New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F4-2

Functional Oxide and Oxynitride Coatings

Moderators: Michael Stueber, Karlsruhe Institute of Technology, Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG

1:50pm **F4-2-2 After-arc Plasma Technique to Modify Chemical States of Surface and Grain Boundaries of 50-nm-thick Conductive ZNO Films to Achieve a Fast-response Hydrogen Sensor**, ***Tetsuya Yamamoto***, *J Nomoto, H Makino,* Kochi University of Technology, Japan*; H Kitami, T Sakemi, Y Aoki,* Sumitomo Heavy Industries, Ltd., Japan*; K Kobayashi,* Kochi University of Technology, Japan*; S Kishimoto,* Kochi National College of Technology, Japan

We report a high-response hydrogen gas sensor based on a 50-nm-thick conductive Ga-doped ZnO (GZO) polycrystalline films. The GZO films were deposited on amorphous glass substrates at a temperature of 200 Celsius by ion plating with direct-current arc discharge. The Ga_2O_3 content in the ZnO targets were 4 wt.%. Control of chemical states of adsorbed oxygen atoms on the ingrain surface and at grain boundaries and of oxygen-related point defects such as oxygen vacancies in the vicinity of the ingrain surface is essential to achieve hydrogen gas sensors showing a very strong and *immediate response* to this gas. We, thus, have been developing a novel after-arc plasma technique to generate electronegative oxygen ion (O^-) for the control of the density and chemical states of the different type of defects above. The analysis of the data obtained by X-ray photoelectron spectroscopy measurements for as-deposited GZO films indicated the presence of oxygen vacancies, O^-, hydroxyl, oxygen molecule and water molecule. On the other hand, XPS study on the GZO films after the exposure to the O^- revealed that the intensity of the peak to the O^{2-} ions on the wurtzite structure of the hexagonal Zn^{2+} ion array increased, whereas the intensity of the peak associated with the O^{2-} ions that are in oxygen deficient regions within the ZnO matrix decreased. The above changes in the intensity of this component may be in connection with the variation in the concentration of the oxygen vacancies. This implied that some of the doped oxygen species should adsorbed on the surface of grain boundaries, trapping carrier electrons. This lead to the formation of a high and narrow energy barrier at a grain boundary in addition to the energy barrier owing to the nature of the grain boundaries such as discontinuity and disorder. In this study, we assume the chemical reaction limiting the performance of hydrogen gas sensors can be as follows: the reaction of hydrogen gas (H_2) with an O^- ion adsorbed on a grain boundary produces water molecule together with a free electron, resulting in a decrease in the electrical resistivity. We confirmed the distinctly enhanced performance of the hydrogen gas sensors with *fast response* within 1 second at a temperature of 330 Celsius. The use of extrinsic O^- ions exposure with the after-arc plasma technique would be an effective way for the achievement of H_2 sensors exhibiting at lower temperature. We will propose a theoretical model of the H_2 sensing mechanism limiting the properties of the H_2 sensor.

2:10pm **F4-2-3 Microstructure and Corrosion Resistance of PVD Hf-coated Mg Alloy after Thermal Oxidation Treatment**, *D Zhang, Z Qi, B Wei,* ***Zhoucheng Wang***, Xiamen University, China

Hf coatings are fabricated on Mg alloy by PVD magnetron sputtering and further submit to thermal oxidation treatment at temperature of 200℃, 300℃ and 400℃, respectively. The surface analysis indicates that new shallow grain boundaries are appeared on the coating surface when the treatment temperature is over 300℃. These changes in microstructure inhibit the permeation of corrosion media into the substrate and decrease the diffusion rates of corrosion products. Moreover, the thickness of the hafnium oxide film resulted from surface oxidation is increased with increasing the treatment temperature. As a result, surface densification and oxidation of the coating induced by the post treatment significantly decreased its susceptibility to corrosion. In addition, the release of the residual stress produced by the post treatment suppresses the delaminating of the coating as Mg is corroded. Consequently, the Hf coating post-treated with 400℃ exhibits more positive corrosion potential, lower corrosion current density and higher polarization resistance than that of the other coating in electrochemical test. However, salt spray test reveals that the Hf coating post-treated with 300℃ provides the most efficient long-term protection for Mg alloy. Scratch test reveals that it was mainly due to the poor adhesion strength resulted from the big difference in thermal expansion coefficients between coating and substrate during the high treatment temperature (400℃).

2:30pm **F4-2-4 HiPIMS Deposition of Ta-O-N Coatings with Modified Surface by Cu Nanoclusters for Water Splitting Application**, ***Jiří Čapek***, *Š Batková, S Haviar, J Houška,* University of West Bohemia, Czech Republic

As reported in [1], Ta-O-N material can provide appropriate properties (i.e., band gap width and alignment) for splitting of water into H_2 and O_2 under visible light irradiation (without any external voltage). This could bring a great possibility to convert the solar light into a useful chemical energy. However, it is still impossible to prepare the Ta-O-N electrodes by conventional (chemical) methods at the temperatures less than 500°C without post-annealing. Moreover, the efficiency of this material for water splitting is limited due to fast recombination rate of photogenerated electrons and holes.

Recently, we have demonstrated [2] in our laboratory that high-power impulse magnetron sputtering is a suitable technique for low-temperature (less than 250 °C) and high-rate (higher than 150 nm/min) deposition of Ta-O-N coatings with tunable elemental composition and optical band gap width. In this work, we focus on a further optimization of deposition conditions (e.g., average pulse target power density, working gas pressure, substrate bias and temperature) in order to reach proper crystal and electronic structures of Ta-O-N coatings with respect to the water splitting application. Moreover, we propose to modify the surface of the coatings by Cu nanoclusters in order to enhance the efficiency of water splitting due to a reduced recombination rate of electrons and holes. For this purpose, we have designed a unique dual magnetron-based system combining the reactive high power impulse magnetron sputtering with a source of metallic nanoclusters. The results of our experiments including the coating properties investigated using atomic force microscopy, spectroscopic ellipsometry and high-resolution SEM and preliminary data on photocatalytic activity are presented in detail.

[1] R. Abe, J. Photochem. Photobiol. C Photochem. Rev. 11 (2010) 179.

[2] J. Rezek et al., Thin Solid Films. 566 (2014) 70.

2:50pm **F4-2-5 New Oxides and Oxynitrides for Thermoelectrics and Hard, Transparent Coatings**, ***Per Eklund***, Linköping University, IFM, Sweden **INVITED**

I present an overview of our experimental and theoretical investigations of $Ca_3Co_4O_9$- and $CaMnO_3$-based systems by reactive magnetron sputtering for thermoelectrics and amorphous oxynitride M-Si-O-N coatings as hard, transparent coatings. We have introduced a two-step sputtering/annealing method for the formation of highly textured virtually phase-pure $Ca_3Co_4O_9$ thin films by reactive co-sputtering from Ca and Co targets followed by an annealing process at 730 °C under O_2-gas flow.The thermally induced phase transformation mechanism was investigated by *in-situ* time-resolved annealing experiments using synchrotron-based 2D x-ray diffraction as well as *ex-situ* annealing experiments and standard lab-based x-ray diffraction [1] . By tuning the proportion of initial CaO and CoO phases during film deposition, the method enables synthesis of $Ca_3Co_4O_9$ thin films as well as Ca_xCoO_2. The same approach is used to synthesize $CaMnO_3$ and $CaMn_xNb_{1-x}O_3$ perovskite oxides on Al_2O_3 (0001), (1-100) and (1-102). Furthermore, amorphous thin films in the Mg/Ca-Si-O-N systems were deposited by reactive RF magnetron co-sputtering from Mg(Ca) and Si targets in $Ar/N_2/O_2$ gas mixtures [2]. The films were found to be homogeneous and transparent in the visible region with high hardness of 21 GPa and elastic modulus of 166 GPa.

3:30pm **F4-2-7 Reactive Magnetron Sputter Deposition of NbO_x Thin Films**, ***Roland Lorenz***, Montanuniversität Leoben, Austria*; M O'Sullivan, D Sprenger, B Lang,* Plansee SE, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

Within this work, niobium oxide thin films were deposited on silicon and glass substrates by reactive dc magnetron sputtering from niobium targets prepared by cold gas spraying. The oxygen partial pressure in the oxygen/argon atmosphere was varied while the overall gas pressure and the applied target current were kept constant. The applied pulsed d.c. substrate bias voltage was set to -50 V and several pulse conditions were used. Scanning electron microscopy was used to investigate the topography of film surface and fracture cross-section. To examine the crystalline structure, X-ray diffraction and Raman spectroscopy was applied. Further, X-ray photoelectron spectroscopy and energy dispersive X-ray spectroscopy were used to measure the oxygen content within the films and to illuminate the chemical bond structure. The optical properties of the films were determined by their reflexion and transmission spectra,

while the electrical thin film resistivity was measured by four point probe. With increasing oxygen partial pressure the film growth rate decreases, while the oxygen content within the films increases. All films grown show a smooth surface and their amorphous microstructure is reflected by both, the fracture cross-sections and the X-ray diffractograms. The increasing oxygen content within the films leads to a transition from non-transparent films to nearly fully-transparent films. This transition is linked to an increase of the electrical resistivity, where films grown at the highest oxygen content show insulating properties.

3:50pm **F4-2-8 Electrical Properties of BiNbO Thin Films Deposited by Dual Co-sputtering**, ***Osmary Depablos-Rivera***, *J Pérez-Alvarez,* Instituto de Investigación en Materiales-UNAM, Mexico*; S Charvet, M Lejeune,* Université de Picardie Jules Verne, France*; S Rodil,* Instituto de Investigación en Materiales-UNAM, Mexico

The bismuth oxide-based materials have been gaining interest because their optical and electrical properties are suitable for applications, such as opto-electronic devices, catalysts in photo-induced processes and clean energy generation areas. The bismuth niobium oxides (BiNbO) system is one of this materials group, and they have been reported as possible candidates for solid electrolytes and high-k dielectric materials for capacitors. In such applications, their synthesis as thin films is desirable. In this work, we propose the use of the dual magnetron co-sputtering technique for the synthesis of the different compounds of the BiNbO system controlling the composition and structure by adjusting the deposition parameters of the two independently driven targets. The films were deposited from an α-Bi_2O_3 and Nb targets; the power applied to the ceramic target was fixed at 30 W (radio frequency), and the power applied to the Nb was varied between 20 and 150 W (DC). The deposition was done under Ar:O_2 (20 volume % O_2) reactive atmosphere. The substrates were borosilicate glass pieces, which were heated at 150 °C. The films deposited at Nb power above 50 W were amorphous, then they were annealed at 600 °C for 2 h in air. The identification of the obtained different phases was done correlating the structural and compositional results by x-ray diffraction and energy dispersive x-ray spectroscopy/x-ray photoelectron spectroscopy, respectively. Four different structures were obtained: solid solutions with different Nb concentrations and defective fluorite-based structure, Bi_3NbO_7, $Bi_5Nb_3O_{15}$ and $BiNbO_4$. The electrical conductivity of the films was measured as a function of the temperature by both DC and AC (impedance spectroscopy) two-probe methods, using Pt electrodes on the film surface and a ring electrode configuration. From the analysis of the data, it was possible to estimate the activation energy for the ionic and or electronic conduction processes. The films presenting the fluorite solid solution structure and the Bi_3NbO_7 phase showed ionic conductor behavior, while the other phases were insulators.

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4:10pm **F4-2-9 Structure and Properties of Magnetron-sputtered Manganese Ferrite Films**, ***Fred Fietzke***, *O Zywitzki,* Fraunhofer FEP, Fraunhofer Institute for Organic Electronics, Germany

Mixed oxides of iron with other metals like zinc, nickel, or manganese have already been used for a long time because of their magnetic properties, especially in electrical engineering as core material of coils and current transformers.

The fabrication of the bodies needed for these applications is usually carried out by sintering technique, in which the details of process management affect the characteristics of the finally produced material in decisive way.

Ferrites as thin film material so far have been little investigated but more and more come into focus of interest for potential applications as electromagnetic shielding or optical absorber.

In the work to be presented, manganese ferrite films with and without the addition of chromium have been produced by reactive pulsed magnetron sputtering of alloyed targets.

Primarily, the influence of substrate temperature and oxygen content in the gas atmosphere on structure and optical properties of the deposited layers have been investigated. The evaluation of the magnetic properties is of more complex nature and will be published at a later date.

Layers with thicknesses between one and two microns have been deposited onto flat samples of polished stainless steel and borosilicate glass. The substrate temperature was in the range from 150°C (without additional heating) to 600°C.

All deposited films show a dark anthracite or black appearance in reflected light and a more or less pronounced transmittance in the infrared region, where the transmission factor is determined by the oxygen content and the onset wavelength of transmission by the metal composition.

Whereas at lower substrate temperatures smooth amorphous films with distinct residual reflectivity are formed, at temperatures above 500°C matt crystalline layers with an absorption coefficient of more than 95% over the whole wavelength range of visible light arise.

The crystalline layers exhibit spinel structure and a surface roughness of more than 100 nanometers. XRD spectra, SEM pictures, and GD-OES profiles will be presented, and the mechanism of layer growth in the different temperature regions will be discussed.

4:30pm **F4-2-10 A Combined Optical and Electronic Structure Analysis of ZnO:Al Films: Bandgap Renormalization and the Burstein – Moss Effects**, ***Neilo Trindade***, Sao Paulo Federal Institute, Brazil*; N Marana, M Junior, J Sambrano, A Tabata, J Silva, J Bortoleto,* Sao Paulo State University, Brazil

ZnO and ZnO:Al are wide-bandgap semiconductors which have many applications, mainly as transparent conducting films. ZnO is one of the most promising candidates to replace ITO because of its low toxicity, availability and low production cost. To reduce the electrical resistivity of this material different types of dopants have been used. The Al3+ ion (0.54 Å) is considered one of the best dopants because it has ionic radius close to the radius of the ion Zn2+ (0.74 Å). As a conductive transparent oxide, ZnO doped with Al (AZO) shows great promise for applications such as emitters in the range UV / blue, photodetectors, transparent electronics and solar cells. Thin films of these compounds were deposited onto glass and silicon substrates by RF magnetron sputtering for the investigation of structural and optical characteristics. In order to produce ZnO:Al, the target composition consisted of 95.3 at.% zinc and 4.7 at. % aluminum. The XRD results show that the films present wurtzite structure and that the crystallinity is significantly improved with the Al incorporation. A high degree of orientation texture with the [001] axis perpendicular to the substrate surface is observed in the doped samples. The Al incorporated films exhibited optical transmittance above 80% in the visible spectrum and a clear absorption band in the infrared due to free carriers. Additionally, the optical band gap around 3.5 eV is significantly above the values for the intrinsic ZnO (~ 3.3 eV). Photoluminescence (PL) measurements showed a broad emission band in the visible region. Narrower PL emission lines at 3.32 and 3.37 eV showed up in Al incorporated films, and were related to excitonic emissions. The experimental results were interpreted using computational modeling based on the Density Functional Theory. The results show that the Burstein-Moss effect plays a central role in determining the optical characteristics of the doped material. In addition, the electronic structure analysis show the dominant effect related to Al incorporation in the films, and that the contribution of aluminum atoms affects mainly the conduction band and Fermi level. The authors would like to thank the financial support of the Brazilian agencies FAPESP (2008/53311-5) and CNPq (555774/2010-4).

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