11±1) nm at 1400 cP which is close to the values obtained for thin films deposited onto solid substrates.

The film formation has been also observed during sputtering of silver, titanium and titanium nitride targets onto high viscosity silicone and polymerized rapeseed oils. The mechanism of the film growth onto the oil surfaces has been discussed from the perspective of NP diffusion rate that is affected by the temperature gradient presenting in the solution due to the heating of liquid by sputtering plasma [3].

Authors thank the FNRS for the financial support through the “SOLUTIoN” project No T.0134.19.

References

[1] A. Sergievskaya, A. Chauvin, and S. Konstantinidis, Sputtering onto liquids: a critical review, Beilstein J. Nanotechnol. 13 (2022) 10

[2] A. Sergievskaya, R. Absil, A. Chauvin, K. V. Yusenko, J. Veselý, T. Godfroid, S. Konstantinidis,Sputtering onto liquids: how does the liquid viscosity affect the formation of nanoparticles and metal films? Phys. Chem. Chem. Phys. (2022) doi:10.1039/D2CP03038A

[3] K. Patel, A. Sergievskaya, A. Chauhan, S. Konstantinidis, Heating of liquid substrate by low-pressure sputtering plasma, J. Appl. Phys.131 (2022) 203301

Sputter deposition in He gas: gas/solid nano-composite or highly porous films synthesis

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Interaction of He ions or helium plasmas with materials has been widely studied, especially in the frame of nuclear fusion. It has been proved that due to its low solubility and high mobility in metals, He is able to diffuse on a long pathway, inducing the formation of vacancies where it can accumulate [1]. This finally may lead to the formation of He filled high pressure nanosized bubbles, which presence inside the material drastically modify the properties. When helium is incorporated at the very near surface, it has been shown that rupture of the metal lattice can occur which induce processes like flaking or the development of a so-called porous fuzz structure [2].

The objective of the present work is to study the deposition of thin films by DC magnetron sputtering in Ar/He atmospheres (or pure He) in order to benefit from this particular behavior of helium in materials. In that aim we coupled simulation of the sputtering, transport and growth processes (using SRIM, home-made software and molecular dynamics) with thin film characterization. Film micro- and nano-structure was analyzed by scanning and transmission electron microscopy. X-ray diffraction was employed to study the crystalline quality. Helium content was measured by proton elastic backscattering spectroscopy. In an attempt to qualify the nature of the vacancy defects, positron annihilation spectroscopy was conducted.

We investigated the sputtering of Si, Al and Zr in helium containing atmospheres [3,4]. We evidenced that, depending on the He proportion in the gas phase and on the element, films of different nature can be elaborated. For instance, in case of Si and Zr, gas/solid nanocomposite films where He is trapped in pores dispersed over the entire thickness [3] are obtained, whereas highly porous nanostructured films are synthesized with Al. All these films exhibit completely different properties than that usually deposited in Ar gas. Thus, playing with the plasma gas, may be a way to broaden the film properties accessible by the magnetron sputtering technique.

We investigated how adding He in the gas phase induces the change of the plasma regime which affects the sputtering of the atoms at the target, but also their transport to the substrate and, consequently, the energy distribution functions of the particles impacting the growing film. Our results allow to give some insight into the mechanisms and species responsible for the formation of such different films [4].

References

[1] L. Pentecoste, P. Brault, A.-L. Thomann, P. Desgardin, T. Lecas, T. Belhabib, M.-F. Barthe, T. Sauvage, Low Energy and low fluence helium implantations in tungsten: Molecular dynamics simulations and experiments, J. Nucl. Mater. 470 (2016) 44–54.

[2] H. Fan, Z. Wu, T. Sun, M. Yang, J. Guo, K. Yang, Y. Li, Efficient plasma-assisted approach in nanostructure fabrication of tungsten, Mater. Des. 89 (2016) 78–84, https://doi.org/10.1016/j.matdes.2015.09.139.

[3] R. Schierholz, B. Lacroix, V. Godinho, J. Caballero-Hernández, M. Duchamp, A. Fernández, Nanotechnology, 26, 2015, 075703

[4] S. Ibrahim, F. Z. Lahboub, P. Brault, A. Petit, A. Caillard,E. Millon, T. Sauvage, A. Fernandez , A.-L. Thomann, Surface & Coatings Technology 426 (2021) 127808

Synthesis, structural and mechanical characterization of ZnZr and ZnMg thin films

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In the last decades magnetron sputtering (and others PVD techniques) became a well-established process because of its capability to generate a large variety of protective coatings against wear and corrosion [1]. In particular, extensive research on coatings designed for biomedical application is carried out. These are generally used to increase the biocompatibility of bulk materials (such as Mg- or Ti alloys [2]), to improve the antimicrobial properties of surgical tools [3] or to develop a new class of biodegradable implants [4]. The most used materials for bioresorbable devices are Mg-, Zn- and Fe-based alloys but they might suffer of microgalvanic corrosion among the intermetallic compounds because of their difference in corrosion potentials. An amorphous material could be a proper solution to overcome this issue since it is characterized by a homogenous structure which may lead to a generalized corrosion with tunable corrosion rates. In this study several Zn_xZr_{100-x} and Zn_yMg_{100-y} thin films with controlled thickness (400-700 nm) have been deposited by tuning the target power's ratio during the RF magnetron co-sputtering process. Figure 1 shows the chemical composition (at.%) of deposited thin films measured by EDX as function of the target power ratio applied. Successively, the film's structure was characterized by XRD, SEM and AFM techniques and the elastic properties have been evaluated by nanoindentation. The presence of the hump in XRD analysis proved a compositional range of amorphization in both systems of alloys (26<x<88 and 45<y<67 at.% Zn). Moreover the position 2θ of the hump is related to the average interatomic distances between atoms (through Ehrenfest law) which are related to the stiffness of the material. Nanoindentation results show an increment of Young's modulus by increasing the Zn content due to the shortening of average atomic distances and formation of strong Zn-Mg/Zr bonds. The SEM cross-section images of thin films in the amorphization range show the presence of corrugations on the fracture surface, typical of amorphous materials. Nevertheless, the roughness of the surface of ZnZr and ZnMg thin films has been evaluated by AFM and for amorphous structure it resulted about 1nm. Since the low roughness, the SEM plane-view looks featureless. Overall, this preliminary study paves the way to develop new class of amorphous coatings with potential impacts for biomedical applications.

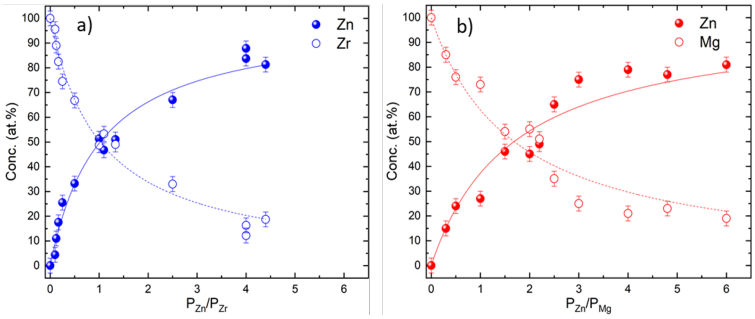

Figure 1: Chemical composition of (a) ZnZr and (b) ZnMg thin films at different target power's ratio.

References

[1] K. Strijckmans et al., Tutorial: Hysteresis during the reactive magnetron sputtering process, Journal of Applied Physics 124, (2018) 241101

[2] M. Qadir et al., Ion-substituted calcium phosphate coatings by physical vapor deposition magnetron sputtering for biomedical applications: A review, Acta Biomaterialia 89, (2019) 14-22

[3] L. Bonilla-Gameros et al., Silver-based antibacterial strategies for healthcare-associated infections: Processes, challenges, and regulations. An integrated review Nanomedicine: Nanotechnology, Biology and Medicine 20, (2020) 102142

[4] Z. Zhang et al., Advances in coatings on magnesium alloys for cardiovascular stents – A review, Bioactive materials 6, (2021) 4729-4757

Reactive oblique angle deposition of Zr- and Ta-based coatings

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The oblique angle deposition (OAD) is nowadays widely used to deposit thin films with controlled microstructure and functionalities. In this work, zirconium- and tantalum-based thin films are prepared by magnetron sputtering using the OAD method in metallic and reactive mode.
The background of the study concerns the protection of the head of artificial hip joint (i.e. hemispherical shape) thanks to multilayer thin films based on Zr and Ta nitrides. For this purpose, a dedicated substrate-holder (Fig. 1) was developed.

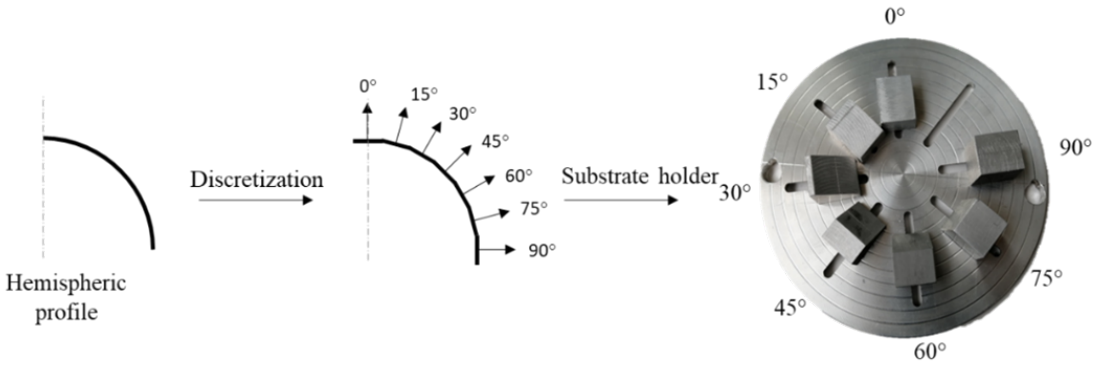

Figure 1: Dedicated substrate holder.

The continuous shape of the half-sphere is discretized into linear segments with an angle variation of 15° between each successive face and distributed at a same radial distance and height compare to a planar holder. As the pressure conditions are also fixed (without or with nitrogen), the only variables remaining are the substrate angles (equal for each compound) and the material-dependent growth conditions (i.e. Zr or Ta, metallic or nitride).
A joint experimental and digital approach is followed to answer some questions and open new ones… SRIM [1], SiMTRA [2] and NASCAM [3] are used for the digital approach, while for the experimental way, surface morphology, column angle, residual stress, composition, and structure are investigated.
Most of these properties present the expected variations with the change of the particles incidence angle. However, the reactive deposition conditions disturb this nice landscape and open several questions…

References

[1] J.F. Ziegler, J.P. Biersack, The stopping and range of ions in matter, Treatise Heavy-Ion Sci., Vol. 6 Astrophys. Chem. Condens. Matter; Bromley, D.A., Ed.; Springer US, Boston, MA, 1985, pp. 93-129.
[2] D. Depla, W.P. Leroy, Magnetron sputter deposition as visualized by Monte Carlo modeling, Thin Solid films 2012, 520, 6337-6354.
[3] P. Moskovkin, S. Lucas, Computer simulations of the early stage growth of Ge clusters at elevated temperatures, on patterned Si substrate using the kinetic Monte Carlo method, Thin Solids Film 2013, 536, 313–317

December 9th

Benefit of monitoring discharge current waveforms in reactive HiPIMS: Tailoring of film chemistry under constant reactive gas flow

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An inherent feature in reactive magnetron sputtering is process instability due to the complex relationship between the fluxes of reactive gas and sputtered metal from the target surface. As an approach to stabilize the reactive process, one could implement reactive High-Power Impulse Magnetron Sputtering (R-HiPIMS) with peak current regulation [1]. The change of shape and amplitude of the discharge current is related to the transition between the reactive process modes. It is explained by a contribution of the ion current due to the significant recycling of ionized sputtered metal in metallic regime, while working gas recycling becomes dominant during the transition and poisoned regimes, due to the low self-sputtering yield of the compound layer formed on the target surface [2].

By utilizing this feature, a feedback control system using pulse frequency was implemented into the HiPIMS generators to maintain a constant peak current independent of reactive gas flow, and to stabilize the reactive process conditions at a given set point. The main concept of the feedback control is to alter the generation of free metal through the pulse frequency to keep the peak current constant and thereby maintain the same compound state at the target surface. For example, the compound layer on the target surface is reduced by the increased pulse frequency as a consequence of the increase of average target power, so that the reactive mode transition enters the metallic regime. In this manner, by altering the average power by controlling the pulse frequency, oxygen partial pressure can be varied even at a constant reactive gas flow.

We demonstrated the capability of this approach to modulate the film chemistry during the deposition process, by adjusting the peak current setpoint to obtain a variety of substoichiometric compositions under constant reactive gas flow for the film growth of several transition metal oxides, TiO_x, AlO_x, MgO_x, ZrO_x and VO_x.

References

[1] T. Shimizu, M. Villamayor, D. Lundin, U. Helmersson, *Process stabilization by peak current regulation in reactive high-power impulse magnetron sputtering of hafnium nitride* J. Phys. D, 49 (2016) 065202

[2]D. Lundin, J. T. Gudmundsson, N. Brenning, M. A. Raadu, and T. M. Minea *A study of the oxygen dynamics in a reactive Ar/O2 high power impulse magnetron sputtering discharge using an ionization region model* J. Appl. Phys., 121 (2017) 171917.

Tailoring of rhenium oxidation state in ReO_x thin films during reactive HiPIMS deposition process and following annealing

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Bulk rhenium trioxide (ReO_3) has an unusually high electrical conductivity [1] and, being nanosized, has promising catalytic properties. However, the production of pure ReO_3 thin films is challenging due to the difficulty to stabilize rhenium in a 6+ oxidation state. Here we present a novel approach for the deposition of ReO_x ($x \approx 1.6–2.9$) thin films using reactive high power impulse magnetron sputtering (r-HiPIMS, t_{ON}=50 μs, t_{OFF}=9 ms, Ip≈0.8 A/cm^2) from a metallic rhenium target in a mixed Ar/O_2 atmosphere [2]. The thin films of ReO_x (≈ 150 nm) on fused quartz substrates were deposited in the gas-sustained self-sputtering regime, observed during r-HiPIMS process according to current waveforms. The influence of the substrate temperature, the oxygen-to-argon flow ratio and post-annealing at 250 °C in the air for 3 h on the properties of the films were studied. The films were studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), UV-Vis-NIR absorption spectroscopy and conductivity measurements. The films were stored in an inert atmosphere till the characterisation to avoid the possible film's degradation in the ambient conditions. The as-deposited films have an X-ray amorphous structure (a-ReO_x) when deposited at room temperature while a nano-crystalline β-ReO_2 phase when deposited at elevated temperatures (150 or 250 °C). The amorphous a-ReO_x can be converted into the crystalline ReO_3 with a lattice parameter of 3.75 Å upon annealing in the air (Fig. 1(a)). During the annealing, a clean piece of quartz was placed on the sample surface to avoid the evaporation of rhenium oxide [3]. The surface morphology of the films is dense without detectable voids when elevated substrate temperatures are used (Fig. 1(b)). Various Re oxidation states are observed on the surface of the films in different ratios depending on the deposition parameters. All samples exhibit electrical resistivity on the order of 10^{-3} Ωcm and optical properties typical for thin metallic films (Fig. 1(c)).

Financial support was provided by ERDF Project no. 1.1.1.1/20/A/057.

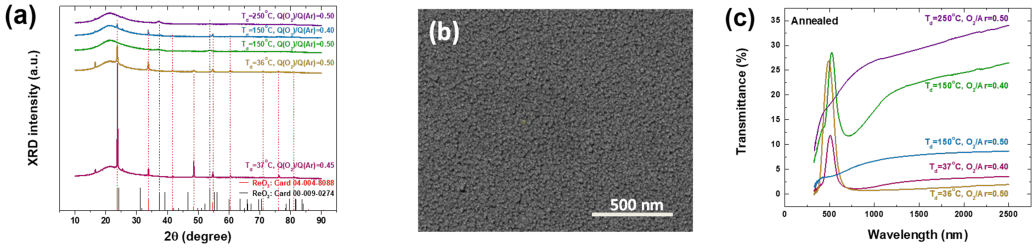

Figure 1: X-ray diffractograms of the annealed rhenium oxide films (a), SEM image of the film deposited at 250 °C (b), and transmittance spectra of the annealed films (c).

References

[1] Evans, H. A. et al., Nat. Rev. Mater. 2020, 5, 196-213

[2] Zubkins, M. et al., Mater. Chem. Phys. 2022, 289, 126399

[3] Polyakov, B. et al., Cryst. Growth Des. 2020, 20, 6147-6156

Molecular dynamics study of the effect of sputtered atom energy distribution on film growth. Comparison between thermal evaporation, dc magnetron sputtering, HiPIMS and bipolar HiPIMS.

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Molecular dynamics simulation is a simulation technique well suited for describing thin films or nanoparticle growth phenomena [1]. Some successful attempts have already been undergone for including specific effects of different magnetron sputtering (MS) deposition techniques [2-4].
In this work, we select velocity initial conditions determined from experimental data (energy resolved mass spectrometry) or SRIM simulations of sputtered atom energy distribution (EDF) for thermal evaporation, dc magnetron, HiPIMS and bipolar HiPIMS. This choice is motivated by approaching experimental conditions as much as possible. Usually, in MD simulation it is achieved by setting a mean kinetic energy or sampling from a uniform energy distribution. This is expected to give a step forward for improving MD simulation prediction ability of sputtered film properties, such as morphology, composition, structure, tribology etc.
For thermal evaporation, a Maxwell-Boltzmann distribution at melting temperature is considered, for dc MS, SRIM EDF are used modified by the transport through the MS reactor. For HiPIMS and bipolar HiPIMS, the kinetic energy of sputtered ions are selected from the experimental energy resolved mass spectra obtained using EQP1000 mass spectrometer (Hiden Analytical). This approach is applied to copper sputtering, for which, HiPIMS Cu+ EDFs are available (Fig. 1).

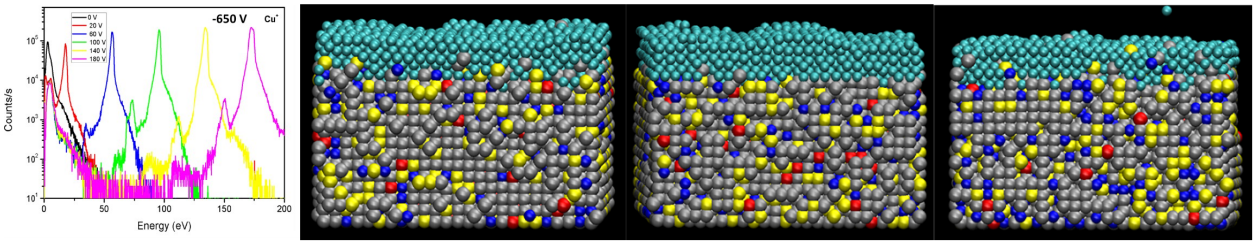

Figure 1: Experimental copper ion Cu^+ EDF in HiPIMS mode (0V) and bipolar HiPIMS for various acceleration voltage recorded 12 cm away from the target. MD dcMS, HiPIMS and bipolar HiPIMS 180V snapshots, from left to right. Color code: cyan Cu, yellow Cr, silver Fe, red Mo, blue Ni.

Growth on a model stainless steel substrate is studied (bcc $Fe_{67}Cr_{17}Mo_2Ni_{14}$, $72\times72\times46$ Å^3 slab with 20000 atoms,). 4300 Cu atoms (+ Cu^+ ions for HiPIMS studies) are released at a periodic rate with random positions above the surface and initial velocities randomly selected in the different EDFs. The ratio Cu^+/Cu is fixed at 10% for all HiPIMS studies. Structures and morphologies of the resulting films will be presented as well as XRD patterns and atomic strain in the films.

References

[1] L. Xie, P. Brault, J.-M. Bauchire, A.-L. Thomann, L. Bedra, J. Phys. D: Appl. Phys. 47 (2014) 224004
[2] M. Kateb, H. Hajihoseini, J. T. Gudmundsson, S. Ingvarsson, Journal of Vacuum Science & Technology A 37 (2019) 031306
[3] M. Kateb, J. T. Gudmundsson, S. Ingvarsson Journal of Vacuum Science & Technology A 38 (2020) 043006
[4] M. Kateb, J. T. Gudmundsson, P. Brault, A. Manolescu, S. Ingvarsson, Surface and Coatings Technology 426 (2021) 127726

Choice of the working point in reactive HiPIMS of oxides

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Reactive High Power Impulse Magnetron Sputtering expands the possibilities for growth control in magnetron sputtering. Substantial ionization of the sputtered material increases the energy input in the growing film with potentially beneficial impact on many performance characteristics. At the same time, the choice of pulse configuration adds an additional level of complexity to the deposition process development. Even the mode of operation (metal or oxide) affects the plasma condition and has to be considered in selection of a working point for a HiPIMS process.

This contribution discusses the interplay between the operating mode in reactive sputtering and the HiPIMS pulse configuration. First, the differences in the ionized flux fraction are highlighted. It is shown that a higher fraction of the metal flux is ionized in the compound mode for the same duty cycle [1]. This is caused by large differences in the metal vapour densities in the respective modes.

HiPIMS affects also the hysteresis behavior. Our simulations indicate that the back-attraction of ionized metal opens a process window where high deposition rate of stoichiometric films may be possible in the metal mode. For the same partial pressure of reactive gas, increased compound fraction is predicted in the deposited film [2]. Interestingly, the sputtering target compound coverage is independent of the back-attraction probability. Despite the lower metal deposition rate in HiPIMS processes, the resulting deposition rate of a stoichiometric compound may be higher than in a corresponding dc process. The model, however, requires further experimental verification in order to assess the impact of other mechanisms, such as the gas rarefaction and refill.

References

[1] Kubart, T.; Čada, M.; Lundin, D.; Hubička, Z. *Investigation of ionized metal flux fraction in HiPIMS discharges with Ti and Ni targets* Surf. Coat. Technol. 238 (2014) 152-157

[2] Kubart, T.; Fernandes, D.F.; Nyberg, T. *On the description of metal ion return in reactive high power impulse magnetron sputtering* Surf. Coat. Technol. 418 (2021) 127234.

Toward energy-efficient physical vapor deposition: routes for densification of $(Ti_{1-y}Al_y)_{1-x}W_xN$ thin films grown with no external heating

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In view of the sustainable development goals and to satisfy the demand for growing dense, hard coatings for protecting temperature-sensitive substrates, the quest for lowering energy consumption during thin film growth by magnetron sputtering becomes of pressing importance. Here, we introduce a method which replaces thermally-driven adatom mobility, necessary to obtain high-quality fully-dense films, with that supplied by effective low-energy recoil generation resulting from high-mass metal ion irradiation of the growing film surface. This approach enables the growth of dense and hard films with no external heating at substrate temperatures Ts $\leq$ 130 °C in a hybrid high-power impulse and dc magnetron co-sputtering (HiPIMS/DCMS) setup involving a high mass (m > 180 amu) HiPIMS target and metal-ion-synchronized bias pulses. Compared to conventional PVD methods, the energy savings are as much as 64%.

First, the effect of the metal ion mass on the densification, phase content, nanostructure, and mechanical properties of metastable cubic $Ti_{0.50}Al_{0.50}N$ based thin films is reviewed. Three series of $(Ti_{1-y}Al_y)_{1-x}Me_xN$ (Me = Cr, Mo, W) films are grown with x varied intentionally by adjusting the DCMS power. Results reveal a strong dependence of film properties on the mass of the HiPIMS-generated metal ions. All layers deposited with Cr^+ irradiation exhibit porous nanostructure, high oxygen content, and poor mechanical properties. In contrast, $(Ti_{1-y}Al_y)_{1-x}W_xN$ films are fully-dense even with the lowest W concentration tested, x = 0.09. We then discuss the effects of the high-mass W^+ irradiation on film properties with W^+ energy E_{W^+} (≈90-630 eV, controlled by substrate bias voltage amplitude V_s) and x (0.02-0.12, controlled by the HiPIMS pulse length). Results reveal that a strong coupling exists between the W^+ incident energy and the minimum W concentration required to grow dense layers. We establish that dense, high-quality coatings can be obtained provided that the $^+$ momentum transfer per deposited metal atom is sufficiently high. Finally, the behavior of $(Ti_{1-y}Al_y)_{1-x}W_xN$ films upon annealing in vacuum up to 1000 °C is demonstrated.

Growth by reactive magnetron sputtering and unusual epitaxial relations of NiO and CrN thin films on r-Al_2O_3

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Epitaxial NiO and CrN thin films were grown on single crystal $Al_2O_3(1\bar{1}02)$ (r-plane sapphire) using reactive magnetron sputtering in Ar/O_2 or Ar/N_2 mixtures. X-ray diffraction in $\omega - 2\theta$ configuration revealed that the NaCl-structured materials NiO and CrN grow with a tilted orientation relative to the substrate, with a tilt angle of $\omega = 16.9°$ determined from an in-depth pole-figure analysis of the NaCl-structured materials on r-plane sapphire. The full epitaxial relations can therefore be described as: (110)$[\bar{2}2\bar{5}]$ $\|$ $(9908)[1120]$ with its mirror symmetry (110)$[\bar{2}2\bar{5}]$ $\|$ $(9908)[1120]$ which contrast to the more commonly observed (100) $[100]$NaCl$\|$ $(1102)[1010]Al_2O_3$.

This characterization and analysis of the epitaxy, crystallography, and growth modes yield a single and identical epitaxial relationship of these two cubic materials on r-plane sapphire, in contrast to earlier studies on NaCl-structured materials (mostly MgO [1]) on r-plane sapphire indicate several different orientation relationships.

The results advance the understanding of growth modes and unusual epitaxial relationships of two cases of metal oxide and nitride films with rock-salt (NaCl) structure broadly used in science and technology on r-plane sapphire.

References

[1] P.A. Stampe, M. Bullock, W.P. Tucker, R.J. Kennedy, Growth of MgO thin films on M-, A-, C- and R-plane sapphire by laser ablation, J Phys D Appl Phys. 32 (1999) 1778. 10.1088/0022-3727/32/15/304

Complex studies of room temperature magnetron sputtering growth of ZnO:Al thin films

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Aluminum-doped zinc oxide (AZO), classified as one of the transparent conductive oxides (TCOs), is wide band gap semiconductor with high optical transparency, low electrical resistivity and high electron mobility. In terms of those features, this class of materials have relevant impact on the development of state-of-the-art electronic and optoelectronic devices, such as touch-sensitive screens, electrodes in light emitting diodes, gas sensors, contacts for solar cells and many others. Moreover, AZO is the hopeful replacement for the commonly used and expensive to manufacture indium tin oxide. There are many different techniques for obtaining thin films of these materials, however the typical methods involve magnetron sputter deposition. In the current research, the emphasis is on optimizing the growth process, by changing selected sputter conditions, in order to control the material features: resistivity, crystalline quality, carrier concentrations, energy band gap, etc.

In this report we present a complex investigation of process conditions to determine in one deposition system which parameter is the one controlling the properties of the films in the biggest part. To achieve that, 100 nm-thick AZO films were deposited using variable argon pressure, target power, different AZO targets and sputtering modes without thermal treatment onto various substrates: silicon, quartz, glass and sapphire. Furthermore, the experiment utilized two different sputtering systems: Leybold Z400 and Gamma 1000C to examine the influence of target-substrate distance and sample spatial distribution on the films resistivity. We applied two AZO targets from different vendors, with the same nominal atomic composition, differing in color. The obtained films were examined in terms of transparency, conductivity, crystalline quality, chemical composition by means of spectral transmission, four-point probe, X-ray diffraction and energy-dispersive X-ray spectrometry, respectively. The aluminum incorporation was measured by secondary ion mass spectrometry. To study the surface chemistry of selected films X-ray photoemission spectroscopy was used. The experimental results mainly show that morphological structure improves with decrease of argon pressure. Transmission with 86% in visible region and resistivity of 1.5×10^{-3} $Omega$.cm were achieved at room temperature, while those features are present usually using high-temperature magnetron sputtering deposition. We argue that this is achieved through the small target to substrate distance and immersion of substrate in the plasma.

This work was supported by the National Centre for Research and Development, Poland, project 'OxyGaN' - M-ERA.NET2/2019/6/2020, by the Hungarian NRDI Fund, grant number 2019-2.1.7-ERA-NET-2020-00002 and by the Israel Ministry of Science, Technology and Space in the frames of the M-era.net Programme.

Long-term antibacterial properties of ZrN-Cu coatings deposited by industrial reactive magnetron sputtering

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Pathogenic microbes such as bacteria and viruses can spread significantly via contaminated surfaces. A way to eliminate the contamination and thus a possible contact-induced transmission of these pathogens is by using antimicrobial coatings. ZrN-Cu coatings containing different amounts of Cu were deposited using the combination of reactive arc deposition and magnetron sputtering in an industrial PVD system. Microstructural studies showed the formation of two distinct ZrN and Cu phases when Cu content was sufficiently high. Hardness and elastic modulus were inversely proportional to the Cu content. The as deposited coatings showed outstanding bactericidal properties against Escherichia coli CCM 3988 and Pseudomonas aeruginosa CCM 1960, especially when Cu content was more than 12 at.% and the exposure time was longer than 40 min. The coatings, however, did not exhibit any significant virucidal properties against SARS-CoV-2 virus. The samples were embedded in our faculty's door handles for six months to study the coatings' long-term efficiency and durability under natural operational conditions. The samples were periodically evaluated and it was observed that the antibacterial efficiency of the coatings gradually deteriorated over time. The sample with the highest Cu content of $\sim$ 30 at.% showed always better performance compared to samples with copper content of $\sim$ 12 at.%.

Structure and properties of Mo-Hf-Y-Si-B-N films deposited by reactive magnetron sputtering

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The purpose of this work is to study the effect of nitrogen concentration on the structural characteristics, mechanical properties, oxidation resistance, and thermal stability of Mo-Hf-Y-Si-B-N coatings.

Magnetron sputtering of the ($MoSi_2$ + 10%MoB) + 20%HfB_2 +4Y segment target was carried out in DC mode on the UVN-2M installation [1] in the medium of Ar+N_2, while the consumption of N_2 was 0, 12.5, 25 and 37.5 ml/min. The deposition of coatings was carried out using the Pinnacle+ 5x5 Advanced Energy power supply. The power was maintained at the level of 1 kW, the residual and working pressure were 0.005 and 0.2 Pa, respectively. Monocrystalline Si (100) and polycrystalline Al_2O_3 were used as substrates.

The microstructure and elemental composition of the coatings were evaluated by scanning electron microscopy on a Hitachi S-3400 microscope with a Noran 7 Thermo prefix for energy dispersive analysis. The elemental profiles of the coatings were obtained by glow discharge optical emission spectroscopy (GDOES) on the Profiler-2 Horiba JY device. The fine structure of the coatings was studied by transmission electron microscopy (TEM) and selected area electron diffraction on a JEM-2100 Jeol electron microscope at an accelerating voltage of 200 kV. X-ray diffraction (XRD) analysis was performed on a D2 Phaser Bruker diffractometer with CuKα radiation. Raman spectra were recorded on the NTEGRA (NT-MDT) instrument using a red laser with a wavelength of 633 nm. Mechanical characteristics were measured using a Nano Hardness Tester CSM at a load of 4 mN. The abrasive resistance of the coatings was evaluated using a Calowear tester when using a diamond abrasive with a dispersion of 1 μm. In situ studies of structural-phase transformations and thermal stability were carried out by the TEM method at temperatures of 20-1000 °C [2]. Heating was carried out using the Gatan 671 holder at a rate of 100 °C/min. The obtained results were analyzed using Olympus Radius and ImageJ software.

According to the GDOES data, all elements in the Mo-Hf-Y-Si-B-N coatings were distributed uniformly. The nitrogen concentration in the coatings increased from 0 to 42 at.% when flow rate raised from 0 to 37.5 ml/min. The growth rate of coatings decreased from 270 to 50 nm/min, which may be due to poisoning of the target. According to the TEM, SAED, and XRD data, all coatings were characterized by an amorphous structure. There was an extreme dependence of hardness and elastic recovery on nitrogen consumption with a maximum of 16 GPa and 57% achieved at a nitrogen consumption of 25 ml/min. The abrasive resistance of the coatings increased linearly with increasing nitrogen concentration. According to In situ TEM, the coatings retained an amorphous structure up to 900 °C, which indicates their high thermal stability. At a temperature of 1000 °C, the coatings partly crystallized with the formation of h-$MoSi_2$ and t-MoB phases.

The study was supported by the Russian Science Foundation (project 19-19-00117-II).

References

[1] Ph. V. Kiryukhantsev-Korneev, Effects of doping with Zr and Hf on the structure and properties of Mo-Si-B coatings obtained by magnetron sputtering of composite targets, Surface and Coatings Technology 442 (2022) 128141

[2] Ph. V. Kiryukhantsev-Korneev, Structure and properties of protective amorphous Zr-B-N coating, Surface and Coatings Technology 4428(2022) 128849

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