New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F1-1

Nanomaterials and Nanofabrication

Moderators: R. Mohan Sankaran, Case Western Reserve University, Sumit Agarwal, Colorado School of Mines

10:00am **F1-1-1 Sculptured Thin Films by Ion Beam Sputtering*, Bernd Rauschenbach,*** *C Grüner,* Leibniz Institute of Surface Modification, Germany

Nanostructures with a three dimensional tailored shapes are promising candidates for a variety of applications. The sputter induced glancing angle deposition technique is a sophisticated method to create nanostructures with custom-made structure geometries. This new technology is characterized, that the sputtered particle flow arrives the substrate under an extremely grazing angle. In the consequence highly porous thin films are produced, which consist of slanted needles. An additionally constant or periodically interrupted substrate rotation during sputter induced deposition is used to tailor structures like chevrons, posts, circular and quadratic spirals or zig-zags. The structure formation is based on geometric shadowing, where the arriving particle flux is supposed to be caught by the top of structure, and no growth occurs in the structure shadow.

In this presentation a report about the growth nanostructures on non-pattered and regularly arranged nanostructures and the growth conditions is given and some applications of such three-dimensional nanostructures are demonstrated. The growth of the nanostructures is studied in dependence on substrate temperature, substrate pre-patterning, substrate rotation speed, and deposition rate using scanning electron microscopy, X-ray diffraction and high-resolution transmission electron microscopy. The metal and semiconductor nanostructures were grown using ion beam sputter induced GLAD in an ultrahigh vacuum chamber [1-4].

Because this process provides precise nanoscale control over the structure and grain orientation characteristics, the mechanical, magnetic and optical properties of the sculptured films may be engineered for various applications. Finally, recent studies on first applications will be presented [5-6].

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10:20am **F1-1-2 The Effect of Thermal Treatment on the Structure and Surface Plasmon Resonance of Ag-coated ZnO Nanoparticles by Sol-gel Method*, Chih-Chiang Wang,*** National Chung Hsing University, Taiwan*; H Shih,* Chinese Culture University, Taiwan

Zinc oxide (ZnO) is an n-type II-VI semiconductor with a hexagonal wurtzite structure, a wide band gap (3.3 eV) and a higher exciton binding energy (60 meV), and has been applied in the field of ultraviolet or visible optoelectronic devices, photocatalyst, gas sensors, solar cells. On the other hand, silver (Ag) nanoparticles show the variable surface plasmon resonance (SPR) properties by controlling the particles shape, size, and density. In this study, the ZnO nanoparticles were fabricated by sol-gel method at the ambient environment. Subsequent baking was conducted at the 500°C in air. The Ag nanoparticles were coated on the ZnO surface by surface decoration process and baked in the lower pressure condition (~10^{-3} torr) at several temperatures (100, 300, and 500°C).

XRD patterns showed that peaks of (100), (002), (101), (102), (110), (103) planes belonged to the pure ZnO nanoparticles as the wurtzite structure. The peak of (111) plane at 38.1°appeared at the baking temperature of 300 and 500°C indicating that the Ag metal and its grain size increased with the increasing baking temperature. The TEM images and SAD patterns indicated that the Ag-coated ZnO nanoparticles kept the same crystal structure with a prominent facets (002) of the ZnO and (111) of the Ag nanoparticles.

The PL spectra displayed a tendency of blue shift in the UV light emission of 3.18 to 3.2eV and 3.08 to 3.1eV, respectively, while the Ag nanoparticles size increased. The former was the intrinsic emission, and the latter was caused by the V_O^+. Raman spectra revealed the peaks at 99cm^{-1} (E_2^{low}), 331cm^{-1} (multiphonon), 439cm^{-1} (E_2^{high}), and 580cm^{-1} (E_1 LO). The intensity of E_2^{low} mode showed the apparent increasing as the baking temperature increased. However, the intensity of multiphonon, E_2^{high}, and E_1 LO mode revealed the opposite tendency. The binding energy in XPS analysis of the Zn2p$_{3/2}$ and Zn2p$_{1/2}$ were observed at 1021.3 and 1044.8eV, respectively. In addition, the deconvolution of Ag3d$_{5/2}$ showed 368.5 (Ag^0) and 367.4(Ag^+)eV. The ratio (Ag^0/Ag^+) increased with the increasing baking temperature, meaning more Ag metals on the Ag-coated ZnO nanoparticles. The UV-Vis spectrum revealed the noticeable peak centered at λ=420nm due to the SPR effect of Ag nanoparticles, and showed the red shift toλ=460nm as the Ag nanoparticles size increased.

10:40am **F1-1-3 In-situ Electron Microscopy of Synthesis, Chemistry and Self-Assembly of Colloidal Nanostructures*, Eli Sutter,*** University of Nebraska-Lincoln, USA **INVITED**

In-situ microscopy, particularly real-time imaging of dynamic processes has developed into an active field of research and is expected to be one of the key enabling techniques for understanding the formation of nanostructures, catalytic reactions, phase transformations, self-assembly, and other central issues in nanoscience and technology. *In-situ* transmission electron microscopy can be used to follow the behavior and measure the properties of nanostructures over a wide range of environmental conditions with resolution down to the atomic scale. Liquid-cell electron microscopy has developed into a powerful technique that allows the imaging of various processes in wet environments, such as liquids, solutions, or colloidal suspensions, and the investigation not only of a wide range of inorganic nanoscale objects but of biological systems as well.

I will illustrate the power of liquid-cell electron microscopy applied to imaging colloidal synthesis (nanoparticles, core-shell structure), electrochemistry (galvanic replacement reactions) and the self-assembly of nanocrystal superstructures in solution. Our results demonstrate that real-time electron microscopy can substantially advance our understanding of a wide range of processes involving nanoscale objects in bulk liquids.

11:20am **F1-1-5 Deposition of PTFE – TiO_2 Composite Coatings Combining Superhydrophobic and Photocatalytic Properties by Reactive pDC Magnetron Sputtering from a Blended Powder Target*, Marina Ratova,*** *P Kelly, G West,* Manchester Metropolitan University, UK

Photocatalytic materials are used as a sustainable approach to air and water purification, water splitting and decontamination and disinfection of surfaces. Superhydrophilicity (water contact angles of 10° or lower) is one of the widely reported features of titania-based photocatalytic surfaces. However, superhydrophobic surfaces (water contact angles of 150° or higher) are often more desirable for environmental cleaning than superhydrophilic ones, as they prevent adhesion of contaminants and microorganisms to the surface and therefore have an anti-fouling effect that helps to prevent the deterioration of photocatalytic properties.

Typically, coatings combining photocatalytic and superhydrophobic properties are produced using chemical methods, such as hydrothermal, liquid phase deposition, etc. Pulsed DC magnetron sputtering is a well-known method for thin film deposition, and photocatalytic coatings in particular. In this work a reactive pulsed DC magnetron sputtering technique using a blended PTFE – titanium dioxide powder target was employed for the production of photocatalytic superhydrophobic coatings. The surface characteristics and photocatalytic properties of the deposited composite coatings were studied with Raman spectroscopy, optical profilometry and scanning electron microscopy. Hydrophobicity was assessed through measurements of water contact angles, and photocatalytic properties were studied via methylene blue dye degradation under UV irradiation. It was found that variations of gas flow and, hence, process pressures allowed deposition of samples combining superhydrophobicity with stable photocatalytic efficiency under a UV light source. Reversible wettability behaviour was observed with alternating light-dark cycles.

11:40am **F1-1-6 The Mechanisms of Growth of Zr-Fe-O Whiskers***, **Jingjing Gu**,* University of North Texas, USA*; P Petry,* University of Rouen, France*; I Hammood, M Carl, R Reidy, S Aouadi,* University of North Texas, USA

Ceramic whiskers are materials with high melting point, low density, good thermal and electric conductivity, and excellent corrosion-resistant materials. Whiskers are usually selected chosen as a reinforcing material in structural composites. In this presentation, whiskers were created by mixing and pressing nanopowders of ZrC, SiC, Y_2O_3, and Fe_2O_3 carbides. The nano-sized powders were then sintered at 1100°C for 6 hours, which resulted in the formation of Zr-Fe-O whiskers that were a few micometers in diameter and millimeters long. A model is proposed that accounts for the formation of these whiskers and for the thermodynamic processes that control whisker diameter.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F1-2

Nanomaterials and Nanofabrication

Moderators: R. Mohan Sankaran, Case Western Reserve University, Sumit Agarwal, Colorado School of Mines

1:30pm **F1-2-1 Accelerated Development of CuSb(S, Se)$_2$ Thin Film Photovoltaic Device Prototypes***, **Colin Wolden**,* Colorado School of Mines, USA **INVITED**

Development of alternative thin film photovoltaic technologies is an important research topic due to the potential of low-cost, high-efficiency solar cells to produce terawatt levels of clean power. The development of unexplored yet promising absorbers can be hindered by complications that arise during solar cell fabrication. Here, a high-throughput, combinatorial sputtering method is applied to accelerate development of photovoltaic devices based on the novel CuSb(S, Se)$_2$ absorbers. These chalcogenide semiconductors have the appropriate band gap (1.1 -1.3 eV), absorption coefficient (10^5 cm^{-1}), and a hole concentration (~10^{17} cm^{-3}) for use in thin film solar cells. However, there are significant challenges to be overcome for these materials to fulfill their potential, particularly with respect controlling the properties of these ternary compounds and integrating them into solar cell architectures. Here, a high-throughput combinatorial method is applied to accelerate development of both the CuSb(S)$_2$ absorber materials as well as their integration into device structures. This approach revealed a three-stage, self-regulated growth process to control absorber purity and orientation. Device integration employed the $CuIn_xGa_{(1-x)}Se_2$ (CIGS) device architecture, and device development is also explored in a combinatorial as a function of absorber quality and thickness using a variety of back contacts. This study yielded initial CuSb(S, Se)$_2$ device prototypes with ~1% conversion efficiency, which was rapidly elevated to ~5% using the approaches described within. Analysis of device performance provides pathways for future improvements.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F3

2D Materials: Synthesis, Characterization, and Applications

Moderators: Haitao Liu, University of Pittsburgh, USA, Jiaxing Huang, Northwestern University, Liping Wang, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences

2:10pm **F3-3 Tunable MoS_2 and MoS_2-based Electrocatalysts by Hot-injection Method for Hydrogen Evolution Reaction***, **Chia-Ling Wu**, P Huang, S Brahma, J Huang,* National Cheng Kung University, Taiwan*; S Wang,* Southern Taiwan University of Science and Technology, Taiwan

Hydrogen has been considered as one of the most promising renewable energy for production and storage to replace petroleum-based energy. The 2D structure and the presence of several effective active sites make MoS_2 an excellent electrocatalyst for hydrogen evolution reaction (HER). However, the most common syntheses nowadays are not only expensive but also time-consuming. Here, we report an efficient, fast and tunable hot-injection method to prepare MoS_2 and MoS_2-MoO_2 composite with/without tributyl phosphate (TBP). MoO_3 with oleic acid (OA) and S powder with oleylamine (OLA) are used as Mo- and S- precursor, respectively. With increasing reaction temperature and time, OA reorganize the octahedral units of MoO_3 and gradually turn into low valence of Mo. Fourier transform infrared spectroscopy (FT-IR) clearly shows the increase/decrease of the intensity of M=O and 2Mo-O bond vibrations. After injecting S-precursor, OLA first reduces Mo-precursor to MoO_2, and then S atoms replace O atoms to form MoS_2. The addition of a drop of tributyl phosphate (TBP) as surfactant in Mo-precursor significantly accelerate the production of MoS_2 via MoO_2 as the intermediate phase ($MoO_3 \rightarrow MoO_2 \rightarrow MoS_2$). The X-ray diffraction (XRD) (Fig.1) shows that the peaks of MoS_2 dominate by adding TBP, and the peaks of MoS_2 and MoO_2 are equal without adding TBP. Scanning electron microscope (SEM) shows the uniform layer like morphology of nanoscale MoS_2. Transmission electron microscopy (TEM) confirms the existence of few-layer MoS_2 with abundant edge sites (Fig.2) and the core-shell MoS_2-MoO_2 structure (Fig.3), respectively. HR-TEM image shows the MoS_2 (002) plane and d-spacing is measured as 0.62 nm. This simple, flexible and tunable synthesis has large potential for the production of MoS_2 and MoS_2-MoO_2 composite. High purity of MoS_2 and MoS_2-MoO_2 composite can combine with other materials for energy conversion and storage. The detailed electrochemical properties on HER will be reported in future.

2:30pm **F3-4 High-throughput Combinatorial Synthesis and Multimodal X-ray Analysis of Co-based Ternary Alloys***, **Janak Thapa**, C Gross, V Hegde, L Ward, S Naghavi, C Wolverton, Y Chung, M Bedzyk,* Northwestern University, USA

Cobalt-based superalloys have excellent high temperature properties such as creep resistance and chemical inertness during applications at elevated temperatures. Potential applications include high performance jet engine turbine blades and ultra-supercritical steam driven power plants. In this work, we undertook efforts to begin filling in the database gap of Co-based ternary systems. Such a database will facilitate the design and development of Co-based superalloys. We have observed new phases in previously empty regions. We use the naturally scalable techniques of photolithography, DC magnetron sputtering, and high-flux X-ray analysis for high-throughput studies. Gamma and gamma-prime phases, which are essential for high-temperature applications of conventional superalloys, are also being identified. High-throughput DFT is being employed to efficiently determine crystal structures based on X-ray data. These phase diagrams will provide a foundation of understanding to accelerate the creation and implementation of novel Co-based superalloys, and potentially other alloy systems.

2:50pm **F3-5 Development and Characterisation of Cost-Effective Graphene Oxide-Nickel Nanocomposite Coatings***, S Qi, X Li, **Hanshan Dong**,* The University of Birmingham, UK

Graphene is a very attractive new carbon-based coating material due to its extraordinary mechanical, thermal, chemical and optical properties. Notwithstanding the fact that some nano/micro scale studies have shown the potential of graphene as tribological and anti-corrosion coatings on Cu and Ni, its application for coatings on other metallic materials has yet to be fully explored. This is mainly due to the high cost and low yield of pristine graphene produced by exfoliation and the difficulties in transferring CVD-grown graphene films onto 3D real engineering surfaces with necessary bonding. Hence, how to cost-effectively deposit large-area graphene coatings on metallic materials for corrosion and wear protection is a scientifically interesting and technologically important research area.

One possible solution is to use relatively low-cost graphene oxide (GO) in metallic matrix composite. In this work, a nickel/GO composite coating was deposited on steel using a purposely developed electrochemical deposition method to ensure homogenous distribution of GO in the matrix. The deposited Ni/GO coatings were fully characterised using XRD, FIB/SEM, Raman and TEM; their mechanical and tribological properties were evaluated using nano-indentation and friction/wear testing. The thermal stability of the Ni/GO coatings was investigated by thermal annealing at 100, 200, 40 and 600ºC for 30min.

The experimental results reveal that transparent and silk-like graphene oxide sheets are randomly distributed in the Ni matrix. As a result, the hardness and Young's module of Ni coating can be increased by 56% and 29% respectively due to the reinforcement and refinement of the matrix by GO sheets; the coefficient of friction is reduced from 0.6 for Ni to 0.4 for the Ni/GO nanocomposites and the wear rate is reduced by about 90%. Most importantly, the thermal stability of Ni coating can be significantly improved by adding GO. For example, when annealed at 400ºC for 30min, while the hardness of Ni coating was reduced by 36% no appreciable reduction in hardness was observed for the Ni/GO nanocomposite coatings.

3:10pm **F3-6 Fabrication of Functional Graphene Reinforced Polyurethane Nanocomposite Coatings with Regular Textures for Corrosion Inhibition***, **Wenjie Zhao**,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

In order to further enhance its anti-corrosion properties as a surface coating for protecting various materials from corrosion, polyurethane (PU) needs to be modified by adjusting the chemical composition and interface structure. In this work, a series of functionalized graphene (FG) reinforced PU nanocomposite coatings with regular texture were fabricated using a replication method. The structural and morphological properties of the as-prepared PU composite coatings were characterized by Fourier transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectrometer, transmission electron microscopy, scanning electron microscopy and atomic force microscopy. Results showed that FG was dispersed homogeneously in the PU matrix after chemical modification. Moreover, the morphology of the obtained coatings showed a circular cone with a diameter of 8 µm spaced 8, 6 and 4 µm apart, respectively. Most importantly, the presence of surface texture and well-dispersed FG effectively enhanced the anti-corrosion properties of the textured FG/PU composite coating. It is attributed to the hydrophobicity and barrier effect of the obtained coatings, which not only reduce the contact and interaction between water and the surfaces, but also increase the tortuosity of the corrosive medium diffusion pathway.

3:30pm **F3-7 Structure and Tribological Properties of TiSiCN Coatings Incorporated with Layered Structure of MAX Phase in Artificial Seawater***, **Jinlong Li**, Y Wang, C Dang, L Wang, Q Xue,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

The TiSiCN coatings were fabricated on Ti6Al4V alloy by arc ion plating at 500 º C. In order to obtain a MAX phase with like graphic layered structure, the different bias voltages were employed during the deposition of the TiSiCN coating. The structure of the TiSiCN coating were characterized using Scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Transmission electron microscopy. The hardness and tribological properties of the TiSiCN coating were evaluated by nanoindentation, potentiostat and ball-on-plate wear tests. All TiSiCN coating shows a coupled structure of a TiN nanocystallite / Si_3N_4 amorphous. When the negative bias voltage increases to 100 V, some Ti_3SiC_2 MAX phase with a like graphic layered structure also is found in the TiSiCN coating. The TiSiCN coating has a higher hardness of 40 GPa. The MAX phase with a layered structure contributes to significantly decrease of the friction coefficient and wear rate of the TiSiCN coating. The imposed protection potential has a positive effect on protecting the coating from electrochemical corrosion. However, the cracks inside the coating will accelerate the coating failure.

3:50pm **F3-8 Graphene: Improving Material Performance by Keeping the Surface Cleaning***, **Haitao Liu**,* University of Pittsburgh, USA

Recent studies showed that graphitic materials can be easily contaminated by airborne and waterborne hydrocarbons. In this talk, I will discuss ways to protect a graphitic surface from airborne contamination. It was shown that a monolayer thick of water film significantly slows down the adsorption of airborne hydrocarbon. The water-protected graphitic surface showed extreme high electrochemical activity; the measured heterogeneous electron transfer rate is even higher than that of a Pt electrode.These results highlight the potential to achieve intrinsic material properties of graphitic materials under ambient environments.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F2-1

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Tomas Kubart, Uppsala University, Angstrom Laboratory, Sweden

8:00am **F2-1-1 An Ionization Region Model of the Reactive Ar/O$_2$ High Power Impulse Magnetron Sputtering Discharge***, **Jon Gudmundsson**,* University of Iceland, Iceland*; D Lundin,* CNRS, Université Paris-Sud, France*; N Brenning, M Raadu, C Huo,* KTH - Royal Institute of Technology, Sweden*; T Minea,* CNRS, Université Paris-Sud, France

In the reactive high power impulse magnetron sputtering discharge experimental findings indicate that there is a significant increase in the discharge current and this current increase appears to follow one of two paths as the discharge enters the poisoned mode. On one hand the current waveform becomes distinctly triangular in shape and on the other hand the current maintains the shape of the non-reactive waveform [1,2]. A reactive ionization region model (R-IRM) is developed to describe the reactive Ar/O$_2$ high power impulse magnetron sputtering (HiPIMS) discharge with titanium target [3]. It is then applied to study the temporal behaviour of the discharge plasma parameters such as electron density, the neutral and ion composition, the ionization fraction of the sputtered vapour and the oxygen dissociation fraction. We study and compare the discharge properties when the discharge is operated in two well established operating modes, the metal mode and the poisoned mode. Using the R-IRM we find that when the discharge is operated in the metal mode Ar$^+$ and Ti$^+$ -ions contribute most significantly (roughly equal amounts) to the discharge current while in the poisoned mode the Ar$^+$-ions contribute most significantly to the discharge current while the contribution of O$^+$ -ions and secondary electron emission is much smaller. Furthermore, we find that recycling of atoms coming from the target, and subsequently ionized, are required for the current generation in both modes of operation. In the metal mode self-sputter recycling dominates and in the poisoned mode working gas recycling dominates, and it is concluded that the dominating type of recycling determines the discharge current waveform.

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8:20am **F2-1-2 Residual Stress Control of Al-rich (Ti,Al)N Hard Coatings by Pulse Duration in High Power Impulse Magnetron Sputtering***, **Tetsuhide Shimizu**, S Takahashi, H Komiya,* Tokyo Metropolitan Univeristy, Japan*; Y Teranishi, K Morikawa,* Tokyo Metropolitan Industrial Technology Research Institute, Japan*; M Yang,* Tokyo Metropolitan Univeristy, Japan*; U Helmersson,* Linköping University, IFM, Sweden

A present study demonstrates the controllability of residual stress of deposited ternary nitride films by regulating pulse duration in high power impulse magnetron sputtering (HiPIMS). Optical emission spectrum (OES) measurements were firstly performed in the plasma of Al-rich Ti$_{0.33}$Al$_{0.67}$ alloy sputtered in an Ar/ N$_2$ gas mixture to analyze ion and excited neutral densities at different peak current intensities and plasma compositions. Based on the OES spectra, specific pulse conditions of 100, 200 and 1000 µs with a same pulse off time of 3000 µs were chosen to deposit (Ti, Al)N films on Si (100) wafer. Residual stress of the deposited films was estimated by a deflection of 50 µm-thick thin glass sheets. Chemical composition, surface morphology and phase composition of the films were analyzed by an energy dispersive spectroscopy, an atomic force microscopy and X-ray diffraction, respectively. Mechanical properties were characterized by using nanoindentation. As results, clear gradual variation from tensile to compressive stress was demonstrated by varying pulse duration from 1000 to 100 µs. A compressive stress was found in the film grown using the shortest pulse duration of 100 µs, which also had the highest Ti ion-to-neutral ratio, while the pulse duration of 200 µs and 1000 µs showed the tensile stress. In particular, the pulse duration of 200 µs showed almost no residual stress but the highest hardness with highest crystallinity of mixed cubic and hexagonal phase. The cause of these tendencies in residual stress between different pulse duration was discussed based on the effect of ionization degree of sputtered species and compositions of the gas and metallic ions in the discharge plasma.

8:40am **F2-1-3 Energetic Deposition of Electronic Materials***, **Jim Partridge**, B Murdoch, N McDougall, D McCulloch,* RMIT University, Australia*; R Ganesan, M Bilek, D McKenzie,* The University of Sydney, Australia*; M Tucker, N Marks,* Curtin University, Australia **INVITED**

Energetic deposition provides increased control over the micro-structural, electrical and optical properties of thin films. In our work, high power impulse magnetron sputtering (HiPIMS) and filtered cathodic vacuum arc deposition systems have been employed to form high quality metal oxide and carbonaceous materials. Electronic and optical applications for these materials including transparent thin film transistors, photo-detection and resistive memory storage devices have been explored. Process and film characteristics will be discussed for materials including ZnO, HfO$_2$, HfO$_x$N$_y$, BN and C. In particular, the plasma and target conditions during HiPIMS growth of metal oxides and carbonaceous materials will be related to microstructural, electronic and optical measurements performed on the films produced. In addition, work will be presented in which ab initio calculations and X-ray absorption spectroscopy have been employed to characterise defects in energetically grown hBN.

9:20am **F2-1-5 Controlled Reactive HiPIMS of Thermochromic VO$_2$ Films at a Low Deposition Temperature (300 °C)***, **David Kolenaty**, J Vlcek, T Kozak, J Houška, R Čerstvý,* University of West Bohemia, Czech Republic

Vanadium dioxide (VO$_2$) is the most interesting thermochromic material due to its reversible phase transition from semiconducting IR transparent state (monoclinic structure) to metallic IR reflective state (tetragonal structure) at around 68 °C. A high IR transmittance modulation makes the VO$_2$–based films a suitable candidate for optical switching applications, such as self-tunable infrared filters, temperature sensing devices and “smart” windows regulating the solar transmission. Current drawbacks limiting the application potential of the VO$_2$ films include high deposition temperatures (> 400 °C) of the films and the necessity to use a substrate bias potential in the case of their magnetron sputter deposition.

Reactive HiPIMS with a feed-back pulsed reactive gas (oxygen) flow control and an optimized location of the oxygen gas inlets in front of the target and their orientation toward the substrate made it possible to form crystalline thermochromic VO$_2$ films at very high values of the maximum target power density of up to 5 kWcm^{-2} in a pulse. The thermochromic VO$_2$ films (80 nm thick) were deposited onto floating glass substrates without any nucleation–promoting “seed” layer at the temperature of 300 °C. The depositions were performed using a strongly unbalanced magnetron with an indirectly water-cooled planar vanadium target (50.8 mm in diameter) in argon-oxygen gas mixtures at the argon pressure of 1 Pa. The duty cycle was set to a constant value of 1%, the voltage pulse durations were 50 µs and 80 µs, and the corresponding repetition frequencies were 200 Hz and 125 Hz, respectively. The deposition-averaged target power density was approximately 13 Wcm^{-2}. The target-to-substrate distance was 150 mm.

The phase composition of the VO$_2$ films was determined by X-ray diffraction. The thermochromic behavior of the films was investigated using a spectrophotometer and spectroscopic ellipsometer equipped with custom designed heat cells to control the measurement temperature of the samples from 25 °C to 100 °C. The temperature-dependent electrical resistivity of the films was measured by a four-point probe. The time-averaged energy distributions of positive ions were measured with an energy-resolved mass spectrometer placed at the substrate position.

The VO$_2$ films prepared at the voltage pulse duration of 50 µs exhibited a high IR modulation (ΔT_{2500nm} ~ 45% between 25 °C and 90 °C), an optical transmittance of about 40 % in the visible region, a large drop in the electrical resistivity (from 5.5×10^{-3} Ωm to 1.5×10^{-5} Ωm) after the semiconductor-to-metal transition, and a lower transition temperature of 58 ˚C than the bulk VO$_2$ (68 ˚C).

9:40am **F2-1-6 High Power Impulse Plasma Magnetron Sputtering – Dawn of Industrialization***, W Gajewski, P Rozanski, P Lesiuk, P Ozimek, **Rafal Bugyi**,* TRUMPF Huettinger Sp. z o.o., Poland

Since the first presentation of the High Power Impulse Magnetron Sputtering (HiPIMS) idea by *Kouznetsov and co-workers* in 1999 the basic architecture of a DC-charged capacitor bank dissipating periodically its energy into the plasma in pulses evolved to a sophisticated electronic device commercially available for industry. In order to meet rigorous requirements of industrial application, engineers have proposed different modifications of HiPIMS power delivery units to make the pulse shape and duration independent on the size of the capacitor bank and time-dependent plasma impedance. Since typically pulses longer than 100 µs are required to reach metal self-sputtering regime, a precise control of voltage and current pulse shape is required during the whole pulse length. Furthermore, for tuning ionization of the plasma species and deposition rate flexibility in power delivery regulation is of a key importance.

This contribution provides a series of case-study examples where HIPIMS was tested and qualified for industrial applications. First, the examples from the hard and decorative coating applications will be discussed. Using the basic facts about the HIPIMS plasma parameters the influence of the modified rectangular-like current peak on the plasma composition and dynamics will analyzed. As next, a novel approach of a flexible and application selectable HiPIMS power delivery control will be presented: *(i)* peak current regulation, *(ii)* pulse frequency, and *(iii)* pulse length. The in-field experiments data will be used to discuss the influence of peak current regulation on the ionization degree of the sputtered species as well as the influence of frequency regulation on the deposition rate.

Finally, tests performed in reactive processes both on metallic and ceramic target materials will complete the discussion on HIPIMS industrialization demonstrating the importance of fast arc detection and suppression algorithms required for a long term stability of industrial processes.

10:00am **F2-1-7 Comparison of CrN from Planar and Rotating Target using Highly Ionized Processes**, ***Holger Gerdes***, *A Themelis, R Bandorf, M Vergöhl, G Braeuer,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

CrN is used in many industrial applications. It provides good electrical conductivity, high hardness, corrosion resistance and high temperature stability. As known from many other investigations high power impulse magnetron sputtering (HIPIMS) lead to significant improved properties.

This presentation will discuss the influence of different HIPIMS techniques on the adhesion, hardness and composition of the thin film. Therefore, the gas composition (ratio between Ar and N2), the working pressure were changed. Additionally, the influence of the sputtering plant and target geometry was investigated. Two sputtering plants were used. The first one, a lab scale one, was equipped with a planar target (132 mm x 224 mm) and the second one with a planar (130 mm x 470 mm) and a rotating (Length of 500 mm) target.

While conventional processes require temperatures in the range of 250 °C and additional biasing the presented films all showed hardness values up to 2900 HV without substrate bias or additional heating.

10:20am **F2-1-8 Molybdenum Thin Films Deposited by High Power Impulse Magnetron Sputtering**, ***Arutiun P. Ehiasarian***, *D Loch,* Sheffield Hallam University, UK

Molybdenum thin films used in chalcopyrite solar cells can influence the Na diffusion rates and the texture of the Cu(InGa)Se_2 absorber according to the microstructure and morphology. The lowest resistivity films are achieved at low working pressure and are accompanied by high residual stress and poor adhesion due to the resulting high energy of the deposited flux. High Power Impulse Magnetron Sputtering was employed to ionise the sputtered flux, achieve high adatom mobility at low energy and influence the growth of Mo back contacts. Pulse durations in the range 60 to 1000 µs, sputtering voltages between 800 and 1500 V and deposition pressures of 2×10^{-3} mbar and 4×10^{-3} mbar resulted in ten-fold variations in the flux ratios of Mo^{1+}/Mo^{0} Mo^{2+}/Mo^{1+}, Ar^{2+}/Ar^{1+} and Mo^{1+}/Ar^{1+} as determined by optical emission spectroscopy and time-resolved plasma-sampling energy-resolved mass spectroscopy. The energy of metal and gas double- and single-charged ions reduced with pulse duration and increased with voltage. The microstructure of the films varied from open columnar with faceted tops to fully dense as observed by secondary electron microscopy. The reflectivity of the films improved by 20% compared to industry-standard materials. The lowest resistivity was in the range of 12 µΩ-cm as observed by four-point probe measurements of 570 nm thick films. The correlation between resistivity, microstructure, crystallographic texture and deposition flux characteristics is discussed.

10:40am **F2-1-9 Epitaxial Growth of Copper Thin Films on Si(001) by HiPIMS**, ***Felipe Cemin,*** Université Paris Sud, France*; G Abadias,* Université de Poitiers, France*; D Lundin, T Minea,* Université Paris-Sud, France

The heteroepitaxial growth of metallic thin films on semiconductor substrates is usually required to provide a special growth direction for subsequent deposition of magnetic ultrathin layers or to reduce the dislocation density of lattice mismatched heterostructures. However, epitaxial relationship may be only obtained if the substrate surface is free of native oxides and contaminants, i.e., an atomic cleaning process is required. Conventional pre-treatment methods include the heating of the substrate at relatively high temperatures (800 °C) and the creation of a hydrogen-termination layer on the substrate surface through chemical etching with hydrofluoric acid. In this contribution we report a new route to grow epitaxial copper thin films at room temperature on silicon(001) wafers covered with native oxide without any prior substrate cleaning process. This method consists in a single-step deposition using high power impulse magnetron sputtering (HiPIMS) and substrate biasing. The studied Cu thin films were deposited onto Si(001) wafers by HiPIMS and conventional direct current magnetron sputtering (DCMS) at different substrate bias voltages. The stress evolution during deposition was monitored *in situ* using the real-time wafer curvature method. The as-deposited Cu films were characterized *ex situ* by X-ray diffraction, focused ion beam scanning electron microscopy, electron backscattering diffraction and atomic force microscopy. It was found that for higher bias voltages, a Cu/Si epitaxial growth is achieved following the Cu(001) [100] // Si(001) [110] orientation relationship in HiPIMS films, while polycrystalline Cu films with [111] preferred orientation are obtained using a DCMS discharge under the same deposition conditions. Detailed investigation of the film structure correlated with the intrinsic stress measurements shows that the substrate bias voltage affects the early growth stages of HiPIMS Cu films on Si, and thus their final microstructures.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F2-2

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Tomas Kubart, Uppsala University, Angstrom Laboratory, Sweden

1:50pm **F2-2-2 HPPMS Deposition from Composite Targets: Effect of Two Order of Magnitude Target Power Density Changes on the Composition of Sputtered Cr-Al-C Thin Films***, **Holger Rueß,*** RWTH Aachen University, Germany*; M to Baben,* GTT-Technologies, Germany*; L Shang,* RWTH Aachen University, Germany*; P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; M Hans,* RWTH Aachen University, Germany*; D Primetzhofer,* Uppsala University, Sweden*; J Schneider,* RWTH Aachen University, Germany

Magnetron sputtering techniques are widely used to synthesize a large number of coatings either from elemental, compound or composite targets. Coatings synthesized by direct current magnetron sputtering (DCMS) from the latter two targets often exhibit a considerable compositional deviation from the target composition, in particular, for targets containing constituents with significant mass differences [1,2]. However, for high power pulse magnetron sputtering (HPPMS), where in contrast to DCMS, a large fraction of film forming species is ionized, the magnitude of compositional deviations has not been investigated.

Hence, the effect of target power density on the composition of sputtered thin films from a Cr–Al–Cr_3C_2 composite target, as Cr, Al and C exhibit significant mass differences, was studied by utilizing DCMS (2.3 W/cm²) and HPPMS (162 and 373 W/cm²) at various substrate bias potentials and temperatures. Independent of the applied power density at the target, all Cr–Al–C thin films deposited at floating substrate potential showed no differences in composition. As the target power density was increased and a substrate bias potential was applied, aluminum deficiencies of up to 18.3 at.% were measured. Based on the measured ion currents at the substrate, preferential re-sputtering of aluminum was suggested to cause the dramatic Al depletion. As the substrate temperature was increased with an applied substrate bias potential of -100 V, the Al concentration was reduced by 8.4 at.% compared to the room temperature deposition. This may be rationalized by thermally induced desorption in addition to the afore mentioned re-sputtering effect.

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2:10pm **F2-2-3 Adherent and Hard DLC Coatings Deposited by HiPIMS in Deep Oscillations Magnetron Sputtering (DOMS) Mode***, **Fábio Ferreira,*** University of Coimbra, Portugal*; A Aijaz, T Kubart,* Uppsala University, Angstrom Laboratory, Sweden*; A Cavaleiro, J Oliveira,* University of Coimbra, Portugal

Diamond-like carbon coatings (DLC) make up the largest proportion of thin film coating solutions applied in the automotive industry, notably for engine applications, drivetrain components and transmission parts. DLC combine high hardness with low friction coefficient, chemical inertness, high thermal conductivity and high refractive index, making them very attractive for a wide range of other applications. In order to comply with the current trends of rising operating temperatures and lower viscosity oils, component manufacturer are currently seeking to develop a new generation of DLCs coatings, with improved properties. The main limitations of the existing DLC solutions stem from high internal stresses and limited thermal stability. The stresses, often in excess of 10 GPa, limit the maximum achievable thickness of hard H-free DLCs due to adhesion problems. H containing DLC coatings, on the other hand, have lower hardness and are typically restricted to operating temperatures below 350ºC. The main objective of this work is to develop a new generation of significantly improved well-adherent and hard DLC coatings, with high sp3/sp2 ratio and good temperature stability. DLC films were deposited by deep oscillation magnetron sputtering (DOMS), a variant of high power impulse magnetron sputtering (HIPIMS). The bombardment energy was controlled by changing the substrate bias. In order to improve the film's adhesion an interlayer was deposited. In this work, the microstructure of the films was characterized using scanning electron microscopy, Raman spectroscopy and X-ray reflectivity. The mechanical properties (Hardness and Young´s modulus) of the films were also characterized.

2:30pm **F2-2-4 Variation of Local Chemical Compositions of (Ti, Al)N Films on Inner Wall of Small Hole deposited by High Power Impulse Magnetron Sputtering***, **Hidetoshi Komiya,*** *T Shimizu,* Tokyo Metropolitan Univeristy, Japan*; Y Teranishi, K Morikawa, M Yang,* Tokyo Metropolitan Industrial Technology Research Institute, Japan

To enhance the tool life as in industrial scale, thin films with anti-adhesive and high wear toughness are required to deposit uniformly on the three-dimensional complicated shape structure. Focusing on the great possibility of high power impulse magnetron sputtering (HiPIMS), the authors have demonstrated its availability and advantages for the industrial applications [1-3]. For the further improvement of film quality the present study focused on controlling chemical composition of thin film at inner wall of sub-millimeter scale small hole, which is specifically important for the crystal phase and mechanical properties. The small hole structure was realized by clamping the comb-shaped stainless steel plate with two flat silicon wafer substrates. To characterize the films properties at different position of inner wall depth, the several analytical techniques were performed. Surface morphology and cross-sectional microstructure of the films on the inner wall were observed using field emission scanning electron microscopy (FE-SEM). Cross-sectional SEM observation was prepared by focused ion beam (FIB). Additionally, the local chemical composition of the (Ti,Al)N films at each position of inner wall depth was analyzed by energy dispersive X-ray spectroscopy coupled with FE-SEM (SEM-EDX), which can achieve the local elemental analysis at micrometer-scaled area on the inner wall. As results, increasing tendency of atomic composition ratio of Ti and that of N / (Ti+ Al) were shown at deeper position of the inner wall. The role of ionization degree of sputtered species and its transportation and distribution into the small-hole structure are discussed by comparing with the film deposited by conventional dc magnetron sputtering.

References

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[2] T.Shimizu et al., *Thin Solid Films*, 581 (2015) pp.39-47

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2:50pm **F2-2-5 A Feasibility Study on the Large-area Graphene Growth by using High Power Impulse Magnetron Sputtering (HIPIMS)***, C Pandey, M Po, D Liou, M Chen, Y Chen,* ***Ju-Liang He,*** Feng Chia University, Taiwan

High Power Impulse Magnetron Sputtering (HIPIMS), known to produce high density plasmas, is utilized to energize carbon ions from graphite substrate as cathode. for growth of large area graphene.

In this work, we aimed at depositing graphene on Copper and Silicon wafer using HIPIMS at temperatures up to 500ºC and substrate bias up to -800V. Vacuum pressures of 0.1 – 0.4 mTorr and deposition times of 5 minutes and 10 seconds were used. At 500ºC and the substrate bias set at -800V, a 7-8 layered graphene film on Copper was obtained for a deposition time of 5 seconds. An interesting feature observed using Optical Emission Spectroscopy showed that increasing the peak power increased the presence of Carbon-ion species in the plasma.

Raman spectroscopy and Raman mapping were carried out to analyze the G, D and 2D band information and I_{2D}/I_G ratios for the samples for qualitative analysis of the graphene layers respectively.

The construction of the synthesized graphene was analyzed through TEM micrographs. At zero substrate bias, amorphous carbon film was deposited on the copper substrate whereas when biased at -800V, multiple layers of graphene were deposited with a thickness of 0.33 nm .

This study showed that modifying the substrate temperature and the biasing voltage has a significant effect on the deposition of carbon atoms on the surface of copper or silicon even at low temperature of 500ºC as compared to the high temperatures used in CVD techniques.

New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F5

Additive-manufacturing-based Methods and Surface Engineering

Moderators: Ramana Chintalapalle, University of Texas at El Paso, Sven Ulrich, Karlsruhe Institute of Technology (KIT)

3:30pm **F5-7 3D-Painted Metals and Alloys: A New Approach to Metal and Alloy Advanced Manufacturing**, *A Jakus, S Taylor,* ***Nicholas Geisendorfer****, D Dunand, R Shah,* Northwestern University, USA

We present a alternative technology to traditional laser and e-beam based metal and alloy additive manufacturing (AM) approaches that utilizes room-temperature extrusion of particle-based liquid inks comprised of metal oxide powder(s), elastomeric binder, and graded volatility solvents to create self-supporting, complex constructs that can be thermochemically reduced and sintered, resulting in metallic constructs. This particular ink formulation results in 3D-printed green bodies that, although comprised of up to 90 vol.% metal, alloy, and/or metal compound particles, can be bent, rolled, folded, cut, and even fused with other similar materials using the ink as an adhesive. The inks may also be used to rapidly create flexible, conformal films via dip-coating and other non-3D-printing methods. We demonstrate that this process can be applied to a variety of ferrous and non-ferrous primary metal and alloy systems to create objects as small as a single cubic millimeter and as large as many cubic centimeters, comprised of structural features as small as 100 µm. In this manner, nano- and micron-scale oxide powders, which are generally far more economical than their metallic or pre-alloyed powder counterparts, can be utilized to rapidly create large scale, user-defined architectures. Mechanical testing of 3D-printed oxide green bodies reveals that tensile and compressive strengths and moduli depend heavily on the concentration of particles within the construct, as well as the size of the comprising particles. None of the green bodies tested, including those comprised of 90 vol.% particles, catastrophically fail under compressive loads, but rather, plastically deform. Inks comprised of a variety of metals - including but not limited to those of iron, nickel, copper, tungsten - are presented along with inks comprised of mixed oxides corresponding to desired final binary and ternary alloy compositions. Oxide green bodies are thermochemically reduced in pure H_2 atmosphere at elevated temperatures to metals and alloys, which then continue to be sintered in H_2 or inert atmosphere. The resulting metallic constructs, although volumetrically reduced due to sintering and to oxide-to-metal density changes, retain their originally shapes without warping, cracking, or sagging. Metallographic and electron microscopic analyses of the resulting metal and alloy structures reveal near fully dense metallic constructs can be achieved with the majority of the systems tested. Finally, we show how this process can be extended towards creating complex, multi-metal/alloy constructs through co-3D-printing of multiple liquid oxide inks.

3:50pm **F5-8 3D Printing of 2D Materials***, A Juhl,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; A Stroud,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA*; W Lai,* University of Dayton/Sensors Directorate, Air Force Research Laboratory, USA*; S Kim,* Human Effectiveness Directorate, Air Force Research Laboratory, USA*; N Glavin, R Berry, G Leuty,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; R Naik,* Human Effectiveness Directorate, Air Force Research Laboratory, USA*; M Durstock,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; P DeRosa,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA*; E Heckman,* Sensors Directorate, Air Force Research Laboratory, USA*;* ***Christopher Muratore****,* University of Dayton, USA

Alternative materials and fabrication techniques are necessary to revolutionize the performance of large scale flexible electronics. Direct printing of electro-optical devices is a promising new fabrication approach, especially for integration of emerging two dimensional (2D) materials which have uncommon and useful combinations of properties, such as tunable band gaps, mechanical flexibility and optical transparency. However, challenges in conventional printing of suspended 2D particles and low performance of printed circuits remain. Here we describe a printing technique based on a novel a selective molecular attachment (SMA) approach for integration of 2D and other materials into printed circuits or devices. Peptide molecules have been identified via phage display techniques that adhere selectively to semiconducting few-layer MoS_2 flakes and graphene. These peptides are dissolved in 'ink' and printed on insulating surfaces to print transistors and other devices. The printed substrates are then dipped in suspensions of graphene and MoS_2 and the particles stick only to the peptide printed surfaces. Simulations of the peptide surface interactions reveal the specific amino acids that bind to substrate and particle. For example we observe that for the HLL peptide adsorbed on MoS_2, the phenylalanine ring had the closest binding position of any amino acid. The other ring residue structures, histidine and the two prolines, were also shown to very close to the surface. The n-term, c-term, and arginine residues were seen to migrate away from the surface. This knowledge enables design of peptides for enhanced adhesion and also for sensing of target molecules in vapor or solution phase. It is anticipated that the exotic combinations of properties found in 2D materials will add unique functionality to devices over standard printed materials and architectures. Here we demonstrate the technique and explore the peptide-surface interactions in SMA processes.

4:10pm **F5-9 Direct Laser Deposition of High Entropy Alloy Coatings on High Temperature Alloys**, ***Daniel Fabijanic****, Q Chao,* Deakin University, Australia*; T Jarvis, X Wu,* Monash University, Australia*; P Hodgson,* Deakin University, Australia

High entropy alloys (HEAs) are relatively a new alloy system comprising of a minimum of 5 principle alloy elements at a concentration between 5-35 atomic percent. Contrary to phase rule prediction many HEA compositions form simple solid solutions. HEAs have attractive properties as bulk or coating materials in elevated temperature applications: high resistance to thermal softening, thermally stable microstructure, low inter-diffusion, and high oxidation resistance. Limited studies have explored the formation of HEA coatings on steel substrates by laser surface melting a static layer of pre-alloyed powders. This technique is restricted to horizontal surfaces, limiting practical implementation. To clad complex shapes an appropriate technique is "blown powder" additive manufacturing (Direct laser deposition, DLD) where powder is delivered to a focused laser on a controllable head. The formation of HEA coatings by this technique is unreported in the literature. This work addresses two main research questions; *Can chemically homogenous coatings be manufactured by the DLD of a blend of 5 elemental powders?* and *Can the DLD process parameters be controlled to eliminate the dilution effect of the substrate?*.

$Al_xCoCrFeNi$ (x=0.3, 0.6 and 0.9) HEA coatings of were produced by single-pass DLD on 253MA austenitic steel and Inconel 600 superalloy using a mixture of blended elemental powders. A three-level parametric study was performed on key variables: laser power, scan speed, spot size, powder feed rate, focal offset and hatch distance. Through thickness elemental composition (GDOES) and phase analysis (XRD) was determined. The coating microstructure (SEM, AsB detector), local homogeneity (EDS) and properties (microhardness) were obtained in cross-section. Increasing Al mole fraction from 0.3 to 0.6 and 0.85 resulted in a change in HEA coating crystal structures from FCC, FCC/BCC and BCC. The compositional mixing between the deposited layer and the substrate was quantified using a proposed mixing factor, which was significantly influenced by the deposition variables, chiefly powder feed rate. Homogenous HEA coating compositions were obtained at a relatively higher powder feed rate.

4:30pm **F5-10 In-situ Impedance Spectroscopy Evaluation of Electrolytic Plasma Polishing Process for Stainless Steels***, V Mukaeva, E Parfenov, R Nevyantseva,* Ufa State Aviation Technical University, Russian Federation*; A Matthews,* ***Aleksey Yerokhin****,* University of Manchester, UK

Electrolytic Plasma Polishing (EPPo) is currently attracting increasing attention due its ability to provide excellent surface finish to components manufactured by various methods, including 3D printing parts of stainless steels, Ti, Cu and Ni alloys. The method is based on anodic dissolution of metals combined with sputtering by glow discharge which is developed in the Vapour Gaseous Envelope (VGE) formed at the surface of the working electrode under the conditions of high-voltage electrolysis. However, how these two different material removal mechanisms coexist and interact with each other remains unclear. To elucidate these relationships in-situ impedance spectroscopy studies of the EPPo process of AISI 420 stainless steel have performed. The impedance spectra have been acquired for the treatments carried out at voltages and temperatures ranging from 250 to 350 V and 70 to 90 ºC respectively. Based on the analysis of impedance spectra, an equivalent circuit was developed, including three kinetic processes with different time constants representing charge transport through the VGE by normal conduction and plasma discharge mechanisms followed by charge transfer across the interface with the metal anode. Physical meanings of the circuit elements have been discussed and dependencies on processing parameters established. These dependencies have been correlated with kinetic characteristics of material removal and quality of surface finish achieved. As a result, optimum conditions for EPPo treatment of AISI 420 stainless steel have been established.

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

Functional Oxide and Oxynitride Coatings

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

8:00am **F4-1-1 Development of Microstructure, Phase Composition and Residual Stresses during Plasma Electrolytic Oxidation (PEO) of Aluminium Alloys***, **Etienne Bousser**, A Yerokhin,* The Univ. of Manchester, UK*; T Schmitt,* École Polytechnique de Montréal, Canada*; A Gholinia, J Donoghue,* The Univ. of Manchester, UK*; D Asquith,* Sheffield Hallam Univ., UK*; A Jarvis,* Univ. of Sheffield, UK*; P Withers, A Matthews,* The Univ. of Manchester, UK

Aluminium alloys are widely used for their high specific strength but because of their lower hardness, these alloys often present a less than ideal resistance to surface degradation. In order to improve the tribo-mechanical behaviour of these materials, Plasma Electrolytic Oxidation (PEO) has been shown to offer better wear performance through increased hardness due to the formation of hard crystalline phases during the oxide growth process at near-to-ambient bulk metal temperatures. Indeed, these coatings are typically non-uniform with a shallow porous top layer which sits on a thicker, dense layer comprising of a mixture of polycrystalline and amorphous oxide phases. In this paper, we investigate the evolution of microstructure, phase content and residual stress states in Al_2O_3 layers formed on aluminium alloys using Pulsed Bipolar PEO processes.

In order to understand the evolution of surface layer microstructure and phase composition during PEO treatments, the layers formed at different process durations were evaluated. In order to characterise appreciable changes in microstructure and crystallography of the formed oxide phases over a small range, the surface layers were characterised by cross-sectional Scanning Electron Microscopy (SEM) while the phase composition and strain states were evaluated by laboratory- and synchrotron-based depth-resolved Grazing Angle X-Ray Diffraction (GAXRD) measurements. Moreover, in order to observe the effects of thermal gradients during coating deposition on the occurrence, size and distribution of the different alumina phases (alpha, gamma and amorphous phases) within the coating microstructure, high resolution Electron Back-Scattered Diffraction (EBSD) was carried out on the coating cross-sections prepared by Xe^+ ion Plasma FIB serial-sectioning and broad Ar^+ ion beam milling.

In this study, we will show that the microstructure and phase content is strongly dependent on the processing method through variations in temperature flux within the forming oxide layer. In addition, the complex distribution of residual stresses as a function of depth and phase content is presented. We will show that overall low compressive residual stresses are present in the coating and are balanced by tensile stresses in the substrate. Finally, it appears that the gamma to alpha phase transformation, which occurs in the inner region of the coating, leads to relaxation of internal stresses in the gamma phase matrix.

8:20am **F4-1-2 Influence of Transition Metal Dopants on the Reactive Sputtering Process of Al_2O_3 Thin Films and their Oxidation Resistance**, ***Bernhard Kohlhauser**, H Riedl, C Koller,* Institute of Materials Science and Tech., TU Wien, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; V Paneta, D Primetzhofer,* Uppsala University, Sweden*; H Hutter,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; P Mayrhofer,* Institute of Materials Science and Tech., TU Wien, Austria

The pursuit of longer lasting workpieces is pushing materials to their limit. To meet the ever growing mechanical and chemical demands, the aid of protective coatings is developing from a surface improvement to an essential necessity. One of the coating materials, that attracts particular attention due to its outstanding oxidation resistance, thermo-mechanical stability and chemical inertness is Al_2O_3. While the thermodynamically stable α–Al_2O_3 (corundum) is limited to high deposition temperatures, the cubic γ-Al_2O_3 can be deposited by DC pulsed or RF reactive sputtering at more workable temperatures but lower growth rates. Reactive DC sputtering yields higher deposition rates but struggles with non-stable deposition conditions due to the formation of isolating Al_2O_3 at the target surface.

To improve the reactive DC sputtering process, we study the influence of small amounts of transition metal dopants such as M = Cr, Nb, Mo, and W on the deposition process as well as the properties of the deposited $(Al_{1-x}M_x)_2O_3$ thin films. The selected concentrations of the dopants in the targets were 2 and 5 at.% each. Resulting dopant concentrations in the thin film were investigated via a combination of energy dispersive x-ray spectroscopy and time-of-flight recoil detection analysis. In comparison to the non-alloyed Al target a significantly improved process stability was observed. The morphology of all coatings is highly dense, smooth and partly columnar with cubic γ-Al_2O_3 crystalline structure. The mechanical properties of the low level Cr, Mo, and W containing coatings are slightly enhanced, e.g. hardness values of about 25 GPa. Transmission electron microscopy is applied to evaluate the influence of the dopant atoms on the morphology and the crystal structure. As a result of the enhanced process stability, the oxidation protection capabilities can be clearly improved by alloying W, Mo, or Cr compared to pure Al_2O_3 thin films, as proven by differential scanning calorimetry and secondary ion mass spectroscopy of isotope tracers.

8:40am **F4-1-3 On the Phase Evolution of Al-Cr-based Intermetallics and Oxides Formed by Cathodic Arc Evaporation**, *V Dalbauer, **Christian Koller**, R Raab,* CDL-AOS TU Wien, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J Ramm,* Oerlikon Surface Solutions AG, Liechtenstein*; M Bartosik, P Mayrhofer,* TU Wien, Austria

The protection of tools and components by only several microns thick hard coatings has evolved to an indispensable element of today's manufacturing and forming process chain. This particular type of surface treatment not only guarantees for enhanced performance of components facing severe mechanical and thermal load, or higher resistance against chemical attacks, but also makes the production cycles more efficient by increasing the duty-cycle and simultaneously lowering material consumption. Owing to their outstanding properties in oxidising and chemically hazardous environments Al-Cr-based oxide coatings represent ideal candidates for the protective application at elevated temperatures. However, the strong dependence of these properties on the microstructure and crystallographic composition in combination with the formation of metastable phases at synthesis temperatures of less than 600 °C still pose a considerable challenge to materials scientists.

We therefore address the phase formation of cathodic arc evaporated $(Al_xCr_{1-x})_2O_3$ coatings with Al-contents x ranging from 0.90 to 0.25 as a function of oxygen partial pressure. Coatings synthesised with a constant oxygen process pressure are compared to gradually-structured films, for which the oxygen flow was slowly increased throughout the deposition process. The growth of metallic films and their transition to oxide phases with M_2O_3 stoichiometry are discussed based on cross-sectional transmission electron microscopy and X-ray nano-beam studies.

9:00am **F4-1-4 Synthesis of Local Epitaxial α-$(Cr_{1-x}Al_x)_2O_3$ Thin Films ($0.08 \leq x \leq 0.16$) on α-Al_2O_3 Substrates by R.F. Magnetron Sputtering***, Y Gao, H Leiste, M Stüber, **Sven Ulrich**,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany

(0001) oriented nanocrystalline α-$(Cr_{1-x}Al_x)_2O_3$ ($0.08 \leq x \leq 0.16$) thin films with a thickness of ~270 nm were grown on *c*-plane α-Al_2O_3 (0001) single crystal substrates at 400˚C by non-reactive reactive radio frequency magnetron sputtering from a segmented ceramic target. The stoichiometric composition of all films was verified by electron probe micro-analysis (EPMA). Only (*000l*) reflections of the films and the substrates were identified from X-ray diffraction (XRD) in Bragg-Brentano geometry. The reflections of the films shift to larger diffraction angle with increasing Al concentration. The mosaic spreading of the (0006) reflex of the films was analyzed to determine the misorientation of the individual crystals with respect of *c*-axis in the films. Transmission electron microscopy (TEM) was carried out in order to study the microstructure and further confirm the orientation and epitaxial relationship of $[0001]_{film}$ // $[0001]_{substrate}$ and $[10\text{-}10]_{film}$ // $[10\text{-}10]_{substrate}$. More information such as lattice parameters *a* and *c*, strain relaxation and epitaxial quality of partial crystal tilting was obtained by reciprocal space mapping (RSM). Further, Raman spectra show a significant shift of phonon frequency with Al concentration. The band gap of the films is between 2.72 eV and 2.85 eV, calculated from visible light absorption spectra. The films nano-indentation hardness and the reduced Young's modulus are in the range of 25.6 - 30.8 Gpa and 216 - 339 Gpa respectively, which vary dependent on the Al concentration.

9:20am **F4-1-5 Thermal Stability of Arc Evaporated Oxide, Nitride, Oxinitride, and Oxide/Nitride Coatings within the Systems Al-Cr-N and Al-Cr-O**, ***Robert Raab,*** CDL-AOS TU Wien, Austria; *C Koller,* TU Wien, Austria; *S Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P Mayrhofer,* TU Wien, Austria

The most common industrially used material systems synthesised by cathodic arc evaporation are nitrides or oxides. Among these, Al-Cr-based films are particularly suitable for a multitude of applications, which not only required a balanced and tailored property spectrum up to 1000°C (and beyond), but also the capability to withstand oxidising and chemically invasive environments. However, increasing demands for higher application temperatures and extended duty cycles, require improvements even for already well-established coatings.

In this regard, we have studied the thermal stability of $Al_xCr_{1-x}N/(Al_xCr_{1-x})_2O_3$ multilayer coatings and compared them with the homogenously grown counterparts $Al_xCr_{1-x}N$, $(Al_xCr_{1-x})_2O_3$, as well as its combination in terms of quaternary Al-Cr-O-N. Therefore, $Al_xCr_{1-x}N$ and $(Al_xCr_{1-x})_2O_3$ multilayers as well as mixtures thereof were synthesised by reactive arc evaporation using powder metallurgically prepared $Al_{0.7}Cr_{0.3}$ targets. By careful adjustment of deposition time and reactive gas configuration, the multilayers could be designed with different bilayer periods and interface types. By reducing the time per layer during the deposition (thus increasing the total number of bilayers), the $(Al_xCr_{1-x})_2O_3$ and $Al_xCr_{1-x}N$ layers have different thicknesses, resulting in decreased bilayer periods from 175 to 30 nm. The quaternary Al-Cr-O-N coatings, were synthesised with different O to N ratios to achieve a similar chemical composition compared to the multilayers.

We used a combination of differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), X-ray powder diffraction (XRD), and hardness investigations after annealing the samples up to 1500 °C in vacuum for one hour to investigate the decomposition of the Al-Cr-based oxide, nitride, oxinitride, and oxide/nitride coatings.

According to DSC/TGA results we can conclude that the thermal stability increases, with increasing total number of layers. We observed a transition from a two-step process of the Al-Cr-based multi-layered coatings with higher bilayer periods as well as the oxinitride coatings with higher N contents, to a one-step process of the $Al_xCr_{1-x}N/(Al_xCr_{1-x})_2O_3$ multilayers with the lowest bilayer periods and the oxinitride coatings with highest O content.

Based on our results we can conclude that a multi-layer arrangement with optimized bilayer period is superior to the monolithically grown $Al_xCr_{1-x}N$, $(Al_xCr_{1-x})_2O_3$, and quaternary Al-Cr-O-N.

9:40am **F4-1-6 Structural Evolution in Reactive RF Magnetron Sputtered $(Cr,Zr)_2O_3$ During Annealing**, ***Ludvig Landälv,*** Linköping Univ., IFM, Thin Film Physics Div. and Sandvik Coromant R&D, Sweden; *J Lu,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *S Spitz, H Leiste, S Ulrich,* Karlsruhe Institute of Technology (KIT), Inst. for Applied Mat. (IAM-AWP), Germany; *M Johansson-Jõesaar,* Linköping Univ., IFM, Nanostructured Mat. And SECO TOOLS, Sweden; *M Ahlgren, E Göthelid,* Sandvik Coromant R&D, Sweden; *B Alling,* Linköping Univ., IFM, Thin Film Physics Div. and Max-Planck-Institut für Eisenforschung GmbH, Sweden; *L Hultman,* Linköping Univ., IFM, Sweden; *M Stüber,* Karlsruhe Institute of Technology (KIT), Inst. for Applied Mat. (IAM-AWP), Germany; *P Eklund,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Physical vapor deposited binary oxide alloys has drawn attention in the past years, often focusing on the Al-Cr-O system [1,2]. The interest for this material system stems from the possibility to stabilize the desired corundum phase, α-Al_2O_3, by introducing other elements to the alloy such as Cr in α-$(Al,Cr)_2O_3$.The corundum structure is stabilized by means of a template growth; Cr forms escolaite Cr_2O_3 which is isostructural with corundum. Exchanging Al with Zr, which is used in many other ceramic alloy systems, creates a new and interesting oxide system with the retained stabilization from Cr, despite Zr's one higher valence than Al and being significantly larger in size. Spitz et al. mapped the Cr-Zr-O system over a wide range of Cr/Zr composition by reactive RF-magnetron sputtering [3], obtaining different phases: solid solution in corundum structure at low Zr-content, cubic-$(Zr,Cr)O_2$ based solid solutions at ~50 at % Zr, and monoclinic/tetragonal solid solution $(Zr,Cr)O_2$ for higher Zr-content. A recent in-situ synchrotron X-ray diffraction study showed the increase in crystallization onset temperature of α-$(Cr,Zr)_2O_3$ and tetragonal $(Zr,Cr)O_2$ from as-deposited amorphous Cr-rich Cr-Zr-O films during vacuum annealing with increasing Zr content (3-15 at %) [4].

In the present study, $Cr_{0.28}Zr_{0.10}O_{0.61}$ coatings were synthesized at 500 °C by reactive RF-magnetron sputtering, to a thickness of about 5 µm. The as-deposited coatings were then vacuum annealed at 750°C, 810 °C, and 870 °C for 5 h each. The microstructure development of the binary oxide compound after annealing was characterized through high resolution state of the art HRSTEM and HREDX-maps, revealing the segregation of Cr and Zr on the nm scale.

The as-deposited films comprise of α-$(Cr,Zr)_2O_3$ solid solutions with a Zr-rich $(Zr,Cr)O_x$ amorphous phase distributed as elongated, in the growth direction, alternating domains. After annealing to 750°C tetragonal ZrO_2 nucleates and grows from the amorphous phase. The ZrO_2 phase is stabilized in its tetragonal (t) structure at these fairly low annealing temperatures, possibly due to the small grain size (<~30 nm). Correlated with the nucleation and growth of the t-ZrO_2 phase is an increase in hardness, with a maximum hardness after annealing to 750 °C, followed by a decrease in hardness upon grain coarsening, bcc metallic Cr phase formation and loss of oxygen during annealing to 870 °C.

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10:00am **F4-1-7 Ternary Oxide Coatings as High-temperature Solid Lubricants**, ***Samir Aouadi,*** *J Gu, D Stone,* University of North Texas, USA; *Y Gao, A Martini,* University of California Merced, USA **INVITED**

This talk will provide an overview of the latest research developments on binary and ternary oxide coatings that have the potential to be used as solid lubricants at elevated temperatures. The review focuses on understanding the major mechanisms that lead to a reduction in friction and/or wear in high temperature lubricious oxides. Changes in the structural, chemical, and electronic properties of these oxides as a function of temperature will be correlated to their mechanical and tribological performance using a range of experimental tools in addition to simulations based on ab initio calculations and molecular dynamics simulation methods. The incorporation of these oxides in adaptive coating designs will also be discussed. Adaptive mechanisms include metal diffusion and formation of lubricant phases at worn surfaces, surface contact tribe-chemical evolution to form phases with low melting point, and the formation of easy-shear oxides. This review also includes a discussion of the industrial applications of these coatings as well as of potential improvements to the coating design and other anticipated future developments.

10:40am **F4-1-9 High-rate Reactive High-power Impulse Magnetron Sputtering of Hf-O-N Films with Tunable Composition and Properties**, ***Jaroslav Vlcek,*** *A Belosludtsev, S Haviar, J Houška, R Čerstvý, J Rezek,* University of West Bohemia, Czech Republic

Oxynitrides are a class of materials with yet unexplored physical, chemical and functional properties, and a great potential for industrial applications.

In this work, reactive HiPIMS with a feed-back pulsed reactive gas (oxygen and nitrogen) flow control and an optimized location (high-density plasma) of the reactive gas inlets in front of the target and their orientation toward the substrate made it possible to produce high-quality Hf-O-N films with a tunable elemental composition, structure and properties at very high deposition rates ranging from 240 nm/min for HfO_2 films [1] to 175 nm/min for HfN films. Basic principles of this method will be given.

The depositions were performed using a strongly unbalanced magnetron with a planar hafnium target of 100 mm diameter in argon-oxygen-nitrogen gas mixtures at the argon pressure of 2 Pa. The nitrogen fractions in the reactive gas flow were in the range from 0 % to 100 %. The repetition frequency was 500 Hz at a fixed deposition-averaged target power density of 30 Wcm^{-2} with the voltage pulse duration of 200 µs (duty cycle of 10 %). The substrate temperatures were less than 140 °C during the depositions of films on a floating substrate at the distance of 100 mm from the target. All films were nanocrystalline and their elemental compositions were varied gradually from HfO_2 to HfN. We present a gradual change of hard (18 GPa), highly optically transparent (extinction coefficient of $5x10^{-4}$ at 550 nm), electrically insulating and hydrophobic (water droplet contact angle of 101°) HfO_2 films into harder (25 GPa), optically non-transparent, electrically conductive (electrical resistivity of $3.2x10^{-6}$ Ωm) and more hydrophobic (water droplet contact angle of 107°) HfN films.

[1] Vlcek, A. Belosludtsev, J. Rezek, J. Houska, J. Capek, R. Cerstvy, S. Haviar, High-rate reactive high-power impulse magnetron sputtering of hard and optically transparent HfO_2 films, Surf. Coat. Technol. 290 (2016) 58.

11:00am **F4-1-10 Thin Films in the M-Si-O-N Systems***, **Sharafat Ali**,* Linnæus University, Sweden*; P Biplab, R Magnusson, G Greczynski, E Broitman,* Linköping University, (IFM), Sweden*; B Jonson,* Linnæus University, Sweden*; J Birch, P Eklund,* Linköping University, (IFM), Sweden

Thin films in the M-Si-O-N systems (Where M= Mg, Ca), were deposited on commercial soda-lime silicate float glass, silica wafers and sapphire substrates by RF magnetron co-sputtering from Mg/Ca and Si targets in an $Ar/N_2/O_2$ gas mixture. Chemical compositions, optical and mechanical properties of the films were investigated using X-ray photoelectron spectroscopy, spectroscopic ellipsometry and nanoindentation. Thin films in the M-Si-O-N system are composed of N and M contents up to 80 at. % and 50 at. %, out of anions and cations respectively. This is very rare in the bulk form. The films were found to be homogeneous and transparent in the visible region. Mechanical properties like hardness and reduced elastic modulus show high values, up to 20 GPa and up to 160 GPa respectively, and show similar compositional dependencies i.e. increase with the N content. The refractive indices range from 1.60 to 2.02 at wavelength 633 nm and is found to increases with increasing N and M contents.

11:20am **F4-1-11 Diffusion between Silica Thin Film Deposited by Reactive Magnetron Sputtering and Glass Substrate during Annealing at High Temperature***, **Jean-Thomas Fonné**, E Gouillart, E Burov, H Montigaud, S Grachev,* Joint unit CNRS/Saint-Gobain UMR 125 - Surface of Glass and Interfaces, France*; D Vandembroucq,* UMR 7636 CNRS/ESPCI/Paris 6 UPMC/Paris 7 Diderot - Physics and Mechanics of Heterogeneous Media Laboratory, France

Industrial processes often involve annealing and/or tempering glass panels coated with thin films. Diffusion of alkali ions from the substrate to the active layers is typically observed during these treatments and can modify properties of these thin films. In order to understand the kinetics and mechanisms of this phenomenon, amorphous silica thin films (pure or doped with aluminum) deposited by magnetron sputtering under reactive atmosphere onto glass substrates have been studied after annealing above the glass transition temperature (Tg). Various techniques such as SIMS, SEM, AFM, XPS, EPMA and Raman Spectroscopy were used for the evaluation of the composition depth profile and the microstructure characterization.

Our investigations show that annealing commercial soda-lime glass substrates coated with silica thin films above Tg leads to migration phenomena between silica and glass with two essential steps:

- A fast migration of alkali ions (especially sodium and potassium) from the substrate to the film is first observed. This transport phenomenon is shown to strongly depend on aluminum doping in silica layers. In particular the alkali ions concentration obtained in the silica layer after annealing scales linearly with the initial aluminium concentration in the silica layer.
- A slow homogenization then takes place at the interface between the silica thin film and the glass substrate. This second phenomenon is controlled by the interdiffusion of the st of all elements. We observe a gradual thinning of the silica layer with the square root of time.

Differents annealing durations and temperatures were studied since these phenomena depend on elements mobility and activity. Moreover the impact of deposition conditions was also studied (like the deposition pressure) since these parameters can have an influence on the silica layer properties.

11:40am **F4-1-12 Investigation of Sputtered Zirconium Oxide Thin Films Deposited at Different Oxygen Partial Pressure***, **Nicky Patel**,* Sardar Patel College of Engineering, India*; K Chauhan,* Chandubhai S. Patel Institute of Technology (CSPIT), Charotar University of Science and Technology (CHARUSAT), India*; S Rawal,* McMaster University, Canada

Reactive magnetron sputtering was used to deposit zirconium oxide thin films by using argon as inert gas and oxygen as reactive gas. The oxygen partial pressure was increased from 17% to 50% and its effect on structural, wettability and tribological properties of deposited zirconium oxide thin films are investigated. The structural characterization by X-ray diffraction confirms formation of (111) peak for zirconium oxide thin films whose intensity decreases with increase in oxygen partial pressure. Atomic force microscopy results indicate increase in surface roughness values with increase in oxygen partial pressure. The average transmittance values of around 80% within wavelength range of 300 nm to 700 nm was observed which proves that zirconium oxide thin films are transparent. Contact angle measurement done for water and formamide liquids indicate zirconium oxide thin films are hydrophobic. The maximum contact angle observed on zirconium oxide thin films are 102.6°and 101.3° for water and formamide liquids respectively. Tribological investigation shows that zirconium oxide thin films coated pins had a reduction of wear when compared to the uncoated pins.

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.

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[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.

Acknowledgements: The research leading to these results has received funding from the BisNano project (125141), PHOCSCLEEN (318977) and the CONACYT (251279), DGAPA-PAPIIT (100116). ODR thanks to CONACYT for the scholarship during the PhD study.

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).

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

FP-3 Monolayer Controlled Deposition of ZnO Thin Films by Catalytic Reaction-assisted Chemical Vapor Deposition, *S Ono, T Saitou, R Tajima, Y Tamayama,* ***Kanji Yasui,*** Nagaoka University of Technology, Japan

The large bandgap (3.37 eV at RT) and exciton binding energy (60 meV) of ZnO [1] have recently stimulated intensive research into optoelectronic device applications, such as light-emitting diodes and laser diodes that operate in the ultraviolet region [2-6]. We have previously developed a new CVD method for ZnO film growth based on the reaction between alkylzinc (DMZn) and high-temperature H_2O generated by a Pt-catalyzed exothermic H_2-O_2 reaction. The resulting ZnO films grown on a-plane (11-20) sapphire (a-Al_2O_3) substrates exhibited excellent optical and electronic properties [7]. Superlattices are often used to enhance the efficiency of optical emission devices. Such structures involve alternating layers with different compositions, with each layer often being just a few molecules thick. It is therefore necessary to be able to control the growth process at the monolayer level. Therefore, in the present study, the applicability of catalytic reaction–assisted CVD using a pulsed gas supply was investigated for monolayer controlled growth of ZnO on a-Al_2O_3 substrates.

Except for the gas supply mode, the CVD apparatus and growth procedure were the same as those previously reported [7]. DMZn gas was supplied to the reaction zone in pulses with durations of 4 and 8 ms, and was reacted with a catalytically generated high-energy H_2O beam effused from a de Laval nozzle. The growth rate per pulse was evaluated based on the final film thickness and the total number of DMZn pulses. Pulse rates of 2 and 4 Hz were used, with the gas being supplied for 30 and 15 min, respectively. For a pulse duration of 8 ms, based on the final ZnO film thicknesses of 1300 and 1400 nm, the deposition rate was 0.36 and 0.39 nm per pulse for a pulse rate of 2 and 4 Hz, respectively. For a pulse duration of 4 ms, based on the final film thickness of 1400 nm, the deposition rate was 0.19 nm per pulse. Since the c-lattice constant of ZnO is 0.52 nm, the thickness of a single molecular layer is 0.26 nm. Therefore, from the above results, the thickness of the deposited layer could be controlled to less than the thickness of a single molecular layer using catalytic reaction-assisted CVD with a 4 ms pulsed gas supply.

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FP-6 Optical and Electronic Properties of MoS2: Joint Theoretical/Experimental Study, ***Miller Eaton,*** *H Sirikumara, H Samassekou, D Mazumdar,* Southern Illinois University, USA; *L Liyanage, M Nardelli,* University of North Texas, USA; *T Jayasekera,* Southern Illinois University, USA

First-principles calculations of the optoelectronic properties of semiconductors using density function theory (DFT) have suffered from slight inaccuracies due to the exchange energy interaction approximations used. The inclusion of the Hubbard parameter U allows for more accurate predictions with a negligible increase in computational time. We use the DFT + *U* approach to perform *ab initio* calculations of the optical and electronic properties of thin film MoS2. We then fabricate pristine MoS2 thin films on BN-buffered silicon substrates via magnetron sputtering. Few-layer films are first confirmed with X-ray reflectivity and diffraction measurements, and then further characterized using variable angle spectroscopic ellipsometry (VASE). Agreement of DFT + *U* predictions with layer specific modeling of VASE data demonstrates the viability of sputtering for large-area growth. This study paves the way for the controlled introduction of chemical dopants to further improve electronic and optoelectronic properties of MoS2 for nanoscale device application.

FP-7 Possibility of Selective and Morphology-Controlled Growth of CuO and Cu_2O Films, ***Tomoaki Terasako,*** *K Ohnishi, H Okada, S Obara,* Ehime University, Japan; *M Yagi,* National Institute of Technology, Kagawa College, Japan

Both CuO (Eg=~1.35 eV) and Cu_2O (Eg=~2.1 eV) exhibit *p*-type conduction. These materials have attracted much attention because of their promising applications, such as photocatalytic water splitting, solar cells, electrode materials for lithium-ion batteries, gas-sensing devices and so on. Chemical bath deposition (CBD) is performed at temperatures typically lower than 100 °C, which allows us to use polymers as substrate materials. In this paper, we will discuss the possibility of the selective and morphology-controlled growth of CuO and Cu_2O films on Au/SiO_2/Si(100) substrates by CBD from the same precursor, *i.e.* $Cu(NO_3)_2 \cdot 3H_2O$ (CuNit).

The CuO films grown from the aqueous solutions of CuNit with the different pH values adjusted by the use of NH_3(aq) were composed of the needle-like grains whose average length increased with increasing pH value. At pH≥10.5, the needle-like grains were organized in the caddis clew-like shapes. The most probable mechanism for assembling the needle-like grains is the "oriented attachment" in which the rotations of the needle-like grains can be driven by torques introduced by the misalignment of the neighboring grains [1, 2]. The appearance of the caddis clew-like shapes is probably due to the imperfect rotation of the needle-like grains caused by the increase in the average length.

The Cu_2O films were grown from the mixed aqueous solutions of CuNit and $C_6H_{12}N_4$ (HMT) with the assistance of a piece of Fe plate immersed in the solution, denoted by "Fe-assisted CBD". No Cu_2O film could be obtained without the immersion of the Fe plate [3]. The reduction from the Cu^{2+} ions to the Cu^+ ions is required for the formation of Cu_2O from CuNit. Oxidation-reduction potential (ORP) measurement during the Fe-assisted CBD process revealed that the ORP exhibited a sudden decrease just after immersing the Fe plate. Moreover, the ORP values during the Fe-assisted CBD were overall low in comparison with those during the usual CBD process. Taking into account the fact that α- and δ-FeOOH were formed on the surface of the Fe plate during the CBD process, the CBD solution in which the Fe plate was immersed had high concentration of electrons contributing to the reduction of Cu^{2+} ions. The preferential growth direction of the Cu_2O film changed from [111] to [100] with increasing CuNit (or HMT) concentration, accompanied with the change from the triangular-plate grains to the four-sided pyramidal grains.

This work was supported by JSPS KAKENHI Grant Number JP26390029.

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FP-8 Thermal Stability of Arc Evaporated Oxide, Nitride, Oxinitride, and Oxide/Nitride Coatings within the Systems Al-Cr-N and Al-Cr-O, ***Robert Raab,*** CDL-AOS TU Wien, Austria; *C Koller,* TU Wien, Austria; *S Kolozsvári,* Plansee Composite Materials GmbH, Germany; *J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P Mayrhofer,* TU Wien, Austria

The most common materials systems synthesised by cathodic arc evaporation for industrial applications are nitrides or oxides (e.g., TiAlN, CrAlN,Al_2O_3,…). Among these, Al-Cr-based films find application in multitude of applications, such as forming or cutting tools, which not only required a consistent performance over a temperature range up to 1000°C and beyond, but also the capability to withstand oxidising environments.

In this regard, we have studied the thermal stability of $Al_xCr_{1-x}N/(Al_xCr_{1-x})_2O_3$ multilayer coatings and compared them with the homogenously grown counterparts $Al_xCr_{1-x}N$, $(Al_xCr_{1-x})_2O_3$, as well as its combination in terms of quaternary Al-Cr-O-N.

We used a combination of differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), X-ray powder diffraction (XRD), and hardness investigations after annealing the samples up to 1500 °C in vacuum for one hour to investigate the decomposition of the Al-Cr-based oxide, nitride, oxinitride, and oxide/nitride coatings.

Based on our results we can conclude that a multi-layer arrangement with optimized bilayer period is superior to the monolithically grown $Al_xCr_{1-x}N$, $(Al_xCr_{1-x})_2O_3$, and quaternary Al-Cr-O-N.

FP-9 Parametric Study of TiN Thin Films Deposited on 316 L Substrates by HiPIMS, *L Melo-Máximo,* ITESM-CEM, Mexico; *F Estrada-Martinez,* Termoinnova S.A. de C.V., Mexico; *D Melo-Maximo,* TRAMES S.A. de C.V., Mexico; ***Joaquin Oseguera,*** ITESM-CEM, Mexico

Thin films of TiN were prepared by High-power impulse magnetron sputtering (HiPIMS) on 316L substrates. The main objective of this work was to evaluate the thin film growth under various conditions, in order to show the effect that process parameters have on the properties of the films. The microstructure and the adhesion of the coatings were studied by the characterization with scanning electron microscopy, optical microscopy, x-ray diffraction and scratch test.

FP-11 Transition Metal Dichalcogenides for Next Generation Semiconductor Devices*, B Sirota,* University of North Texas, USA, U*; A Waite, N Glavin,* Air Force Research Laboratory, USA*; C Muratore,* University of Dayton, USA*; S Krylyuk, A Davydov,* National Institute of Standards and Technology, USA*;* ***Andrey Voevodin,*** University of North Texas, USA

New advances in technology encourage the proliferation of next generation electronic devices. Two dimensional semiconductor materials such as MoS_2, WS_2, $MoTe_2$, $MoSe_2$ and similar compounds have gained significant interest for their capabilities due to their size, flexibility, optical transparency, and tunable electronic bandgap. In addition, ultra-thin amorphous BN has gained recent interest as a dielectric material due to its large band gap, flexibility, optical transparency, and low temperature processing compatible with polymer substrates. Herein, we present a study on 2D transition metal dichalcogenides prepared by physical vapor deposition (MoS_2) and mechanical exfoliation ($MoTe_2$). We also examine their heterostructures with pulsed laser deposited ultra-thin amorphous BN layer, and integrated into electronic devices. Proof-of-concept field effect transistors with 2D semiconductors serving as the channel material are made using conventional electronic beam lithography and lift off. Microstructure, electronic and optical properties are determined and compared to devices made from traditional techniques in the recent literature. These results demonstrate the functionality of 2D transition metal dichalcogenide layers and their heterostructures with amorphous ultra-thin BN as a use for electronic devices with advanced functionality.

FP-13 Microscopic Barrier Mechanisms and Interface Damage Behavior of Two-dimensional Nanomaterials*,* ***Pu Jibin****, L Wang, J Xue,* Key Laboratory of Marine New Materials and Related Technology, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, China

The serious surface damage of high-tech facilities in the marine and spatial environment has become a key problem that restrains the reliability and life span of marine engineering facilities and spacecrafts. The common mechanism of material damage in the marine and spatial environment is infiltrated and eroded by the medium of external environment. Two-dimensional nanomaterials (graphene, hexagonal boron nitride, disulfide, etc.) have a wide coverage of surface area and excellent mechanical, electrical, thermal and obstructing properties. So they have natural advantages as materials of resisting ion penetration and atomic oxygen erosion in the marine and spatial environment. By studying the influence of the electronic structure, electric conductivity, thermal conductivity, layer number, surface functional group and defect degree of two-dimensional nanomaterials on obstructing marine medium and atomic oxygen and the influence of the controllable dispersion, ratio, distribution pattern and multi-scale interface of two-dimensional nanomaterials on the damage of composite coatings, this paper expounds the obstructing regulation mechanism of two-dimensional nanomaterials so as to provide theoretical guidance for developing new-type long-life materials of marine protection and spatial anti-atomic oxygen.

FP-14 Corrosion Performance of Waterborne Epoxy Coating using Non-covalent Dispersion of Graphene as Inhibitor*,* ***Shuan Liu****, H Zhao,* Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China*; P Jibin,* Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, P. R. China, China*; L Wang,* Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

To improve the anticorrosion performance of waterborne epoxy coating and expand its practical applications, Graphene was initially stabilized by sulfonated polyaniline in aqueous solution, and its structure and dispersant performance were investigated by SEM.TEM Raman and AFM respectively. Then the corrosion behaviour of different composite coatings in 3.5% NaCl solution was studied based on a series of electrochemical measurements. Results indicated that graphene could be dispersed uniformly in water. Sulfonated polyaniline was not only a graphene dispersant but also an corrosion inhibitor. The addition of well-dispersed graphene into waterborne epoxy coating improved corrosion protection significantly compared with neat waterborne epoxy coating.

FP-16 Production and Testing of Enhanced Photocatalytic Coatings onto Nanoparticles by Magnetron Sputtering*, P Kelly,* ***Marina Ratova****, G West,* Manchester Metropolitan University, UK

Magnetron sputtering is a well-established technique for the deposition of high quality metallic and ceramic coatings onto a wide range of substrate materials and forms. It is not generally suitable, though, for the coating of fine particulates (particle sizes from 10s of nm to 100s of µ m). This paper, however, describes the use of an oscillating mechanism to manipulate particulates under two co-planar magnetrons, such that uniform coverage of the particles is achieved.

This technique has been used to deposit a range of coatings onto photocatalytic anatase titania nanoparticles (PC500), with the aim of overcoming some of the limitations of this material, specifically rapid charge carrier recombination and low visible light activity. The materials selected include bismuth tungstate, a visible light active photocatalyst, which can increase charge carrier numbers and lifetimes through semiconductor coupling with titania; and carbon, which can be used as a dopant to increase overall activity. The bismuth tungstate coatings were deposited by reactive magnetron co-sputtering from two targets. Two strategies were used for carbon doping; direct sputtering from a carbon target and reactive sputtering using CO_2 as a process gas.

The nanoparticles were characterised by SEM, EDX, TEM, XRD and BET surface area measurements. Photocatalytic activity was assessed using an acetone degradation test under visible light irradiation, in which the rate of CO_2 evolution was measured as a function of the surface area of the sample. Preliminary results indicate that the bismuth tungstate coatings, where the Bi/W content is in the ratio of 2:1 can significantly increase the visible light activity of the titania product. The mechanism through which this enhancement occurs is discussed in terms of more efficient separation of the charge carriers and the inherent activity of the coating.

FP-17 3D Printing of Metal Oxide Semiconductor?*,* ***Chuong Nguyen,*** University of Auckland, New Zealand*; J Leveneur,* GNS Science, New Zealand*; M Taylor, J Metson,* University of Auckland, New Zealand

Ion-induced reduction can potentially provide two important features for metal oxide semiconductors: amorphous state and tuneable contact resistance. It is well known that ion bombardment causes amorphitization of target materials. Ion fluence can also be controlled to reduce oxide to metallic state in various proportions, tuning the metal – semiconductor contacts from Schottky to Ohmic.

This study involved argon ion bombardment on multi-valent iron oxides. The reduction extents, in terms of oxidation state and effective depths, as a function of ion fluence is characterized by energy-resolved x-ray photoelectron spectroscopy (ERXPS), complemented by x-ray absorption of near-edge structure (XANES). The correlation is assessed against the transport of ions (TRIM) simulation. Our early results indicate a possible method to build up a functionally graded thin-film transistor layer by layer using physical vapor deposition (PVD) coupled with a supplementary ion gun.

FP-18 A Proposal for Laser Annealing Process with Continuous Wave Nd:YAG Laser (λ_o = 532 nm) for Photovoltaic CIGS Thin Films: Effect of Laser Annealing Time on Optical and Electrical Properties*,* ***MyoungHan Yoo****, D Lee,* Chosun University, Republic of Korea*; Y Jun,* Hyobjin Jeongbo Co., Inc., Republic of Korea*; P Ko, N Kim,* Chosun University, Republic of Korea

$CuIn_{1-x}Ga_xSe_2$ (CIGS) thin-film solar cells are strongly considered as an absorber layer in light-weight and flexible thin-film solar cells . For preparing CIGS thin film at low cost, critical problems still remained in the selenization process of the sputtered Cu-In-Ga precursors by using H_2Se vapor, such as highly toxic H_2Se, poor adhesion to the back contact and the slow rate of reaction. A non-selenization process was proposed to be developed for fabricating CIGS thin film by these authors; however, the annealing temperature was over the decomposition temperature of the typical flexible polymer substrates. A novel method by using a rapid laser annealing process has also been proposed and investigated to demonstrate the feasibility of crystallization and grain growth for CIGS thin film. In our prior study, a continuous wave (CW) second harmonic wavelength of Nd:YAG (λ_o = 532 nm) laser was selected to improve the microstructure of CIGS thin film with a change of the laser optical power from 2.25 to 3.00 W for 200 sec. CIGS chalcopyrite (112), (220/204) and (312/116) phases were formed in the laser-annealed CIGS thin films, but the weak diffraction peaks of Cu-Se related phases were also observed due to the insufficient energy for the grain growth. In this study, the laser annealing time was controlled to accomplish long-range atomic diffusion, chemical reactions and grain growth with a considering mass-production manufacturing. The crystal structures and chemical compositions of the laser-annealed thin films were analyzed by X-ray diffraction and energy-dispersive X-ray spectroscopy as a function of laser annealing time. The effects of them on the optical properties and electrical characteristics of CIGS thin films were examined by using an UV-Visible spectrophotometer and a Hall Effect measurement system. Not only sufficient crystal structure but also excellent optical and electrical properties were obtained by this rapid laser annealing process for CIGS thin film. Acknowledgement: This work (Grants No. C0267866) was supported by Business for Academic-industrial Cooperative establishments funded Korea Small and Medium Business Administration in 2015.

FP-20 Production of Ag Clusters by Plasma Gas Condensation and their Incorporation in an a:C Sputtered Matrix*, I Carvalho,* University of Coimbra, Portugal*; **Sandra Carvalho**,* University of Minho, Portugal*; A Cavaleiro,* University of Coimbra, Portugal

Ureteral stents are essential tools in contemporary urologic practice. However, urethral stents present complications at the level of microbial colonization leading to recurrent infections, being of extreme importance the development of new materials. In this way, the main propose of this study is to develop a new material aiming to improve biocompatibility, corrosion resistance, elasticity and, most especially, to reduce or eliminate adverse reactions in the body due to microbial colonization. A silver delivery device composed of a DLC coating embedded with Ag clusters, covering the existing stent material, is proposed.

Firstly, it is necessary evaluate the Ag clusters formation with respect to their size and shape since these parameters will controls the silver ion release and consequently the antimicrobial performance. In this sense, Ag clusters were produced by plasma gas condensation process consisting in a gas aggregation cluster source connected to a main deposition chamber. The work pressure in the main chamber and gun was 4 x10^{-3} Pa and 100 Pa, respectively to produce Ag clusters, which will be incorporated in a:C matrixes with a current density applied of 2.4 up to 9.2 mA cm^{-2}.

The clusters growth was evaluated in static and rotation mode. Current density applied to Ag target was kept constant at 7.6 mA cm^{-2}. TEM results show that the deposition in rotation mode (2 rpm) leads to a decrease in the clusters mean size, 25 nm to the static mode to 15 nm to the rotate mode. In both modes, the clusters shape is spherical, however in the rotate mode the clusters appear to aggregate. The crystalline structure of Ag clusters was evaluated by the selected area diffraction patterns and the results show the formation of fcc crystalline Ag.

FP-22 Biocompatible Thin Film Intermetalic $Ti_{3-x}AuO_x$, ***Vladimir Vishnyakov**,* University of Huddersfield, UK*; B Beake,* Micro Materials Ltd, UK*; J Devitt,* University of Huddersfield, UK

Titanium-gold intermetallics (both materials being biocompatible) are well suited as a replacement for hard tissue, and represents an opportunity to develop new medical applications in the field of arthritis, rheumatic and musculoskeletal diseases. It has been reported by other groups that intermetallics have the additional advantage, in right composition and crystallinity, of having a hardness value as high as 8 GPa. This high degree of hardness makes material exceptionally valuable for load-bearing body implants, for example. It is also know that the incorporation of relatively small amounts of oxygen, at the level of few atomic percent, can lead to titanium hardening. On the other hand, a small percentage of oxygen is almost inevitably incorporated in the titanium thin films during Physical Vapour Deposition (PVD). Ion sputtering of elemental titanium and gold targets with argon has been used to deposit $Ti_{3-x}AuO_x$ (where $0.03<x<0.1$) onto various substrates in pure Ar or Ar/O atmosphere. Energy Dispersive X-Ray Spectroscopy (EDX) and X-Ray Diffraction (XRD) have been used to assess the film composition and crystalline structure. Even at the highest level of investigation, the oxygen content in the films remain crystalline and its hardness can increase to almost 10 GPa. In addition, nanoscratching reveals certain loss of ductility as oxygen content increases.

FP-24 Features of Incident Particle Flux determining Growth Rates and Electrical Properties of Indium Tin Oxide Films Deposited by Ion-plating with dc Arc Discharge*, **Hisashi Kitami**, T Sakemi, Y Aoki,* Sumitomo Heavy Industries, Ltd., Japan

We have investigated the factors limiting growth rates and electrical properties of indium tin oxide (ITO) films on glass substrates (@ 200 °C) deposited by ion-plating with dc arc discharge. We clarified the incident particle fluxes during film growth under the deposition conditions; the pressure in the deposition chamber of 0.18 – 0.71 Pa and the discharge current of 150 A. The resulting thickness of the ITO films was 150 (±3 %) nm. The carrier concentration of the ITO films was 1.0×10^{21} (±3 %) cm^{-3}.

We measured the incident particle fluxes of the neutral atoms and ions for each species at the substrate level using a mass-energy analyzer (Hiden, EQP300), a Langumuir probe and a diaphragm gauge during the deposition. To clarify the factors limiting the growth rate and Hall mobility ($\mu_{\text{-H}}$) of ITO films, we analyzed the relationship between the growth rates, $\mu_{\text{-H}}$, and the incident fluxes of In species and O species.

As the pressure increased, the fluxes of In$^+$ (>10 eV) ions and O$^+$ (> 10eV) ions decreased and the fluxes of In$^+$ (<10 eV) ions and O$^+$ (< 10eV) ions increased. We found that the fluxes of In$^+$ (>10 eV) ions were dominant factor to limit the growth rate. The sticking coefficient of In species should be dependent on the incident energy into the substrate. As the fluxes of In$^+$ (> 10eV) ions and/or O$^+$ (> 10eV) ions increased, $\mu_{\text{-H}}$ increased. The $\mu_{\text{-H}}$ was governed by the microstructure and carrier concentration of the films, which originated in the incident energy fluxes (> 10eV) of In$^+$ ions and/or O$^+$ ions under the current deposition conditions. We will discuss it in more detail.

FP-25 Development and Microstructure Characterization of Single and Duplex Nitriding of UNS S31803 Duplex Stainless Steel*, L Varela,* University of São Paulo, Brazil*; C Pinedo,* Heat Tech & University of Mogi das Cruzes, Brazil*; H Dong, X Li,* University of Birmingham, UK*; **André Tschiptschin**,* University of São Paulo, Brazil

The microstructural changes involved in single Low Temperature Plasma Nitriding - (LTPN) and Duplex Nitriding (DN): High Temperature Gas Nitriding (HTGN) + Low Temperature Plasma Nitriding (LTPN), surface treatments of UNS S31803 were studied. Specimens of UNS S31803 duplex stainless steel (DSS) were (i) single low temperature plasma nitrided (LTPN) and (ii) duplex nitrided (DN) using high temperature gas nitriding (HTGN), followed by low temperature plasma nitriding (LTPN). In both cases, LTPN was carried out at 400°C for 20 h, in a 75%N_2+25%H_2 atmosphere. HTGN was carried out at 1200ºC, under a 0.1 MPa high purity N_2 gas atmosphere, during 8 hours. The microstructure of the as received material was composed by ferrite and austenitic stringers, aligned in the rolling direction. The results showed that LTPN of the UNS S31803 duplex stainless steel promotes the formation of a duplex modulated structure composed by 2.5 µm thick, 1509 HV hard, expanded ferrite (α_N) regions, and 3.0 µm thick, 1362 HV hard, expanded austenite (γ_N) regions on ferrite and austenite grains, respectively. Intense coherent ε-Fe_3N nitride precipitation inside expanded ferrite was observed. ε-Fe_3N nitrides precipitated with an orientation relationship [111] α_N // [120] ε-Fe_3N, leading to increased microhardness of the expanded ferrite regions. After the first step of the duplex nitriding treatment (HTGN) a 550 µm thick, 330 HV hard, nitrogen rich, fully austenitic layer formed at the surface of the specimens, by transformation of ferrite stringers into austenite. The second nitriding step (LTPN) led to the formation of a homogeneous expanded austenite layer, 1144 HV on top of the thick fully austenitic layer, formed during the first step. The duplex treatment resulted in a more homogeneous, precipitate-free, microstructure and a better transition between the mechanical properties of the hardened outermost layer and the softer substrate.

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