New Horizons in Coatings and Thin Films
Room Grand Hall - Session FP
Symposium F Poster Session

FP-2 Adjusting the Oxidation Behaviour of Arc Evaporated $Al_{1-x}Cr_x$ Intermetallics and Substoichiometric Oxides*, Valentin Dalbauer,* CDL-AOS at TU Wien, Austria*; J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; C Koller,* CDL-AOS at TU Wien, Austria*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Initiated by our recent works on intermetallic Al-Cr-Fe droplets [1–3], which indicate the ability to trigger the nucleation of corundum-structured $(Al,Cr,Fe)_2O_3$ crystallites, the oxidation behaviour of intermetallic Fe-doped $Al_{0.70}Cr_{0.30}$ coatings and corresponding substoichiometric oxides was investigated. The structure and composition of the outermost oxide scale and the oxidation temperature at which it forms is determined by the initial microstructure. Columnar intermetallic coatings, for instance, oxidise via an outermost metastable Al_2O_3 scale, which transforms into the thermodynamically stable corundum-phase starting at 1000–1050 °C. However, nano-composite–like structures, present in substoichiometric coatings, show a more diverse oxidation at the surface and complex elemental separation within the unoxidised material In the present work, we extent our studies on the oxidation and oxide phase formation to intermetallic and substoichiometric coatings prepared from powder-metallurgically produced $Al_{1-x}Cr_x$ cathodes with nominal compositions of x=0.10, 0.25, 0.30, 0.50, and 0.75. The structural evolution of the outermost scale and coating underneath—studied by X-ray diffraction and cross-sectional electron microscopy—is related to the Cr content, oxygen flow rate during the synthesis process and the oxidation conditions.

[1] C.M. Koller, J. Ramm, S. Kolozsvári, J. Paulitsch, P.H. Mayrhofer, Role of droplets and iron on the phase formation of arc evaporated Al-Cr-oxide coatings, Surf. Coatings Technol. 276 (2015) 735–742. doi:10.1016/j.surfcoat.2015.05.012.

[2] C.M. Koller, R. Hahn, J. Ramm, S. Kolozsvári, P.H. Mayrhofer, Microstructural modifications in powder-metallurgically produced Al0.675Cr0.275Fe0.05 targets during cathodic arc evaporation, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 34 (2016) 21603. doi:10.1116/1.4938407.

[3] C.M. Koller, A. Kirnbauer, R. Hahn, B. Widrig, S. Kolozsvári, J. Ramm, et al., Oxidation behavior of intermetallic Al-Cr and Al-Cr-Fe macroparticles, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 35 (2017) 61601. doi:10.1116/1.4986928.

FP-3 Distribution of Dislocations in ZnO Thin Films Grown on a-plane Sapphire Substrates using a Reaction Between Dimethylzinc and High-temperature H_2O Generated by a Catalytic Reaction*, T Saito, R Ibe, A Kato,* Nagaoka University of Technology, Japan*; A Hashim,* MJIIT, Universiti Teknologi Malaysia, Malaysia*; **Kanji Yasui,*** Nagaoka University of Technology, Japan

ZnO is highly useful for applications such as short-wavelength optoelectronics and transparent conductive electrodes [1]. We have developed a new CVD method for ZnO film growth using a reaction between dimethylzinc and catalytically generated high-temperature H_2O. ZnO films grown on a-plane (11-20) sapphire (a-Al_2O_3) substrates at temperatures of 773-873 K exhibited excellent optical and electronic properties [2]. However, the electronic properties were dependent on the film thickness: ZnO films thinner than 500 nm showed inferior electrical properties, namely, a low Hall mobility (<100 $cm^2V^{-1}s^{-1}$) and a high residual carrier concentration (>10^{18} cm^{-3}). The room-temperature electron mobility increased from 30 to 190 $cm^2V^{-1}s^{-1}$ as the film thickness increased to ~3 µm. The mobility also increased significantly as the temperature was decreased to approximately 110-150 K, but decreased at temperatures below 100 K for films thicker than 500 nm. On the other hand, the mobility was almost independent of temperature for films thinner than 500 nm. These results suggest that a region with a high defect density exists near the film-substrate interface. To evaluate the crystal quality of the ZnO film along the growth direction, cross-sectional transmission electron microscopy was performed and the defect density was determined. The ZnO epitaxial film that was studied had a thickness of 4.5 µm and a room-temperature electron mobility of 187 $cm^2V^{-1}s^{-1}$. The dislocation density estimated using Ham's method [3] was found to be lower near the film surface than near the film-substrate interface. The combined density of all dislocations (edge, screw, and mixed) in the top 1.5 µm of the film was approximately 1.1×10^9 cm^{-2}, while in a 30-nm-thick region near the interface, it was approximately 1.6×10^{11} cm^{-2}.

References

[1] B. K. Meyer et al., Phys. Stat. Sol. B, **241** (2004) 231.

[2] K. Yasui et al., MRS Symp. Proc., **1315** (2011) 21.

[3] R. K. Ham, Philos. Mag., **6** (1961) 11.

FP-4 Structural and Optical Properties of ZnO Films Grown on Ion-Plated Ga-Doped-ZnO-Based Buffer Layers by Atmospheric-Pressure Chemical Vapor Deposition using Zn and H_2O as Source Materials*, Tomoaki Terasako,* *Y Ochi,* Ehime University, Japan*; M Yagi,* National Institute of Technology, Kagawa College, Japan*; J Nomoto, T Yamamoto,* Kochi University of Technology, Japan

Zinc oxide (ZnO) with a direct band gap energy of ~3.37eV at RT and a large exciton binding energy of ~60 meV is one of the promising materials for the optoelectronic devices. Chemical vapor deposition (CVD) is an effective way for obtaining films with good crystalline quality over large area. We have reported the successful growth of highly oriented ZnO films on *c*- and *r*-plane sapphire substrates by atmospheric-pressure CVD (AP-CVD) using Zn powder and water (H_2O) as source materials [1,2]. In this paper, we demonstrate AP-CVD growth of undoped ZnO films on ion-plated Ga-doped-ZnO (GZO)-based buffer layers and discuss their structural and optical properties in terms of substrate temperature, source supply ratio of Zn to H_2O and growth time.

The 200-nm-thick GZO films/quartz substrates deposited by ion-plating with dc arc discharge were used as substrates [3]. The AP-CVD apparatus had a horizontal furnace and a vaporizer for H_2O. The horizontal furnace consisted of two temperature zones: one was used for heating the substrate and another for vaporizing high purity Zn powder. Substrate temperature (T_S) was changed in the range from 550 to 725 ºC. Temperatures of zinc source and the H_2O vaporizer were kept at 700 and 54 ºC, respectively. Both the vapors of Zn and H_2O were transported onto the substrate with nitrogen carrier gaseous.

With increasing T_S from 550 to 700 ºC, the growth rate increased exponentially from 13 to 68 nm/min. The analysis of XRD measurement results showed that the ZnO (002) peak was dominant for all the samples, indicating highly *c*-axis orientation. The FWHM value of the (002) peak increased with increasing T_S. SEM observation revealed that the surface morphology strongly depended on T_S. The films grown at T_S of 550 and 575 ºC composed of round-structure grains with the average widths of 161 and 244 nm, respectively. With increasing T_S, the grains became less round and more angular in their shape together with an increase in the average width. At a T_S of 650 ºC, the average width of the grains was 410 nm. Further increase in T_S from 650 to 675 ºC enhanced the lateral growth of the grains.

Photoluminescence (PL) spectra of the films grown at T_S of 550 and 575 ºC were dominated by the near-band-edge (NBE) emission at wavelength of ~380 nm. The PL intensity of the green band emission at wavelength of ~480 nm relative to that of the NBE emission increased with increasing T_S, suggesting that the film composition became more oxygen deficient.

[1] T. Terasako *et al.*, Thin Solid Films **516** (2007) 159-164.

[2] T. Terasako *et al*., J. Vac. Sci. Technol. B **27** (2009) 1646-1651.

[3] J. Nomoto *et al.*, Thin Solid Films **601** (2016) 13-17.

FP-5 Synthesis and Optical Characterization of Nickel Oxide Thin Film obtained by SOL-GEL Method using Nickel Acetate and Citric Acid as Precursors*, Jhonathan Castillo,* *D Mateos, B Valdez, N Nedev, M Curiel, N Rosas, O Pérez,* Universidad Autónoma de Baja California, Mexico

Nickel oxide (NiO_x) has attracted much attention because it is a promising p-type semiconductor with excellent chemical stability and attractive optical and electrical properties as transparent conductive film. This material can be used in thin film transistors, electrochromic devices, batteries and gas sensors, among others. There are several methods to obtain NiO_x. However, most of these methods are expensive because typically the films are deposited in vacuum, e.g., reactive sputtering, High Power Impulse Magnetron Sputtering (HiPIMS) and Chemical Vapor Deposition (CVD).

In this work we obtain pure NiO_x thin films via sol-gel method, employing nickel acetate, citric acid and ethyleneglycol as main precursors. The synthesis consist in mixing 1:1 of $Ni(OCOCH_3)_2 \cdot 4H_2O$ and citric acid in DI water. The pH was adjusted to 8.0 and finally ethyleneglycol was added. The solution was stirred vigorously at 90°C until light green colored gel was formed. The sol-gel solution was deposited on quartz substrate by spin-coating technique and annealed at 410°C in air atmosphere. The annealing temperature was determined previously by thermogravimetric analysis.

EDS analysis reveals the presence of Ni and Oin the deposited thin films. Raman spectroscopy indicates the characteristic peak of NiO_x at 520 cm^{-1}. FTIR measurements show two characteristic peaks at 405 cm^{-1} and 1041 cm^{-1}, which correspond to the Ni-O stretching vibrational modes. UV–VIS absorption spectrum measured after heat treatment corresponds to NiO_x. The transparency and film thicknesses were determined by Spectroscopic Ellipsometry.

The obtained results prove that high purity NiO_x thin films may be obtained at low-cost by sol-gel method. The deposited layers are attractive for application in electronic and optoelectronic devices as transparent and semi-conductive materials.

FP-8 Exploring the Visible Light Photocatalytic Activity of the ZnO - RGO Hybrid - Nanostructures by Sol-gel Process*, **Chih-Chiang Wang,*** National Chung Hsing University, Taiwan*; H Shih,* Chinese Culture University, Taiwan

Carbon-based material, like the graphene, exhibits the unique 2-D structures, e.g., sp^2-conjugated C atoms, highly electronic conductivity, larger specific surface area, better chemical stability. Hence, it attracts various attentions in many fields, like the photocatalysts, solar cells, energy storage, etc. ZnO is an n-type semiconducting material with a wide direct band gap (3.3eV), hexagonal wurtzite structure and higher exciton binding energy (60meV), and has been applied in the field of photocatalyst, gas sensors, and solar cells. In this study, the pristine and ZnO-RGO hybrid-nanostructures were fabricated by sol-gel method at the ambient environments. Subsequent baking was conducted at the 500℃ under $4x10^{-3}$torr.

XRD showed that peaks of (100), (002), (101), (102) and (110) planes belonged to the pure ZnO as the wurtzite structure, but no RGO-related peaks appeared at 24˚ of the ZnO-RGO hybrid-nanostructures. The SEM images revealed that the sheet-structures appeared in the adding RGO samples and TEM-SAD showed the RGO patterns, suggesting that the RGO was covered by the ZnO nanoparticles which has confirmed the XRD results. Raman spectra exhibited the decreasing ratio of I_D/I_G from 1.2 to 0.8 while the ZnO combined with the RGO, meaning that ZnO fixed the defects inside the RGO and increased the sp^2-carbon domain.

UV-vis. spectra revealed the characteristic peak of ZnO at 375nm, and the absorbance increased with the increasing RGO concentrations. PL spectra exhibited two emission regions at NBE and DLE, and displayed the decreasing tendency while the RGO contents increased, indicating that the recombination of electrons and holes was hindered by the adding of RGO. The specific surface area (BET) showed the increasing profile from 4 to $18.5m^2/g$ while the RGO contents was from 0 to 6400ppm, while the grain size decreased from 31 to 26nm. The results suggested that the RGO could inhibit the grain growth of ZnO, therefore, the BET values increased. The visible light photocatalytic tests revealed that the efficiency of pristine ZnO, $ZnO\text{-}RGO_{400ppm}$, $ZnO\text{-}RGO_{800ppm}$, $ZnO\text{-}RGO_{1600ppm}$, $ZnO\text{-}RGO_{3200ppm}$, $ZnO\text{-}RGO_{6400ppm}$ were 10%, 50%, 94%, 95%, 96%, and 94%, respectively, after 15min illuminating time. Furthermore, the rate constant was smaller than $0.012min^{-1}$ while the RGO was lower than 400ppm. On the other hand, the rate constant larger than $0.04min^{-1}$ while the RGO was higher than 800ppm. Both of which confirmed the results of photocatalytic efficiency. In summary, the RGO should be able to inhibit the recombination of electrons and holes, and increase the BET values, as followed by the enhancing of the photocatalytic efficiency under the visible light.

FP-9 Suppression of Moisture-induced Electrical Instabilities in High-mobility ZnON TFTs Fabricated from HiPIMS-made ZnON Films*, K Thorwarth,* ***Rajesh Ganesan,*** EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Trant,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; H Hug,* EMPA Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Bilek, D McKenzie,* The University of Sydney, Australia

The effects of water absorption on the Thin Film Transistor (TFT) devices fabricated from zinc oxynitride (ZnON) films deposited by direct current magnetron sputtering (DCMS) and high-power impulse magnetron sputtering (HiPIMS) have been investigated. When exposed to moisture at room temperature, DCMS-made ZnON TFTs exhibited a smaller mobility, lower threshold voltage, increased carrier concentration and higher subthreshold slope with a deteriorated electrical stability under positive gate voltage. However, for the set of similar conditions, TFT devices made from HiPIMS-deposited ZnON films exhibited relatively stable electrical characteristics than that of the ones made by DCMS. The enhanced performance of ZnON films deposited by HiPIMS could be attributed to the high film density and the amorphous nature which is free of crystallographic defects. Such film characteristics reduce the formation of oxygen vacancies and the bonding of zinc and nitrogen, and thus hold the efficiency of electrical behavior of the films intact.

FP-12 Tribo-mecanical Characterization of Ti/TiN/AlN Thin Film Produced by HiPIMS*, **Joaquin Oseguera,** D Melo-Máximo,* ITESM-CEM, Mexico*; L Melo,* TRAMES S.A. de C.V., Mexico

High power impulse magnetron sputtering (HiPIMS) has the capability of yielding a highly ionized flux of gas and sputtered materials by applying high power in short pulses to the targets. Ti/TiN/AlN thin films were deposited using a homemade reactor with two non-balanced magnetrons by reactive sputtering; co-deposition was produced on a 4140 T tool steel AISI-SAE designation. From the process, optical emission spectroscopy was performed and the combination of voltage pulses and the current was measured, the parameters process were changed (temperature, gas composition, and adhesion layer). The microstructures of thin solid films were characterized by X-ray diffraction and scanning electron microscopy, scratch tests, hardness and friction coefficients were determined.

FP-13 Synthesis and Characterization of Bismuth Cuprate Thin Films Produced by Co-Sputtering*, D Franco-Pelaez, O Depablos-Rivera,* ***Sandra Rodil,*** Universidad Nacional Autonoma de Mexico, Mexico

One of the most important challenge of the humanity is the production of sustainable energy, the increase in energy consumption and the use of coal reserves could come several environment problems and high cost solutions. Semiconductors based on bismuth oxide present a band gap in the visible light, so is possible to use these materials in the production of hydrogen by photoelectrochemical water splitting. We report the synthesis of cuprate bismuth thin films deposited by reactive magnetron co-sputtering, metallic copper and bismuth oxide (Bi_2O_3) targets were used to deposit cuprate bismuth on FTO (fluorine doped tin oxide), glass (fused silica) and silicon substrates. For the copper target it was necessary to vary the applied power (DC) from 3 to 60 Watts finding that the best option is 10 Watts, while at the bismuth oxide target 30 Watts (RF) were applied. The coatings were grown under reactive environment with Ar: 28 sccm and O_2: 12 sccm and heating the substrates at 200 ° C. However, the as-deposited coatings were amorphous and it was necessary to perform a heat treatment at 500 ° C in static air for 2 hours to obtain the tetragonal structure. The X-ray diffraction confirmed the formation of the tetragonal phase ($CuBi_2O_4$) coexisting with copper oxide, the optical and electronic properties were measurement by UV-VIS spectrometry and Mott- Schottky plots, finding that the optical band gap is ~ 1.4 to 1.6 eV and the films presented an p-type conductivity with a flat band potential of 0.4 eV. The photocurrent was evaluated as a function of the thickness.

Acknowledgements: CONACYT scholarship and project 251279.

FP-14 Synthesis of Zn /ZnO Nanoparticles using Atmospheric Plasma Discharge in Solution to Mitigate the Stress Corrosion Cracking in the Simulated Primary Water Environment*, **Sang-Yul Lee,** S Kim, M Song,* Korea Aerospace University, Republic of Korea*; S Kim,* Korea Institute of Industrial technology, Republic of Korea*; J Kim,* University of Incheon, Republic of Korea

Zn injection is known to cause changes in composition as well as in crystalline morphology of the oxide layers, which is responsible for mitigating corrosion on the Ni-based alloys in the simulated primary water [1]. Conventionally Zn precursors such as dimethyl zinc, diethyl zinc, zinc hydroxide, zinc carbonate, and zinc acetate are used for Zn injection and this, however might cause additional problem due to the formation of other corrosive ions (OH^- , CO_3^{2-}, and CH_3COO^-) [2].

To eliminate this problem, in this study, pure Zn nanoparticles were synthesized by atmosperic plasma discharge process in aqueous solution for the mitigation of primary water stress corrosion cracking (PWSCC). Zn nanoparticles with various sizes were synthesized using SPP and were applied for the treatment of Ni-based alloy samples at simulated primary water environment (300ºC, 150 bar). The Zn treatment duration was controlled in the range from 0 to 240 hours. As-obtained oxide films after various Zn treatment durations were investigated using X-ray diffractometry (XRD) analysis. The Zn-treated and non-treated U-bend type Ni-based alloy samples were subjected to very harsh corrosion test under simulated PWR environments, i n which the conditions were Na_2S of 1.0 M and NaOH of 1.0 M. To measure the corrosion behavior of Zn-treated and non-treated Ni-based alloy samples, electrochemical potential analysis was performed by Potentiostat/Galvanostat. Diffraction patterns exhibited that stable oxide films with a spinel structure of $ZnCr_2O_4$ would form with increasing Zn treatment duration. It is postulated that the exchange reaction between Zn and Fe/Ni cations occurred extensively so that the dense and compact Zn spinel structure responsible for the corrosion inhibition formed [1]. Zn treated Ni-based alloys exhibited a low electrochemical potential (ECP) value comparing with non-treated Ni-based alloys. In addition, the results from U-bend test showed that the PWSCC in Zn-treated Ni-based alloy samples was much retarded comparing with non-treated Ni-based alloys.

[1] J. Huang, X. Liu, E. H. Han, and X. Wu, *Corrosion Science***53**, 3254 (2011)

[2] M. Mahdavian and R. Naderi, *Corrosion Science***53**, 1194 (2011)

Acknowledgement

This work was supported by the National Research Foundation of Korea (NRF) grants funded by the Korea Government (NRF-2016R1D1A1A09918072)

FP-15 Vanadium Nitride Thin Films Grown by High Power Impulse Magnetron Sputtering*, H Hajihoseini,* ***Jon Tomas Gudmundsson****,* University of Iceland, Iceland

Thin vanadium nitride films were grown on SiO_2 by reactive high power impulse magnetron sputtering (HiPIMS). The film properties were compared to films grown by conventional dc magnetron sputtering (dcMS) at similar conditions. We explored the influence of the stationary magnetic confinement field strength on the film properties and the process parameters. Furthermore, for both dcMS and HiPIMS the deposition rate is lower for strong magnetic confinement. Structural characterization was carried out using X-ray diffraction and reflection methods as well as atomic force microscopy (AFM) and scanning electron microscope (SEM). For reactive growth of vanadium nitride the HiPIMS process produces denser films with lower surface roughness than dcMS does. Lowering the magnetic field strength increases the deposition rate significantly for reactive HiPIMS while it increases only slightly in the reactive dcMS case. The films grown by HiPIMS with strong magnetic confinement exhibit higher density and lower roughness. We find that the operating pressure, growth temperature, cathode voltage and film thickness has influence on the properties of HiPIMS grown vanadium nitride films. The films are denser when grown at high temperature and cathode voltage and low pressure < 1 Pa. Density of those films are inversely proportional to its thickness and thicker films consist of larger grain size. In all conditions, higher density coincide with lower surface roughness. Thus, the deposition method, the magnetic field strength, growth temperature, cathode voltage, film thickness and growth pressure have a significant influence on the film quality and structural properties, including the grain size for the various orientations.

Author Index

Bold page numbers indicate presenter