

New Horizons in Coatings and Thin Films Room San Diego - Session F2-1

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Jon Tomas Gudmundsson, University of Iceland

10:00am **F2-1-1 On Recycling in High Power Impulse Sputtering Magnetrons**, *Jon Tomas Gudmundsson*, University of Iceland, Iceland; *N Brenning, M Raadu*, KTH-Royal Institute of Technology, Sweden; *T Petty, T Minea, D Lundin*, Université Paris-Sud, France

We will discuss a framework on how to quantify and understand large discharge currents in high power impulse magnetron sputtering (HiPIMS) discharges by investigating the role of self-sputter(SS-) recycling and working gas recycling. We find that above a critical current density $J_{crit} \approx 0.2$ A/cm², a combination of self-sputter recycling and working gas-recycling is the general case. The relative contributions of these recycling mechanisms, in turn, influence both the electron energy distribution and the stability of the discharge [1]. For high self-sputtering yields, above $Y_{ss} \approx 1$, the discharges become dominated by SS-recycling, contain only a few hot secondary electrons from sheath energization, and have a relatively low effective electron temperature. Here, stable plateau values of the discharge current develop during long pulses, and these values increase monotonically with the applied voltage. For low self-sputtering yields, below $Y_{ss} \approx 0.2$, the discharges operated above J_{crit} are dominated by working gas recycling, have a significant sheath energization of secondary electrons and a higher effective electron temperature, and the current evolution is generally less stable. For intermediate values of Y_{ss} the discharge character gradually shifts between these two types. In addition, these new insights on ion recycling have been applied to a series of selected sputter materials. For high currents a discharge with Al target develops almost pure self-sputter recycling, while a discharge with Ti target exhibits close to a 50/50 combination of self-sputter recycling and working gas-recycling [2]. However, if the Ti target is operated in a reactive Ar/O₂ gas mixture, it is found that working gas-recycling is dominating [1] and that the Ar⁺-ions contribute almost solely to the discharge current [3].

[1] N. Brenning et al. Plasma Sources Sci. Technol. (submitted 2017)

[2] C. Huo et al., J. Phys. D: Appl. Phys. 50 354003 (2017).

[3] J. T. Gudmundsson et al. Plasma Sources Sci. Technol. 25, 065004 (2016).

10:20am **F2-1-2 Electron Density at the Sheath Edge of a HiPIMS Plasma**, *A Hecimovic, Julian Held, V Schulz-von der Gathen, W Breilmann, C Maszl, A von Keudell*, Ruhr-Universität Bochum, Germany

In High power impulse magnetron sputtering (HiPIMS) a magnetron discharge is operated with short, high-voltage pulses with a length in the order of 100 μ s at power densities of several kW/cm², creating a highly dense plasma. At high discharge currents, the plasma is not homogeneous but is instead organized into distinct zones of high plasma emission which rotate in ExB direction with velocities of about 10 km/s. The strong emission indicates an elevated electron density inside those so called "spokes". Up to now, no measurement of the electron density inside the spokes has been performed. In this contribution, small inserts in the target surface were used to probe the local current density. Simple sheath theory was then applied to derive the electron density at the sheath edge. The electron density was found to be a few 10^{20} m⁻³. The electron density inside the spokes was about 25% higher than in the plasma between the spokes.

10:40am **F2-1-3 Spatially Resolved Investigation of Transport and Redeposition Processes during HiPIMS by Means of Optical Diagnostics and In-vacuum XPS Analysis of Magnetron Targets**, *Sascha Monje, V Layes, A von Keudell*, Ruhr-University Bochum, Germany; *T de los Arcos*, University Paderborn, Germany; *V Schulz-von der Gathen, C Corbella*, Ruhr-University Bochum, Germany

The distribution of redeposited species and their oxidation states were evaluated with in-vacuum X-ray photoelectron spectroscopy (XPS) of magnetron targets after reactive and non-reactive high power impulse magnetron sputtering (HiPIMS). The investigation was performed for various metal targets (all circular with 50 mm diameter). In addition to regular targets, 'composite' targets were used which are made of a regular metal target, where a second cylindrical shaped metal insert is located in the racetrack center. The insert of these targets acts as a marker for the species transport in the plasma.

The HiPIMS discharge was used at several power conditions and was characterized with a fast imaging CCD-camera as well as optical emission spectroscopy (OES). The target surface composition was evaluated with XPS after an in-vacuo transfer to an UHV chamber.

With the characterization of the plasma on one hand and the redistribution of material on the other hand, it was possible to connect the transport and the discharge behavior. It was found that the lateral transport and redeposition of species are influenced by the appearance of spokes. Furthermore, a correlation between oxidation state and the local surface condition has been found.

11:00am **F2-1-4 Time-resolved Ion Energy and Charge Distributions in Pulsed Cathodic Arc Plasmas of Nb-Al Cathodes in High Vacuum.**, *Siegfried Zoehrer*, Montanuniversität Leoben, Austria; *A Anders*, Lawrence Berkeley National Laboratory, USA, and now at Leibniz Institute of Surface Engineering (IOM), Germany; *R Franz*, Montanuniversität Leoben, Austria

Cathodic arcs are utilized in industry for a wide variety of applications. For instance, to synthesize functional thin films and coatings, to form energetic metal ion beams for ion implantation, or in high current switches. Although there has been tremendous progress in the last decades, the physics responsible for the observed plasma properties are still a matter of dispute. That is particularly the case for multi-element cathodes, which can play an essential role in all given examples. An often overlooked criterion, especially in DC arc plasma analysis, is the typically occurring neutral background of metal atoms in cathodic arcs. It perturbs initial ion energy and charge distributions, which makes it difficult to get information of the near-cathode plasma and also to relate effects to the cathode composition. Therefore, we use a recently developed method to record time-resolved ion charge state and energy distributions in pulsed vacuum arc plasmas from Nb-Al cathodes. This model system consists out of three different Nb-Al compositions, as well as pure Nb and Al cathodes. The results visualize ion detections of 600 μ s plasma pulses, extracted 0.27 m from the cathode resolved in energy and time. They show a heavy influence of neutrals on ion charge state fractions and, to a lesser extent, on ion velocity distributions, which can be observed in the time evolution of these properties. Subsequently, fundamental hypotheses applying to multi-element cathodes, like the „velocity rule“ or the „cohesive energy rule“ are tested on their applicability to early and late stages of the pulse. The results also show a strong material dependency, which appears for initial as well as saturated ion charge states and velocities. That leads to a quite different behavior for single-element cathodes and Nb-rich/Al-rich multi-element cathodes, where the latter generally show lower velocities and less multiply charged Nb ions. Apart from their fundamental character, these findings can be useful for optimizing or designing plasma properties for applications by actively utilizing effects on ion distributions caused by multi-element cathode materials and charge exchange with neutrals.

11:20am **F2-1-5 Investigations on the Substrate Bias Influence on Reactive High Performance Plasmas**, *K Bobzin, T Brögelmann, N Kruppe, Martin Engels*, Surface Engineering Institute - RWTH Aachen University, Germany

High performance plasma processes are subject of several studies. For the high power pulse magnetron sputtering (HPPMS) and hybrid processes composed of HPPMS and direct current magnetron sputtering (dcMS), respectively, investigations regarding correlations between plasma and coating properties and the process parameters have been carried out. These investigations especially focus on the HPPMS pulse parameters frequency f and pulse-on-time t_{on} , the power density at the target and the process gas pressure. However, another important aspect with respect to industrial coating processes is the substrate bias, which is used to accelerate ionized coating forming species to the substrate. This acceleration results in dense and homogeneous coatings due to subplantation of these species into the coating. In order to understand this mechanism, the correlation of substrate-sided plasma properties and the resulting coating properties is a reasonable approach. Nevertheless, it is complicated to implement substrate-sided plasma diagnostics which are closely adapted to industrial coating processes using substrate bias. Hence, the present work focuses on strategies to conduct quantifiable investigations on the high performance plasma properties using substrate bias. These investigations were conducted for reactive HPPMS and dcMS/HPPMS (Cr,Al)N and (Cr,Al)ON processes. The coating systems were chosen, since they are widely used as protective coatings for many tool applications. The strategies were developed for the plasma diagnostics optical emission spectroscopy, Langmuir probe and energy resolved mass spectroscopy in an industrial scale coating unit. A varying substrate bias with values from $U_b = 0$ V to $U_b = -250$ V was used to validate the developed

Monday Morning, April 23, 2018

methodology. The results on the substrate-sided plasma properties like the chemical composition, ionization or Debye sheath thickness were correlated with (Cr,Al)N and (Cr,Al)ON coating properties, i.e. the morphology by scanning electron microscopy, the chemical composition by means of glow discharge optical emission spectroscopy, residual stress by means of cantilever sensor chips as well as the universal hardness and the indentation modulus by nanoindentation. The correlation was conducted using an artificial neural network (ANN). With the developed methodology it was possible to identify significantly changing plasma properties at the substrate side when varying the substrate bias. The correlating coatings properties and the output data of the ANN were used to validate the methodology for the analysis of industrial coating processes.

11:40am **F2-1-6 The Impact of a Positive Pulse in HIPIMS Films, Jason Hrebik**, Kurt J. Lesker Company, USA

HIPIMS technology is on the rise and starting to be qualified in more and more applications in the thin film coating industry. Low power HIPIMS options have enabled more R&D with the technology and as a result, new ways of utilizing and optimizing the technology has been found and published.

Test data will be presented showing various performance advantages of applying a positive pulse (reversing the voltage on the target) during HIPIMS applications. During HIPIMS applications a negative pulse at extremely high densities is applied to the target creating a highly ionized plasma at the target surface. Applying a positive pulse prior to the negative pulse extinguishing extends the plasma and repels metal ions that have not recirculated yet toward the substrate. As a result, higher deposition rates, higher ion fraction, denser films, and less film stress is achieved. In addition, the positive pulse option has a significant effect on reactive coating application in that the positive pulse neutralizes the target resulting in fewer arcs, minimizing the disappearing anode effect.

Data will show that the increase in sputtering rate as a result is approximately 15%. Increasing voltage also has a positive impact on the rate. In addition, the higher density and reduced film stress will be shown in provided performance data.

Parameters can be adjusted to optimize performance for various process requirements such as Height of Pulse, Width of Pulse, and Delay of Pulse. This is a key feature of the technology due to the fact that there are variable requirements based on the application that may need to be tuned and altered. Examples of how these changes can alter performance will be presented.

New Horizons in Coatings and Thin Films

Room San Diego - Session F2-2

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Jon Tomas Gudmundsson, University of Iceland

1:30pm F2-2-1 Effect of Bias Voltage during Deposition by Deep Oscillation Magnetron Sputtering of AlN Films for Acoustic Biosensors, L Melo-Máximo, ITESM-CEM, Mexico; J Lin, Southwest Research Institute, USA; AbrilErendira Murillo, O Salas, J Oliva-Ramírez, J Oseguera, B Garcia-Farrera, ITESM-CEM, Mexico; D Melo-Máximo, Tecnológico de Monterrey-Campus Estado de México, Mexico

Deep Oscillation Magnetron Sputtering (DOMS) has an excellent potential to produce AlN films with the required features for biosensing applications. In the present study, AlN films deposited on Si wafers were extensively characterized to assess this potential. The films were produced varying the substrate potential and the resulting microstructures examined by glancing angle x-ray diffraction, scanning electron microscopy coupled with energy dispersive microanalysis, optical profilometry, scratch testing and atomic force microscopy. The results indicate that there is a strong effect of the potential applied to the substrate on the structure of the Al/AlN/Al films an intermediate bias voltage results in the highest (002) oriented films.

1:50pm F2-2-2 Modification of Niobium Surface Properties by High-temperature Nitrogen Plasma based Ion Implantation Aiming Aerospace Applications, Rogério Oliveira, O Aguiar, National Institute for Space Research - INPE, Brazil; A Oliveira, Federal University of São Paulo, Brazil; L Hoshida, Plasma Laboratory, Brazil; M Araujo, M Silva, C Mello, E Ferreira, National Institute for Space Research - INPE, Brazil; V Liccardo, Aeronautical Institute of Technology, Brazil

High temperature nitrogen plasma based ion implantation (HT-NPBII) has been successfully used to treat pristine niobium. The method has shown to be a convenient alternative to treat the surface of Nb in comparison with coating and alloying, mainly when physical and chemical properties of the raw metal must be preserved, as required in many technological applications, like in aerospace sector. In this non-line-of-sight process, the workpiece immersed in plasma is heated by electron bombardment during the off-time of high negative voltage pulses used to implant nitrogen positive ions into the surface of niobium. The precise control of the heating temperature and the adjustment of the implantation energy and duty cycle of the pulses allow to tailoring the N-implantation depth and its concentration. Thus, relatively thick (6-7 μm) layers enriched with nitrogen and very thin ones (less than a hundred of nanometers) can be achieved. It is reported for the first case, a remarkable presence of niobium nitrides for samples treated by HT-NPBII at 1200 °C, 7 keV/ 30 μs / 400 Hz, leading to the improvement of mechanical and tribological properties of the metal, as well as the enhancement of the oxidation resistance. For the second case (700 °C/ 5 keV/ 20 μs / 300 Hz), nitrogen atoms occupy interstitial spaces in the crystal lattice. The treatment of superconducting niobium cavities under these parameters caused the enhancement of two orders of magnitude of the respective quality factors. Such cavities find application in particle accelerators or playing the role of electromechanical transducers of resonant-mass gravitational wave detectors. A complete set of characterization is presented herein, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), glow discharge optical emission spectroscopy (GDOES), scanning electron microscopy (SEM/FEG), Vickers hardness, thermogravimetric analysis (TGA) and tribology measurements.

2:10pm F2-2-3 High-Power Impulse Magnetron Sputtering Coatings for Extreme Environments, Frédéric Schuster, CEA, France; A Ferrec, Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, France; J Wang, Nanyang Technological University, Singapore; M Ougier, CEA, France; A Quenardel, Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, France; M Sall, M Schlegel, F Lomello, A Michau, H Maskrot, F Balbaud, CEA, France

The rise of low carbon energy, in particular nuclear energy, requires the development of new materials resistant to extreme environments with very often combined stresses: high-temperature oxidation, irradiation, wear and corrosion, frequently in concentrated media. During the last years and especially due to the development of HiPIMS (High Power Impulse Magnetron Sputtering) technologies, industrial developments that could not be considered in the past are now possible thanks to the progresses made by PVD (Physical Vapor Deposition) processes.

Applications for protective coatings concern the whole nuclear fuel cycle, specifically the development of EATFs (Enhanced Accident Tolerant Fuels) in order to increase the resistance in loss of coolant accidental conditions. The protection of components operating in concentrated nitric acid in case of reprocessing plants is also of particular interest to increase drastically their lifespan, as wear-resistant components for valves and the protection against corrosion of nuclear waste storage steel containers.

To address these issues, various studies led CEA to develop over the last few years a wide range of HiPIMS coatings, from simple monolithic metals, metallic alloys, self-healing Cr/Ta nanometric multilayers, to more complex nanocomposites compositions in Cr-Si-N and Ti-Si-N ternary systems but also simple and mixed oxides such as ZrO₂ and ZrSiO₄.

HiPIMS benefits from several advantages in comparison with conventional cathodic magnetron sputtering because of its highly energetic and ionized nature. HiPIMS combines the assets of ionized and pulsed PVD processes to achieve denser coatings, stronger adherence with substrates and better thickness conformities which can be crucial for coatings exposed to harsh environments.

The main driver of the integrated and agile approach we elaborated is rapid industrialization of coating processes. That is the reason why we carry out technological demonstration of components at industrial scale very quickly. This whole research is therefore executed in pilot-scale installations followed by industrial prototype facilities.

2:30pm F2-2-4 Reactive High-power Impulse Magnetron Sputtering of Al-O-N Films with Tunable Composition and Properties, Jaroslav Vlček, A Belosludtsev, J Houska, R Čerstvý, S Haviar, 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 [1,2].

In this work, a modified version of HiPIMS, called Deep Oscillation Magnetron Sputtering, with a feedback 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 Al-O-N films with a tunable elemental composition, structure and properties. We give the basic principles of this method, maximizing the degree of dissociation of both O₂ and N₂ molecules in a discharge plasma, which leads to a replacement of very different reactivities of the O₂ and N₂ molecules with metal atoms on the surface of growing films by similar (high) reactivities of atomic O and N.

The depositions were performed using a strongly unbalanced magnetron with a planar aluminium 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 %. Voltage macro-pulses, composed of 10 voltage micro-pulses (pulse-on time of 20 μs and pulse-off time of 30 μs), with a total length of 500 μs and repetition frequency of 350 Hz were used for all depositions with a maximum target power density up to 675 Wcm⁻² during pulses at a deposition-averaged target power density of 8.5 Wcm⁻². The substrate temperatures were less than 120°C (no external heater) during the depositions of films on a floating substrate at the distance of 100 mm from the target. A pulsed reactive gas (O₂ and N₂) flow control made it possible to produce hard (11–19 GPa) and highly optically transparent (extinction coefficient $\leq 1 \times 10^{-4}$ at 550 nm) Al-O-N films with gradually changed elemental compositions from Al₂O₃ into AlN.

[1] J. Rezek, J. Vlček, J. Houska, R. Čerstvý, High-rate reactive high-power impulse

magnetron sputtering of Ta-O-N films with tunable composition and properties, Thin Solid

Films 566 (2014) 70–77.

[2] A. Belosludtsev, J. Houska, J. Vlček, S. Haviar, R. Čerstvý, J. Rezek, M. Kettner,

Structure and properties of Hf-O-N films prepared by high-rate reactive HiPIMS with

smoothly controlled composition, Ceram. Int. 43 (2017) 5661–5667.

2:50pm F2-2-5 Fabrication of Ti BC N Coatings using a Superimposed HiPIMS and MF Deposition System, Yu-Wen Su, J Lee, Ming Chi University of Technology, Taiwan

Recently, the TiBCN hard coating has attracted lots of attentions owing to its wide range of hardness and coefficient of friction values, which are

caused by adjusting the chemical composition of N and C and resulting phases. Meanwhile, the superimposed high power impulse magnetron sputtering (HiPIMS) and middle frequency (MF) power system has been developed to improve the low deposition rate of traditional HiPIMS without sacrificing its high target peak power density. In this study, a superimposed HiPIMS and MF power system was used to grow TiBCN coatings. The pure Ti and TiB₂ targets were adopted during deposition. The reactive gas mixture consisted of nitrogen and acetylene. A plasma emission monitoring system was employed to grow coatings under different Ti target poisoning regime. Various acetylene gas flow rates were added during deposition. The phase of each coating was studied using the X-ray diffractometer. The microstructures of thin films were examined by the field-emission scanning electron microscopy and transmission electron microscopy. Atomic force microscopy was employed to analyze the surface roughness of films. The nanoindentation, scratch and pin-on-disk wear tests were used to evaluate the hardness, adhesion and tribological properties of thin films, respectively. Effects of the Ti target poisoning status and flow rates of acetylene on the microstructure, chemical composition, phase, deposition rate and mechanical properties of TiBCN were studied in this work.

3:10pm F2-2-6 Effect of Peak Current on the Ti-Cu Thin Film Deposition by High Power Impulse Magnetron Sputter Deposition, Ying-Chai Chen, Y Lin, National Changhua University of Education, Taiwan; W Wu, Da-Yeh University, Taiwan

The improvement in the performance and durability of medical implants and surgical tools is an important issue. Therefore, various surface coatings have been applied onto these implants and tools to enhance their functional properties and lifetime. It is known that several metal ions (Cu²⁺, Ag⁺, Zn⁺) exhibit antibacterial effect which fit such a purpose. Among these metal ions, Cu represents a very promising one because of its lower toxicity and higher cytocompatibility. However, the hardness and the adhesion of Cu thin film to the Ti6Al4V substrates require further improvement. As a result, an asymmetric bipolar high-power magnetron sputtering (HiPIMS) technique was used to deposition Ti-Cu thin films using two different targets of Ti and Cu due to Ti can provide a better mechanical property. The peak currents of the Ti and Cu targets were individually varied from 80 to 200A. The thin films were deposited on different substrates, including Si wafer, Ti6Al4V, and a flexible substrate. The microstructure, composition, mechanical properties, antibacterial effect, and biocompatibility of the resulting Ti-Cu thin films were then investigated and reported.

3:30pm F2-2-7 Deposition of Ag-Cu Thin Film on Flexible Substrate using High Power Impulse Magnetron Sputtering, Yu-Hsuan Hsu, W Wu, Da-Yeh University, Taiwan

In high power impulse magnetron sputtering (HiPIMS) technique, a highly ionized flux from both the sputtering gas and target material occurs due to the input of a high power in a short pulse. The quality of the deposited film is thus improved, especially the adhesion, density, and surface roughness. Furthermore, the deposition temperature of HiPIMS is much lower than that of the conventional magnetron sputtering. Therefore, the selection of substrates is much wider. In this study, a HiPIMS technique was used to deposit bimetallic Ag-Cu coatings under an asymmetric bipolar mode. The Cu target current was varied from 80 to 200 A as the Ag target current was fixed at 50 A. The deposition temperature is lower than 50°C. During the deposition, the plasma was diagnosed using optical emission spectroscopy (OES). Flexible substrates, including plastic PET and PEN were used for the deposition. The bioapplication of the Ag-Cu thin films were examined and reported.

3:50pm F2-2-8 Preparation of Anatase TiO₂ Thin Films by Reactive HiPIMS, F Cemin, Université Paris-Sud, France; J Keraudy, Linköping University, Sweden; T Minea, Université Paris-Sud, France; Daniel Lundin, Université Paris-Sud/CNRS, France

Titanium dioxide (TiO₂) is one of the most investigated semiconducting materials for a wide range of applications, e.g., in photocatalysis (for water splitting, decomposition of pollutants, self-cleaning windows), memory capacitors and transistors (dielectric material), lithium-ion batteries (as anode material), gas and humidity sensors, anti-reflective coatings, etc. Compared to the rutile phase, the anatase phase possesses the highest photocatalytic activity and the best properties for lithium-ion intercalation, which are critical factors for the performance of energy-related devices/applications. Although most HiPIMS studies on TiO₂ phase formation are focused on the rutile phase, there is some evidence that anatase (or a mixture of anatase-rutile) grows preferentially under conditions of relatively weak ion bombardment of the growing film.

However, the reported deposition conditions are often contradictory with no obvious choice of pulse parameters, gas pressure, substrate-to-target distance, etc. In this contribution we have therefore investigated the HiPIMS growth conditions required specifically for anatase TiO₂ and systematically studied the phase formation, microstructure and chemical composition as a function of mode of target operation (metal-transition-compound modes) as well as of external process parameters (substrate temperature, working pressure, and peak current density). Phase pure anatase films were deposited at power normalized deposition rates of more than a factor 10 higher compared to what has previously been reported. Also the crystal quality was improved by using ion bombardment of weak to moderate intensity. Furthermore, the reactive HiPIMS process of TiO₂ was characterized using a new reactive ionization region model (R-IRM). The model provided insight into the temporal behavior of the discharge plasma parameters such as electron density, the neutral and ion composition, the ionization fraction of the sputtered vapor, the oxygen dissociation fraction, and the composition of the discharge current for various discharge conditions.

4:10pm F2-2-9 Vapor Phase Nanoparticle Synthesis, Guiding and Self-assembly, Ulf Helmersson, Linköping University, Sweden INVITED

The synthesis of nanoparticles using low-pressure plasma have the reputation that it "cannot be easily managed for production of material in large quantities". [1] However, it has recently been shown, independently by two groups, that it is possible to achieve a dramatic increase in nanoparticle productivity in using pulsed plasmas. [2,3] This is of great interest since low-pressure plasma methods opens up the potential for design of a diversity of nanoparticles directly followed by the distribution of the generated nanoparticles on surfaces or in the assembly of the nanoparticles into nanostructures using guiding electric or magnetic fields. Electric field can be used since nanoparticles in a plasma generally attains a negative potential, while magnetic fields require that the nanoparticles have ferromagnetic properties. In this presentation, the role of high-power pulsed plasmas for the increased nanoparticle yield, will be discussed and results of nanoparticle assembly into pillars, nanowire and nanotrusses, will be presented. Matrixes of pillars assembled from Ag-nanoparticles are generated by the use of a grid in front of the substrate forming an electrostatic lens by applying suitable potentials on the grid and the substrate. By placing the grid on a movable stage, 3D-printing behavior can be achieved. In the synthesis of ferromagnetic Fe- and Ni-nanoparticles, the use of an external magnet placed behind the substrate promotes the self-assembly of the nanoparticles into wires and trusses, forming conducting nanostructures with large surfaces. The use of these structures in an electrocatalytic water-splitting experiment demonstrates the structures great potential for the use as different electrodes.

[1] A. Bouchoule, ed. *Dusty Plasmas: Physics, Chemistry, and Technological Impacts in Plasma Processing*. Wiley,

New York (1999)

[2] O. Polonski, T. Peter, A.M. Ahadi, A. Hinz, T. Strunskus, V. Zaporojtchenko, H. Biederman, F. Faupel, Huge increase in gas phase nanoparticle generation by pulsed direct current sputtering in a reactive gas admixture. *Appl. Phys. Lett.* **103**, 033118 (2013).

[3] I. Pilch, D. Söderström, M.I. Hasan, U. Helmersson, N. Brenning, Fast growth of nanoparticles in a hollow cathode plasma through orbit limited ion collection. *Appl. Phys. Lett.* **103**, 193108 (2013).

New Horizons in Coatings and Thin Films

Room San Diego - Session F2-3

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Jon Tomas Gudmundsson, University of Iceland

8:00am F2-3-1 Ultra-thick CrN/AlN Superlattice Coatings Deposited by a Combination of Plasma Enhanced Magnetron Sputtering and High Power Impulse Magnetron Sputtering, Jianliang Lin, R Wei, Southwest Research Institute, USA

Plasma enhanced magnetron sputtering (PEMS) is an advanced version of conventional magnetron sputtering by generating a global plasma, in addition to the magnetron plasma, in the entire deposition system using hot filament thermionic emission to enhance the ionization and bombardment. As one version of high power impulse magnetron sputtering (HiPIMS) technique, deep oscillation magnetron sputtering (DOMS) generates large oscillation high power pulses to achieve a high ionization fraction of target species for reactive HiPIMS sputtering. Both DOMS and PEMS aim at utilizing a highly ionized plasma to improve the structure and properties of the coatings. In this paper, ultra-thick CrN/AlN superlattice coatings (20 μm) were deposited on steel substrates by reactive sputtering using a combination of PEMS and DOMS techniques. These coatings were deposited at different PEMS plasma discharge currents (0 to 4 A) which represent different levels of low energy ion bombardment. The bilayer thickness of the nanolayers was controlled in the range of 4 to 7 nm. The microstructure of the coatings gradually changes from long columnar grains to extremely dense structure with an increase in the PEMS discharge current. These thick CrN/AlN coatings show very high hardness and excellent adhesion. The high temperature wear resistance of selected coatings was measured using a high temperature pin-on-disc tribometer in the ambient air from 600 °C to 900 °C. The solid particle erosion resistance of these ultra-thick CrN/AlN coating was evaluated and compared with other thick hard coatings, e.g. CrN, TiN, TiSiCN, etc., using an air jet sand erosion tester.

8:20am F2-3-2 Deposition of DLC Coatings by HIPIMS to Arc Mixed Mode, Holger Gerdes, R Bandorf, J Rösler, M Vergöhl, G Braeuer, Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

The deposition of hard carbon or diamond-like carbon (DLC) films is still of high interest, especially in combination with high power impulse magnetron sputtering (HIPIMS). In automotive applications, the use of hydrogen-free, so-called ta-C coatings is well established. The ta-C are mainly deposited by arc processes, suffering increased roughness due to high energetic macro-particles. Introducing a HiPIMS to Arc mixed mode by M. Lattemann et al. opened the scene for combining the high density sputtering of smooth coatings with the high energy processing by arc. In 2015 Ganesan et al. reported on the deposition of ta-C films with high sp³-content from a 3 inch target.

This presentation will show an approach for upscaling a HiPIMS-Arc mixed mode to an industrial sized cathode (0.5 m). The process parameters and basic aspects on how to design a pulse for transitioning into an arc will be discussed. The investigations by optical emission spectroscopy (OES) showed clearly an indication on generating carbon-ions. The Vickers hardness of prepared films were measured and showed first results with a hardness of up to 3500 HV.

8:40am F2-3-3 Performance Improvements of Tungsten and Zinc Doped Indium Oxide Thin Film Transistor by Fluorine Based Mixing Plasma Treatment with a High-K Gate Dielectric, Yu-Chuan Chiu, P Liu, D Ruan, M Yu, K Gan, T Chien, Y Chen, P Kuo, S Sze, National Chiao Tung University, Taiwan

This study investigates the physical analysis and electrical characteristics for amorphous tungsten and zinc doped indium oxide thin film transistor (a-InWZnO TFT) with a high-k gate insulator, which is applied by fluorine based mixing plasma treatment. Compared with the traditional InGaZnO TFT, the tungsten dopant was proposed as excellent carrier suppressor, which may improve the reliability significantly. However, the carrier mobility was also slightly inhibited by the dopant. In order to achieve good stability and high carrier concentration simultaneously, the fluorine based mixing plasma treatment was introduced in the device process. The fluorine plasma is used as a method to passivate carrier traps within the channel or at the channel/dielectric interface, which can effectively improve the channel conductivity. In addition to that, the oxygen vacancies

are also increased in the back channel region by only fluorine plasma treatment. This may result that a extreme high carrier mobility at the back channel surface which can't be control by a reasonable gate bias. With a mixing plasma process, this phenomenon can be suppressed. Furthermore, a high-k gate insulator is applied for improving the ability of gate control. In this report, the devices with CF₄ + N₂O plasma treatment show a high field-effect mobility of $\sim 25 \text{ cm}^2/\text{V}\cdot\text{s}$, a high On/Off current ratio of $\sim 6 \times 10^6$ and a small subthreshold swing of 0.1 V/decade for a best interface quality for all samples. This research proposes that the fluorine based mixing plasma treatment may be an effective approach to improve the interface quality for novel metal oxide TFT fabrication.

9:00am F2-3-4 Effect Of Craters Formation On Deep Hardening Under Pulsed Electron Beam Treatment, Thierry Grosdidier, Laboratoire d'Excellence Design des Alliages Métalliques pour Allègement de Structures (Labex DAMAS), France; Y Samih, Laboratoire d'Etude des Microstructures et de Mécanique des Matériaux (LEM3), France; C Dong, Key Laboratory of Materials Modification, Dalian University of Technology, China

Techniques like the intense pulsed electron beams (IPEB) or intense pulsed ion beams (IPIB) generally induce surface melting, evaporation followed by rapid solidification and quenching which are accompanied by the formation of stress waves. As a result, surface/near surface properties such as corrosion and wear resistances can be improved while the generation of structural defects such as vacancies and dislocation loops also affect the depth of the samples and can lead to sub-surface hardening. While the improved wear resistance and corrosion resistance have been attributed to several complementary factors (surface hardening, nanostructure formation) the mechanisms responsible for the deep hardening are much less understood.

In the case of IPEB, the large pulse duration (about 800 ns under High Current Pulsed Electron Beam) and, accordingly, the low rate of energy input, does not provide with the formation of the dynamic stress wave and the increase in dislocation density was entirely provided by the action of the quasi-static thermal stresses. In their modelling approach, Quin et al. [1] suggested that the subsurface initial melting that is associated with the specific energy distribution of the electron beam could create an additional source of plastic deformation via the recoil impulses that are generated as a consequence of crater eruptions.

To the authors knowledge however, there is no experimental work that has been carried so far to undoubtedly verify the effectiveness of the formation of craters on hardening the surface and subsurface of HCPEB treated samples. The aim of the present paper is to investigate experimentally the contribution of the potential crater bursts on modifying the deep hardening phenomena. To this end, the HCPEB technique has been applied under similar processing conditions on two stainless steels of very close chemistry but having different potential for crater formation.

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9:20am F2-3-5 Mechanical Property Evaluation of ZrCN Films Deposited by a Hybrid Superimposed High Power Impulse- Middle Frequency Sputtering System, Q Tang, Y Wu, National Taipei University of Technology, Taiwan; Jyh-Wei Lee, Ming Chi University of Technology, Taiwan

High power impulse magnetron sputtering (HiPIMS) is a relatively new physical vapor deposition technology, which is characterized by its ultra-high peak current, peak power density and high-density plasma to achieve unique thin film mechanical properties, such as high hardness, good adhesion and good wear resistance. Recently, a superimposed HiPIMS-middle frequency (MF) power system has been proved to increase the deposition rate of HiPIMS technique effectively. In this study, a superimposed HiPIMS-MF power system was used to deposit the ZrCN films with different carbon content on hardened tool steel disks and silicon wafer substrates. The phase of each coating was studied by means of the X-ray diffractometer. The microstructures of thin films were examined by a field-emission scanning electron microscopy. Atomic force microscopy was used to characterize the surface morphology and roughness. The nanoindentation and scratch tests were used to evaluate the hardness and adhesion properties of thin films, respectively. The pin-on-disk wear test was employed to study the tribological property of coating. Effects of carbon content on the microstructure, mechanical and tribological properties of ZrCN coatings were further discussed in this work.

New Horizons in Coatings and Thin Films Room San Diego - Session F1

Nanomaterials and Nanofabrication

Moderators: Ulf Helmerson, Linköping University, Vitezslav Stranak, University of South Bohemia

1:50pm F1-2 Kinetic Engineering of Crystal Phases in Core-shell Nanowires: Heteroepitaxial Radial Growth of Wurtzite and Zincblende Structured AISb Shells on InAs Nanowires, Hanna Kindlund, R Zamani, A Persson, S Lehmann, R Wallenberg, K Dick, Lund University, Sweden

AlSb and InAs are III-V semiconductors belonging to the so-called 6.1 Å family, with room-temperature band-gaps of 1.61 and 0.36 eV, respectively. Their combination, especially to form low-dimensional heterostructures, is important to develop devices with potentially new applications based on the band-lineups that these heterostructures form. While zincblende (ZB) is the stable structure of conventional bulk III-V semiconductors, it has been shown that low dimensional structures such as nanowires can be grown in the wurtzite (WZ) crystal phase. Previous studies have also demonstrated the growth of nanowires composed of segments with both ZB and WZ crystal structures.¹⁻⁴

Here, we use Au-seeded InAs nanowire core templates with engineered lengths of axial WZ and ZB segments and demonstrate selective, heteroepitaxial radial growth of AlSb on either ZB- or WZ-InAs nanowire segments. We grow InAs/AlSb/InAs core-double-shell nanowires on InAs(111)B substrates by metal-organic vapor phase epitaxy (MOVPE). The precursors used are trimethylindium (TMIn) and arsine (AsH₃) for the growth of InAs core templates, and triisobutylaluminum (TTBAL) and trimethylantimony (TMSb) for AlSb. Using scanning electron microscopy, transmission electron microscopy, electron tomography, and energy-dispersive x-ray spectroscopy, we determine the AlSb shell thickness, crystal-phase, and nanostructure as a function of the shell growth temperature (390 < T_s < 490 °C).

We find that ZB and WZ structured AlSb shells grow epitaxially around the ZB and WZ segments of the InAs core, respectively. Interestingly, the WZ structured AlSb shells are thicker than the zincblende AlSb shells at 390 < T_s < 450 °C with thickness increasing with decreasing growth temperature. In contrast, the ZB-AlSb shell thicknesses increase little with increasing T_s. In addition, detailed electron tomography studies show that the thicker WZ-AlSb shells form on the {11-20} facets rather than on the more commonly grown {1-100} sidewall facets. These results indicate that the growth of WZ-AlSb is preferred over the thermodynamically stable ZB-AlSb at lower growth temperatures. We attribute this behavior to kinetic limitations of MOVPE of AlSb on ZB and WZ phases of InAs.

References:

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3. S. Assali, L. Gagliano, D.S. Oliveira, M.A. Verheijen, S.R. Plissard, L.F. Feiner, and E.P.A.M. Bakkers, *Nano Lett.* **15**, 8062 (2015).
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2:10pm F1-3 Understanding the Friction of Sub-nanometer Thick Ionic Liquids (ILs), A Lertola, Lei Li, University of Pittsburgh, USA

Ionic liquids show promise as lubricants for nano- and micro-electromechanical systems (NEMS/MEMS). When deposited on solid substrates as thin films, these liquids can exhibit solid-like layering structure, which makes them ideal as nano-lubricants. Moreover, ionic liquids are “designer” materials with many possible molecular structures and tunable properties. In this work, we have investigated the friction of various nanometer-thick ionic liquids. While many previous studies showed the impact of cation, we found a dramatic difference in the friction coefficients for 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM) and 1-Ethyl-3-methylimidazolium tris(pentafluoroethyl) trifluoro phosphate (EMIM FAP), suggesting that anion structure also bears a significant effect on the friction. The effect of water at the interface has also been investigated and the friction profiles of the ionic liquids proved resistant to moisture manipulations. Film thickness, uniformity and adhesion to the substrate were also studied to relate molecular structure and surface morphology to tribology performance. The
Tuesday Afternoon, April 24, 2018

significance of these results in terms of ILs as potential MEMS lubricants will be discussed.

2:30pm F1-4 Facile Synthesis of MoSe₂ Nanoplates on Black Phosphorus Nanosheets for Enhanced Hydrogen Evolution Reaction Performance, Wan Li, City University of Hong Kong, Hong Kong; D Liu, J Wang, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, China; M Huang, City University of Hong Kong, Hong Kong; N Yang, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, China; L Liu, Peking University Shenzhen Graduate School, China; X Peng, G Wang, City University of Hong Kong, Hong Kong; X Yu, Shenzhen Institutes of Advanced Technology, Chinese Academy of Sciences, China; P Chu, City University of Hong Kong, Hong Kong

Today, seeking for cost-effective and efficient electrocatalyst is desired because hydrogen evolution reaction (HER) has been highly recognized as a promising approach to produce clean and renewable energy. MoSe₂ is an attractive candidate due to its fascinating properties. Unfortunately, aggregation as well as low conductivity restricts its developments. Here we report a smart strategy that MoSe₂ nanoplates adhered on the surface of BP nanosheets through van der Waals interactions, aiming to increase conductivity and expose much more active sites simultaneously. It is found that the prepared MoSe₂-BP exhibits an enhanced electrocatalytic performance with a lower onset potential (200 mV), a smaller Tafel slope (109 mV dec⁻¹) and excellent stability. Such this performance can be attributed to the support provided by BP, which benefit efficient electrons transfer and prevent MoSe₂ from aggregating.

2:50pm F1-5 Synthesis and Magnetic Properties of Mn_xZn_yFe_{3-x-y}O₄ Nanoparticles Prepared using a Co-precipitation Method, Kuan-Wei Chen, J Ting, National Cheng Kung University, Taiwan

(Mn, Zn) ions were doped into Fe₃O₄ to form Mn_xZn_yFe_{3-x-y}O₄ nanoparticles for enhancing the magnetic property of. The Mn_xZn_yFe_{3-x-y}O₄ nanoparticles were synthesized through an easy, one-step, and quick aqueous co-precipitation method. Iron(III) chloride [FeCl₃·6H₂O], manganese(II) chloride [MnCl₂·4H₂O], and zinc chloride [ZnCl₂] were dissolved into hydrochloric acid to form the precursor solution. NH₄OH was then added into the precursor solution as reagent to the pH value. After vigorous agitation of the pH-adjusted precursor solution, precipitates were then collected. To investigate the microstructure, chemical composition, and magnetic properties, the obtained nanopowders were characterized using field emission scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffractometry, electron Spectroscopy, and a superconducting quantum interference measurement device. The effects of Mn and Zn ion additions on the chemical composition and magnetic properties are presented and discussed. The and mechanism of Mn_xZn_yFe_{3-x-y}O₄ nanoparticle formation is also discussed.

3:10pm F1-6 Effects of Nano Particles on the Thermal Stability and Scratch Resistances of Epoxy Coatings, Mourad Boumaza, K Rawaziz, King Saud University, Saudi Arabia

Coatings are susceptible to damage caused by scratch and/or abrasion and thermal instability. Clearly, the consumer prefers to retain the aesthetic appearance of coated materials and for this reason clear coats used on automobiles must have good scratch and abrasion resistance. An added problem is that scratches may also cause damage to the underlying substrate. Scratch resistance can be obtained by incorporating a greater number of cross links in the coating's binder but unfortunately highly cross linked (hard) films have poor impact resistance due to less flexibility. A less cross linked (softer) film will show better performance with regard to other properties such as anti-finger print and impact resistance but will have less scratch and abrasion resistance

On the other hand thermal performance of materials is crucial in many industries, ranging from pharmacy, battery and aerospace and electronics to construction industries. For optimum thermal stability, heat dissipation, bonding and homogeneity are key parameters of thermal characterization and thermal conductivity, Many researchers recently worked on thermal stability of epoxy/nanoparticles coatings by using different types of nanoparticles

The purpose of this work is to investigate the effect of inorganic nanoparticles on scratch resistance and thermal properties of epoxy/Polyamid coating system. The nano composite coatings are formulated by incorporation of various types of nanoparticles (ZrO₂, ZnO, SiO₂, and Fe₂O₃) with 2 wt. % loading for each type of nanostructure.

The results showed that all the composite coatings with 2% loadings of Nanoparticles increased and passed the impact test of 120 lbs/in as

Tuesday Afternoon, April 24, 2018

compared to the unreinforced coating which cracks at 112 lbs/in. However the impact value for EPZN remains the highest and showed 57% increase in the impact resistance. Similarly the Scratch resistance for all the samples increased in all compositions, while EPSI was found to have highest Scratch load. The increasing trend in the scratch hardness values can be attributed to the improvement in the adhesion between composite coating and metal substrate.

Thermal analysis of these nano composites revealed that the addition of SiO₂ and ZrO₂ enhanced the thermal stability of the nano composite coating, while Fe₂O₃ and ZnO reduce the thermal stability due to catalytic effect of these nanoparticles, which facilitate the thermal degradation process.

3:30pm F1-7 Corrosion Study of Silane-functionalized Graphene Oxide Coatings on Copper, Mohsin Ali Raza, Z Rehman, F Ghauri, University of the Punjab, Lahore, Pakistan

This research work aims to produce corrosion resistant silane-functionalized graphene oxide (GO) coatings on copper (Cu) metal. Two types of precursor graphite (flakes and powder) were utilized to synthesize GO following improved Hummers' method, and resulting GO was labelled as FGO and PGO, respectively. GO was deposited on copper metal, which was made anode and platinum was made cathode, from GO/water suspension by electrophoretic deposition (EPD). Silane functionalization was performed by immersing GO-coated samples in 3-aminopropyltriethoxy silane (APTES) solution. The role of precursor graphite, deposition time, surface roughness of substrate, and post-treatment of GO coating with silane on corrosion protection ability of GO coatings was studied. Characterization of GO and silane-functionalized GO coatings was performed by X-Ray diffraction, atomic force microscopy, Fourier transform infrared spectroscopy and scanning electron microscopy. Optimum EPD parameters for the development of uniform coatings were found to be 5 V and 30 sec with GO/water concentration of 1:10. Corrosion behavior of GO and silane-functionalized GO samples was studied by Tafel analysis, electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) in 3.5 % NaCl solution. The results showed that precursor graphite effects quality of GO, and consequently the corrosion behavior of the GO coatings. PGO-coated Cu deposited at optimized parameters showed better corrosion protection compared to FGO-coated Cu. Tafel analysis showed that PGO coating and silane-functionalized PGO coating developed at optimized parameters enhanced corrosion resistance of Cu by ca. 6x and 25x, respectively, compared to bare Cu. Tafel results were well validated by EIS and CV.

3:50pm F1-8 Growth of MnO₂ on Carbon Materials for Electrochemical Capacitor, Chia-Jung Tu, M Wu, National Changhua University of Education, Taiwan; W Wu, Da-Yeh University, Taiwan

Manganese oxide (MnO₂) has attracted intensive attention and been widely used as catalysis, ion exchange, molecular adsorption, biosensor, and electrodes for lithium ion batteries and supercapacitors due to its low cost, abundance and environmental-friendliness. For supercapacitors, MnO₂ is the most investigated oxide for pseudocapacitors on the basis of its high theoretical specific capacitance of 1370 Fg⁻¹. However, the theoretical specific capacitance of MnO₂ has rarely been achieved due to its poor electrical conductivity. Therefore, a hybrid electrode architecture which incorporates nanostructured MnO₂ on high-surface-area conductive carbon materials was used to improve the electrical conductivity and the specific capacitances. In this study, activated carbon fiber cloth (CFC) and vapor grown carbon nanofiber (VGCNF) was used as the carbon support material. The pretreatment condition of the vapor grown carbon nanofiber were first discussed. Then, nanostructured MnO₂ was grown on activated carbon fiber cloth and vapor grown carbon nanofiber using three different wet chemical methods and conditions. It was observed that different concentration of the precursor KMnO₄ play a crucial role in the crystal growth of MnO₂, which result in different morphology.

4:10pm F1-9 Fabrication of a CMOS Compatible Ferroelectric Tunnel Junction Memory, Fabian Ambriz-Vargas, Énergie, Matériaux et Télécommunications, Canada; G Kolhatkar, Institut National De La Recherche Scientifique, Canada; R Nouar, A Sarkissian, PLASMIONIQUE Inc, Canada; M Gauthier, A Ruediger, Institut National De La Recherche Scientifique, Canada

Semiconductor memories are the key component of any electronic device. Among the different types of semiconductor memories, Dynamic Random Access Memory (DRAM) is the most used memory in the semiconductor market. However, the continue miniaturization of the electronic devices leaded to reach the DRAM physical limits. Then, new types of

semiconductor memories based on different physical approaches are now attracting attention. One candidate to replace DRAM technology is the Ferroelectric Tunnel Junction memory (FTJ), which offers advantages such as a low operating energy, high operation speed (read/write access; ~10ns/10ns), high endurance (10⁶ cycles) and non-volatility.

Recently, it was reported the successful fabrication of the first FTJ devices. They were based on perovskite tunnel barriers such as barium titanate (BaTiO₃), bismuth ferrite (BiFeO₃), lead titanate (PbTiO₃) etcetera. However, FTJs based on perovskite tunnel barriers require of specific substrates (strontium titanate, SrTiO₃) and high processing temperatures (~700°C) which makes them incompatible with the complementary metal oxide semiconductor process (CMOS). In comparison to perovskites, Hafnium-Zirconium oxide (Hf_{0.5}Zr_{0.5}O₂) films offer advantages such as CMOS compatibility as well as ferroelectric properties in ultrathin form.

Thus, in the present work, we report on the fabrication of the first FTJ memory device based on a CMOS compatible tunnel barrier Hf_{0.5}Zr_{0.5}O₂ (6 unit cells thick, ~3nm thick film) on an equally CMOS compatible TiN electrode. Such a device will give rise to a new generation of semiconductor memory devices.

4:30pm F1-10 Polyacrylonitrile Nanofibers Prepared via Electrospinning for High-efficiency PM2.5 Capture Application, Kuan-Nien (G.N.) Chen, Unaffiliated; J Ting, National Cheng Kung University, Taiwan

TiO₂ surface-residing electrospun PAN nanofibers with controllable density of TiO₂ on the fiber surface were prepared by means of an electrospinning technique and microwave hygrothermal method. The nanofiber diameter was controlled by the voltage, precursor viscosity, and flow rate during the electrospinning process. The surface morphology was controlled by adding TiO₂ with different concentrations. The surface chemistry was optimized to enhance PM adsorption. SEM, TEM and XRD pattern analyses demonstrated that TiO₂ was formed and resided on the nanofiber surface, and surface chemical composition was analyzed by XPS. Selected samples were evaluated for filtering efficiency by examining the particle counter (CEM) and the removal efficiency was calculated by comparing the PM particle number concentration before and after filtration.

New Horizons in Coatings and Thin Films Room San Diego - Session F4-1

Functional Oxide and Oxynitride Coatings

Moderators: Jörg Patscheider, Evatec AG, Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG, Marcus Hans, RWTH Aachen University

8:00am **F4-1-1 Self-healing Thermal Barrier Coating System for Prolonged Lifetime**, **Willem Sloof**, Delft University of Technology, Netherlands
Thermal barrier coatings (TBCs) are applied on aircraft and industrial gas turbine engines protecting the operating components from demanding high temperature environments. However, the thermal mismatch leads to generation of stresses in the TBCs resulting in micro-cracks that grow and coalesce, leading to ultimate failure of the coating. A new, unique self-healing thermal barrier coating for turbines and other thermally loaded structures has been developed in order to realize a significant extension of the lifetime of critical high-temperature components.

The concept is based on novel Al_2O_3 coated MoSi_2 particles embedded in the TBC layer, typically consisting of yttria partially stabilized zirconia (YPSZ) [1]. Upon high-temperature exposure in an oxidising environment the embedded MoSi_2 particles react to form a viscous silica (SiO_2), which fills the cracks and re-establishes adherence in the TBC. Subsequently the SiO_2 reacts with the matrix forming zircon (ZrSiO_4), which is a load bearing and solid crystalline ceramic phase. This new concept involves the creation of an inert, oxygen impenetrable, shell of alumina (Al_2O_3) around the actual healing agent, which prevents premature triggering of the healing reaction. With this approach, the healing mechanism will become active only when a crack penetrates the alumina shell.

The MoSi_2 particles are alloyed with boron to promote the kinetics of the healing reaction and filling of crack gap with amorphous silica [2]. For manufacturing the self-healing TBC by atmospheric plasma spraying, encapsulation by selective oxidation of aluminium, added to the healing particles, proved to be successful. The core of the encapsulated and embedded healing particles remained intact when exposed to high temperatures in air for long times.

In furnace cycle tests, mimicking TBCs in applications, the crack damage evolution due to mismatch in thermal expansion is determined. The lifetime of the self-healing TBC in the furnace cycle tests compared to a similar TBC but without healing particles, was prolonged and the scatter in the lifetime data reduced making the self-healing TBC more reliable.

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8:40am **F4-1-3 TiO_2 Thin Films Deposited onto PET by High Power Impulse Magnetron Sputtering for Photocatalytic Degradation of Carbendazim**, **R Marcelino**, Universidade Federal de Minas Gerais, UFMG, Brazil; **M Ratova**, **B Delfour-Peyrethon**, Manchester Metropolitan University, UK; **C Amorim**, Universidade Federal de Minas Gerais, UFMG, Brazil; **Peter Kelly**, Manchester Metropolitan University, UK

Photocatalysis has been widely studied for the removal of contaminants of emerging concern from water. The use of the catalyst in a powdered form results in high surface area, but hinders the catalyst recovery. An alternative approach is to deposit the photocatalyst onto a flexible substrate material that can conform to the shape of a reactor vessel. Titania (TiO_2) in the anatase phase is the most widely used photocatalyst, but when deposited by conventional magnetron sputtering, the coating usually requires elevated temperatures or post-deposition annealing in order to form the desired crystalline structure. This precludes the use of thermally sensitive substrates. However, deposition in HiPIMS (high power impulse magnetron sputtering) mode allows the deposition of anatase titania in a single stage process directly onto polymeric substrates. This paper, therefore, presents data on the performance of photocatalytic thin films of titania deposited onto polyethylene terephthalate (PET) supports via HiPIMS. Photocatalytic activity of the coated film was assessed by the degradation of the photostable fungicide carbendazim (CBZ) in aqueous

solution, in the presence of a photosensitizing agent, reaching 35% of CBZ removal under UV-A and visible radiation. The reusability of the coatings was implied by negligible drop in activity after 5 cycles. The titania coatings have been characterized by SEM, XRD and UV-vis spectroscopy.

9:00am **F4-1-4 Thermal Stability of Structure and Enhanced Properties of Zr-Ta-O Films with Low and High Ta Content**, **Petr Zeman**, **S Zuzjakova**, **J Vlíček**, **J Rezek**, **R Čerstvý**, **J Houska**, **S Haviar**, University of West Bohemia, Czech Republic

Development of novel multicomponent ceramic oxide systems is the promising way how to extend application potential of binary oxides. Zirconia is one of the most studied oxide ceramic materials because of its excellent chemical inertness and good mechanical, electrical, optical and thermal properties. Tantalum pentoxide used as thin-film material exhibits interesting electrical and optical properties. The limit for an application of these oxides is the stability of their structure and properties at elevated temperatures.

The present study focuses on investigation of the thermal stability of the structure and optical and mechanical properties of Zr-Ta-O films with a low and high Ta content. Two ternary Zr-Ta-O films ($\text{Zr}_{25}\text{Ta}_5\text{O}_{70}$ and $\text{Zr}_5\text{Ta}_{25}\text{O}_{70}$) and two binary films (ZrO_2 and Ta_2O_5) were prepared by reactive high-power impulse magnetron sputtering of a single Zr-Ta target (with a varying Ta fraction in the target erosion area) in argon-oxygen gas mixtures using a pulsed reactive gas flow control. The films were deposited either without any external substrate heating or at 400°C onto Si substrates at a floating potential. In the as-deposited state, the structure, microstructure, mechanical and optical properties of the films were analyzed and their thermal stability in air in a temperature range of $700^\circ\text{C} - 1300^\circ\text{C}$ investigated.

We found that highly optically transparent Zr-Ta-O films exhibit a higher hardness, a higher refractive index and an enhanced thermal stability of the as-deposited structure and optical and mechanical properties than the corresponding binary oxides. The $\text{Zr}_{25}\text{Ta}_5\text{O}_{70}$ film is a single-phase material with a nanocrystalline structure corresponding to the ternary $\text{TaZr}_{2.75}\text{O}_8$ phase. This as-deposited phase is stable up to a maximum temperature investigated (1300°C) and the film retains its hardness of 19 GPa and refractive index of 2.25 (measured at 550 nm) even after annealing to 1000°C in air. The $\text{Zr}_5\text{Ta}_{25}\text{O}_{70}$ film exhibits an amorphous structure in the as-deposited state with its thermal stability up to 800°C , which is by about 100°C more than in the case of the Ta_2O_5 film. At higher temperatures a crystallization of a coarse-grained $\beta\text{-Ta}_2\text{O}_5$ phase occurs. The thermal stability of mechanical and optical properties will be discussed and presented in more detail.

9:20am **F4-1-5 Electrophysical Properties of Nanoparticle-Added PEO Coatings on Aluminium**, **Noratiqah Yaakop**, **B Mingo**, **L Qiang**, **Z Wang**, **A Yerokhin**, **A Matthews**, University of Manchester, UK

Oxide ceramic coatings produced by Plasma Electrolytic Oxidation (PEO) in electrolytes with nanoparticle additions have been gaining increasing attention. Many electrical and electronic applications such as capacitors, resistors and integrated circuits would benefit from dielectric surface layers produced by green and facile PEO technology. The PEO coatings produced with incorporation of nanoparticles directly from electrolyte are known to be denser, however the influence of nanoparticle additions on electrophysical properties of such coatings requires further investigation.

The PEO coatings have been produced on AA6082 alloy samples using a pulsed bipolar current mode with 1-3 kHz frequency. The composition of the dilute alkaline electrolyte and the concentration of alpha alumina nanoparticles additions were varied from 10 to 30 g/l. Since incorporation of nanoparticles allowed coating porosity to be reduced, thin yet dense PEO coatings with thickness ranging from 10 to 30 micron have been produced in relatively short treatment times, varied from 5 to 15 min.

A Mott-Schottky analysis was performed on the coatings to determine the concentration charge carriers and the flat band potential. For that, electrochemical impedance spectroscopy (EIS) was conducted at increasing potentials from 0 to 1.3 V vs. OCP with step size of 100 mV. The capacitance of the coatings was calculated by fitting the experimental data to an equivalent circuit and a linear relationship between the inversed squared capacitance and applied voltage was found. The dielectric strength of the studied materials was evaluated in the metal-oxide metal configuration by applying an increasing DC voltage until the coating breakdown is achieved. Morphology of the coatings was studied by scanning electron microscopy (SEM) and phase composition of the coatings was analysed by X-ray diffraction. Correlations were sought between

Wednesday Morning, April 25, 2018

characteristics of surface morphology, phase composition and electrophysical properties of the studied coatings.

The results indicate that the electrophysical properties of PEO coatings are comparable and in some cases even better compared to epoxy-based materials used, up to now, for insulated metal substrates. Additionally, these coatings present higher thermal stability and lifetime which makes them potential candidates for electronic applications.

9:40am **F4-1-6 Titania Films Deposited by Constant Current High Power Impulse Magnetron Sputtering**, *Arutiun P. Eghisarian, D Loch*, Sheffield Hallam University, UK; *A Heisig, J Neidhardt*, Von Ardenne Anlagen Technik, Germany

TiOx films were produced by reactive High Power Impulse Magnetron Sputtering (HIPIMS) of a pair of metallic targets in an Ar-Oxygen atmosphere. During the HIPIMS process a fast rise and a constant current was maintained during the pulse by regulating the voltage. This resulted in the elimination of stability issues associated with runaway currents and target poisoning for oxygen flows ranging from 10 to 50% of the total gas flow. Time-resolved optical emission spectroscopy revealed that the plasma discharge developed through stages of gas ionisation, gas rarefaction and metal sputtering, the latter associated with cooling of the electron temperature. Evidence is presented of metal ionisation and atomic oxygen sputtering from the target at low pressure and produced in the gas phase at high partial pressure. Films were deposited without intentional heating or substrate biasing and had good transparency. The thickness uniformity was < 2% across a 100x100 mm area. The refractive index increased continuously as the oxygen flow reduced from 45 to 13% reaching a maximum value of 2.55 at a wavelength of 550 nm compared to 2.47 for bipolar pulsed sputtered films. The extinction coefficient in the HIPIMS coatings was of the order of 0.003, similar to bipolar pulsed sputtered films. The films were metallic (non-transparent) at 10% Oxygen flow. The films comprised a mixture of rutile and anatase phase with HIPIMS deposition producing higher fractions of rutile compared to bipolar pulsed DC operation. The hardness of the films and its relation to process conditions are discussed.

10:00am **F4-1-7 Study on Silicon Carbide Based Metal Oxide Semiconductor Capacitor with Magnetron Sputtered ZrO₂ High-k Gate Dielectric**, *S Mourya, J Jaiswal, G Malik, B Kumar, Ramesh Chandra*, Indian Institute Of Technology Roorkee, India

A silicon carbide (SiC) based two terminal metal oxide semiconductor (MOS) capacitor with magnetron sputtered zirconium oxide (ZrO₂) as a high-k dielectric material using titanium (Ti) gate has been synthesized at room temperature. The structural, morphological and compositional analysis of the dielectric layer has been carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), Atomic force microscopy (AFM), energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The current-voltage (I-V) and capacitance-voltage (C-V) characteristics of MOS capacitor were studied at room temperature by applying the dc bias gate voltage swept from -3V to 3V for both, high and low-frequency operation on a probe station. The thermal stability of the MOS capacitor is of critical importance for use in the fabrication of electronics for deployment in extreme environments. Hence, the effects of post-deposition annealing (PDA) temperatures (200-1000 °C) on the electrical properties of MOS capacitor have been investigated. MOS characteristics of Ti/ZrO₂/SiC/Ti capacitor were correlated with structural and morphological properties of an insulating dielectric layer at different PDA temperatures. It has been observed that a synergetic contribution of lowest effective oxide charge, semiconductor-oxide interface-trap density and total interface-trap density improve the electric breakdown field of MOS capacitor for PDA samples.

10:20am **F4-1-8 On the Importance of the Energy of Negative Ions in Achieving Uniform and High-quality Magnetron Sputtered AZO Films**, *Fanping Meng*, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

Spatial distribution of highly energetic negative ions inherent in magnetron sputtering of oxides has long made low temperature deposition unsuitable for high quality films uniform over relatively large areas. Here we examine the distributions of both structure and physical properties of magnetron sputtered Al-doped ZnO (AZO) films deposited at low temperatures (≤ 393 K) in which the bombardment from the negative oxygen ions was systematically studied by changing the discharge voltage (i.e., ion energy) and the substrate position (i.e., ion flux). The film structure was characterized by X-ray diffraction, Raman spectroscopy, and transmission electron microscopy; and the electrical and optical properties were

obtained by a Hall system and Spectroscopic Ellipsometry. We found (i) that uniform yet high quality AZO films ($< 4 \times 10^{-4} \Omega \text{ cm}$) can be obtained only when the energy of the negative ions was set below a threshold; (ii) that the ion flux exerted an ever-decreasing effect on the structural uniformity as the ion energy was reduced; and (iii) that a set of structural criteria, incorporating crystallite quality (orientations, size, lattice spacing) and point defects, were derived for low resistivity AZO films. The benefit of lowering the ion energy is then explained in terms of the favorable competition between radiation-induced defect generation and the subsequent dynamic annealing. These findings may pave a way for large-area coating of high quality AZO films at low temperatures.

11:20am **F4-1-11 Combinatorial Thin Film Materials Science: Limitations and Opportunities for Combining Experiments and DFT Based Theory**, *Jochen M. Schneider*, RWTH Aachen University, Germany **INVITED**

The combination of modern electronic structure calculations with the highly efficient combinatorial thin film composition-spread method constitutes an effective tool for knowledge based materials design of hard and wear resistant coatings, energy conversion materials as well as of thin film metallic glasses. Besides elastic properties and phase stability also the interaction of the coating with the ambient can be described based on quantum mechanics. In the talk predictions of the interaction of coated tool surfaces with gases contained in the atmosphere as well as materials to be formed are discussed. Hard coatings used for forming operations of Al and Polymers are investigated and experimental data characterizing these interactions will be discussed. Furthermore, the implications of the presence of point defect for the thermal stability of TiAlN [1] will be analyzed and hybridization implications for the damage tolerance of thin film metallic glasses will be presented [2]. Limitations and opportunities of combining modern electronic structure calculations with combinatorial thin film synthesis und spatially resolved characterization techniques will be discussed.

New Horizons in Coatings and Thin Films Room San Diego - Session F4-2

Functional Oxide and Oxynitride Coatings

Moderators: Jörg Patscheider, Evatec AG, Anders Eriksson, Oerlikon Balzers, Oerlikon Surface Solutions AG, Marcus Hans, RWTH Aachen University

1:50pm **F4-2-2 On the Thermal Stability of Cathodic Arc Evaporated ($Al_{1-x}Cr_x$)₂O₃ Thin Films**, *Valentin Dalbauer*, CDL-AOS at TU Wien, Austria; *J Ramm*, Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *S Kolozsvári*, Plansee Composite Materials GmbH, Germany; *C Koller*, CDL-AOS at TU Wien, Austria; *P Mayrhofer*, Institute of Materials Science and Technology, TU Wien, Austria

The thermo-mechanically excellently performing α -alumina (corundum-type) is a perfect candidate to protect tool or component surfaces suffering from mechanical loads in hazardous atmospheres. Thus α -alumina protective coatings significantly extend the tool-lifetime especially in oxidising environment and at high temperatures. However, a major concern is the formation of amorphous phase fractions and/or metastable Al_2O_3 polymorphs during low-temperature physical vapour deposition, which can effectively be counteracted by alloying with Cr, where the phase composition of $(Al_{1-x}Cr_x)_2O_3$ coatings strongly depends on the Cr content.

With respect to industrial application, the knowledge about structure-property-relationships of $(Al_{1-x}Cr_x)_2O_3$ as a result of thermal exposure is of utmost importance. We therefore study the structural evolution of arc evaporated $(Al_{1-x}Cr_x)_2O_3$ coatings, which have been prepared by $Al_{0.75}Cr_{0.25}$, $Al_{0.70}Cr_{0.30}$, $Al_{0.50}Cr_{0.50}$, or $Al_{0.25}Cr_{0.75}$ cathodes.

The Cr-rich $(Al_{0.49}Cr_{0.51})_2O_3$ and $(Al_{0.23}Cr_{0.77})_2O_3$ coatings crystallise in a single-phase corundum-type structure (α - $(Al,Cr)_2O_3$) with pronounced columnar and faceted growth. Contrary, the Al-rich $(Al_{0.72}Cr_{0.28})_2O_3$ and $(Al_{0.69}Cr_{0.31})_2O_3$ coatings are multi-phased with a large metastable cubic-structured phase fraction and α - $(Al,Cr)_2O_3$.

Upon annealing to 800 and 950 °C, the metastable phases transform into a γ -type phase—with only minor indications for an intermediate θ -structure—and further to an α -type solid solution for temperatures above ~1080 °C. This structure stays stable up to the highest temperature tested, 1500 °C. The accompanied formation of bcc Cr phases indicates the decomposition of metallic droplets with—depending on the annealing conditions—subsequent oxidation of Al. Annealing within the spinodal-regime up to 6 h did not result in any phase separation towards α - Al_2O_3 and α - Cr_2O_3 .

Thermo-mechanical properties of $(Al_{1-x}Cr_x)_2O_3$ show a stronger dependence on the microstructure than on the crystal structure of the as-deposited coatings. Although exhibiting a multi-phase constitution, Al-rich coatings demonstrate higher hardness than the single-phased α - $(Al_{0.23}Cr_{0.77})_2O_3$ coating, which consists of tapered crystallites. Highest H and E values of ~22 Gpa and ~300 Gpa are obtained for $(Al_{0.49}Cr_{0.51})_2O_3$, which combines a dense microstructure with a dominant α -character. Upon vacuum annealing—and therewith associated structural transformation and densification—H and E of the Al- and Cr-rich coating compositions converge with peak values of H ~27 Gpa and E ~450 Gpa at 1050 °C.

2:10pm **F4-2-3 Phase Evolution of RF Magnetron Sputtered Cr-rich (Cr,Zr)₂O₃ Coatings Studied by In-Situ Synchrotron Experiments during Annealing in Air or Vacuum Conditions**, *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; *D Ostach*, Zentrum für Material- und Küstenforschung GmbH, Germany; *M Ahlgren*, *E Göthelid*, Sandvik Coromant R&D, Sweden; *B Alling*, Linköping Univ., IFM, Theoretical Physics division and Zentrum für Material- und Küstenforschung GmbH, Sweden; *L Hultman*, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *M Stüber*, Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany; *J Birch*, *P Eklund*, Linköping Univ., IFM, Thin Film Physics Div., Sweden

Physical vapor deposited binary oxide alloy hard coatings draw increasing attention, often focusing on the Cr-stabilized corundum α - $(Al,Cr)_2O_3$ phase by means of a template growth or alloying; Cr forms escolaita Cr_2O_3 that is isostructural with corundum [1,2]. A new and interesting oxide is obtained by exchanging Al with Zr in the Cr-Zr-O system. Spitz *et al.* explored $(Zr,Cr)_2O_3$ phases with respect to the Cr/Zr metal ratio in coatings prepared by reactive RF-magnetron sputtering, e.g., a solid solution α - $(Cr,Zr)_2O_3$

corundum structure at low Zr-content ($< \sim 12$ at %), a cubic- $(Zr,Cr)_2O_3$ based solid solutions at ~18 at % Zr, and a monoclinic/tetragonal solid solution $(Zr,Cr)_2O_3$ for higher Zr-content [3]. The as-deposited corundum structured coating from this study was the focus of an isothermal annealing study performed in vacuum with posterior HR TEM-characterization. It showed decomposition of a α - $Cr_{0.28}Zr_{0.10}O_{0.61}$ coating into tetragonal ZrO_2 and bcc chromium upon loss of oxygen [5]. In another study on the Cr-rich part of the $(Cr,Zr)_2O_3$ -system, as-deposited amorphous coatings were investigated by means of *in-situ* synchrotron X-ray diffraction during annealing in vacuum. This showed the increase in crystallization onset temperature for both α - $(Cr,Zr)_2O_3$ and tetragonal phases $(Zr,Cr)_2O_3$ with increasing Zr content (3-15 at %) in the as deposited coatings [4]. The phase-stability of such coatings are, however, expected to depend also on ambient atmosphere during service.

In order to study the effect of annealing atmosphere on the phase evolution of α - $(Cr,Zr)_2O_3$ coatings, we use *in-situ* synchrotron radiation experiments performed in air and in vacuum. We find that the phase evolution in α - $(Cr,Zr)_2O_3$ coating samples differs significantly depending on annealing atmosphere conditions: with retained α - Cr_2O_3 after air annealing with accompanying formation of tetragonal ZrO_2 and decomposition of the α - Cr_2O_3 structure if annealed in vacuum with formation of tetragonal ZrO_2 and possible monoclinic ZrO_2 after cooling to room temperature. The difference in phase evolution results in significant nano hardness difference ~22 and 8 GPa respectively and a largely changed microstructure observed with posterior HR-TEM characterization.

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[2] Khatibi, A., et al. Acta Materialia, 2013, **61**(13): p. 4811-4822.

[3] Spitz S., et al. Thin Solid Films, 2013, **548**: p. 143-149

[4] Rafaja D., et al, Thin solid Films, 2016, **516**: p. 430-436

[5] Landälv L., et al, Acta Materialia, 2017, **131**: p. 543-552

2:30pm **F4-2-4 Thick HS-PVD γ - Al_2O_3 Coatings for Challenging Cutting and Die Casting Applications**, *K Bobzin*, *T Brögelmann*, *C Kalscheuer*, *Martin Welters*, Surface Engineering Institute - RWTH Aachen University, Germany
In the last decades crystalline physical vapor deposition (PVD) Al_2O_3 coatings offered their great potential due to outstanding properties such as high hot hardness, high oxidation resistance and high wear resistance, especially concerning cutting and die casting applications. However, the properties of alumina strongly depend on the formed crystallographic phase. Thereby, the thermodynamically stable α - Al_2O_3 phase is the technical most interesting, exhibiting superior mechanical properties. The deposition of α - Al_2O_3 by chemical vapor deposition (CVD) is well-established, but requires high process temperatures. Thus, the deposition of α - Al_2O_3 on temperature sensitive-materials is not possible. Another promising candidate concerning cutting and die casting applications is γ - Al_2O_3 . Depending on the initial conditions, the formation of the γ - Al_2O_3 phase starts at $T \geq 450$ °C, allowing lower deposition temperatures. Regarding the wear protection of turning tools, a higher coating thickness ($s \geq 10$ μ m) and thus a larger wear volume are beneficial. However, this requirement is hard to fulfill by typical PVD processes. A possibility to deposit thick PVD alumina coatings is the High-Speed PVD (HS-PVD) technology. In the present work thick, $s \geq 20$ μ m, γ - Al_2O_3 films are deposited on cemented carbides at a substrate temperature range between $T = 500$ °C and $T = 850$ °C, by means of HS-PVD. A thick, metallic (Cr,Al) bond coat was employed to improve the adhesion of γ - Al_2O_3 . In order to analyze the influence of the bond coat regarding the adhesion of the coatings, scratch tests were conducted, as it is important regarding cutting and die casting operations. For determining the coating morphology and thickness, scanning electron microscopy (SEM) was used. Phase analysis was carried out by X-ray diffraction spectroscopy (XRD). The mechanical properties universal hardness (HU) and indentation modulus (E_{IT}) were determined by means of nanoindentation. Furthermore, thermal stability of the coatings was investigated via thermal exposure tests. Regarding the use in high temperature applications, especially the formation of γ - Al_2O_3 at substrate temperatures of $T \approx 850$ °C indicates that the use of the coatings is possible at equal high temperatures without phase transformation. The HS-PVD γ - Al_2O_3 coatings were compared to thin γ - Al_2O_3 films deposited by magnetron sputtering (MS), as they are state-of-the-art in industry. The comparison emphasizes the advantages of the coatings deposited by means of HS-PVD.

Wednesday Afternoon, April 25, 2018

2:50pm **F4-2-5 HiPIMS Deposition of Ta-O-N Coatings for Water Splitting Application**, Jiří Čapek, Š Batková, J Houska, S Haviar, University of West Bohemia, Czech Republic; T Duchoň, Charles University, 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 H₂ and O₂ 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 a big challenge to prepare Ta-O-N electrodes exhibiting efficient water splitting performance.

In this work we first demonstrate that high-power impulse magnetron sputtering is a suitable technique for low-temperature (less than 250 °C) deposition of Ta-O-N coatings with a controllable oxygen to nitrogen (O/N) ratio and thus their properties. The band gap width of the coatings can be tuned for an effective visible light absorption at preserved proper alignment of the band gap with respect to the water splitting reactions. Subsequently, we focus on an optimization of the structure of the coatings with respect to the transport of the generated electron-hole pairs. For this purpose, the Ta-O-N coatings were either prepared at an elevated substrate temperature (up to 850 °C - limit of the substrate heater) or annealed in a vacuum furnace (up to 900 °C) after the deposition. The carried out X-ray diffraction analyses indicate that the coatings prepared at the elevated temperatures consist of a mixture of oxides and/or nitrides, while the annealed coatings (with a proper O/N ratio) are characterized by a single TaON phase. Moreover, the resulting TaON phase can be highly textured when a proper seeding layer (e.g., Pt) is used. This structure is very promising for the water splitting application due to a possibly reduced recombination rate of photogenerated electrons and holes.

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3:10pm **F4-2-6 Evolution of Microstructure and Mechanical Properties of Graded TiAlON Thin Films Investigated by Cross-sectional Characterization Techniques**, Nina Schalk, M Tkadletz, V Terziyska, Montanuniversität Leoben, Austria; M Deluca, Materials Center Leoben Forschung GmbH, Austria; J Keckes, C Mitterer, Montanuniversität Leoben, Austria

In the last years, oxynitrides have emerged as a new class of materials due to their tunable properties. Within the present work, a graded TiAl(O)N film was grown by magnetron sputter deposition, using TiAl targets with an Ti/Al atomic ratio of 40/60, constant nitrogen and stepwise increasing oxygen partial pressures over the film thickness. The microstructural evolution of the film was investigated by transmission electron microscopy and synchrotron X-ray nanodiffraction. The first layer, grown without the addition of oxygen, showed a dual phase structure consisting of a prevalent wurtzite phase fraction and a subordinate face centered cubic (fcc) phase fraction. The addition of small amounts of oxygen resulted in the stabilization of the fcc phase and the wurtzite phase vanished. With increasing film thickness and thus, increasing oxygen content, the texture of the fcc phase changed from dominating (111) to (100). Further, with increasing oxygen content increasing amounts of an additional amorphous phase fraction were observed. In the first layers, tensile residual stresses in the range of 1 – 2 GPa were determined, which turn compressive towards the film surface. Cross-sectional nanonindentation revealed increasing hardness and elastic modulus with increasing oxygen content in the first layers, however, towards the film surface the hardness decreases, which can be related to the increasing amounts of an amorphous phase fraction.

3:30pm **F4-2-7 Hard Transition Metal Oxynitride Thin Films: From Synthesis to Applications**, Filipe Vaz, J Borges, Minho University, Portugal
INVITED

The aim of this talk is to focus on the design, synthesis, properties and applications of different types of oxynitride protective and functional thin films and coatings. Multifunctional stable and metastable oxynitride coatings are expected to fill a gap between nitride and oxide based coatings. Therefore, they are considered to be of unique interest in fundamental research. Moreover, due to their combination of high oxidation resistance, chemical inertness, good mechanical properties at elevated temperatures and friction behavior, they have a wide application field. In fact, oxynitride thin films are rapidly emerging from the research laboratory, and there are actually several examples of successful industrial applications. Protective applications, decorative coatings for high-quality consumer products, gas barriers, optoelectronics, microelectronics, solar cells, are among the most important areas in which oxynitrides are revealing promising results.

Nevertheless, there is still a huge need for a comprehensive discussion of their fundamental properties and in-service response as a function of the different designs and basic characteristics.

This talk is focused on the development and understanding of the materials themselves and on relationships and knowledge-based correlations between process parameters, synthesis and growth, micro structure evolution and properties, providing a forum to discuss current and future applications of this class of thin films and coatings.

New Horizons in Coatings and Thin Films Room San Diego - Session F3

2D Materials: Synthesis, Characterization, and Applications

Moderators: Eli Sutter, University of Nebraska-Lincoln, USA, Liping Wang, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences

8:00am **F3-1 Crystallization Kinetics of Photonically Annealed Two Dimensional Materials and Heterostructures**, *R Vila*, Stanford University, USA; *R Rao*, *B Maruyama*, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *E Bianco*, Air Force Research Laboratory, Materials and Manufacturing Directorate/Rice University, USA; *N Glavin*, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *Chris Muratore*, University of Dayton, USA

Synthesis capability for uniform growth of two-dimensional (2D) materials over large areas at lower temperatures without sacrificing their unique properties is a critical pre-requisite for seamless integration of monolithic van der Waals materials or their heterostructures into novel devices, especially on flexible substrate platforms. Developing effective strategies to synthesize 2D materials, such as MoS₂ and other transition metal dichalcogenides necessitates a fundamental understanding of the thermodynamics and kinetics controlling nucleation and growth processes. To elucidate crystallization mechanisms we utilize *in situ* Raman spectroscopy during photonic crystallization of amorphous 2D films to directly probe the diffusion-limited kinetics while eliminating contributions from factors adding extreme variability to growth mechanisms such as precursor delivery and gas-phase reactions. We employ a high-throughput autonomous experimentation technique to perform studies in rapid succession on the same substrate, while precisely monitoring temperature by analysis of Stokes/Anti-Stokes peak shifts on rigid (SiO₂/Si) or flexible (polydimethylsiloxane or PDMS) substrates. Preliminary results during isothermal heating reveal that nucleation of amorphous 2D MoS₂ occurs very rapidly and the crystallization rate follows an Arrhenius temperature relationship, yielding an energy barrier of 1.03 eV/atom that corresponds to sulfur diffusion. A correlation between crystallization rate and crystal quality was also observed, as the technique allows *in situ* measurement of atomic defect concentrations. Comparison to theoretical results will allow use of the empirically determined activation barrier for diffusion-limited crystallization as a mechanistic fingerprint in TMD compounds with varying degrees of atomic mass-mismatch. Photonically annealed crystalline 2D materials derived from amorphous precursor films demonstrate device-quality performance, enabling correlation of device properties (i.e., lateral photodetectors and others) to the structure, composition and defect density resulting from different crystallization conditions.

8:20am **F3-2 The Application of Pulsed Laser Deposited a-BN for Temperature and Oxidation Resistance of 2D MoTe₂ Semiconducting Devices**, *Benjamin Sirota*, University of North Texas, USA, United States of America; *N Glavin*, Air Force Research Laboratory, Materials and Manufacturing Directorate, USA; *C Muratore*, University of Dayton, USA; *S Krylyuk*, *A Davydov*, National Institute of Standards and Technology, USA; *A Voevodin*, University of North Texas, USA

Pulsed laser deposition (PLD) of ultra-thin (2-10 nm) amorphous boron nitride (a-BN) films was previously shown to provide a wide band gap insulating material with excellent breakdown and dielectric characteristics [1,2]. The process enables large area coverage at near room temperatures which make it an attractive deposition technique for the use in with two-dimensional (2D) semiconducting materials; such as few monolayer thick transition metal chalcogenides (TMDs). 2D TMDs provide unique physical properties needed for electronic and opto-electronic devices, however they are also prone to degradation by oxidation, especially at elevated temperatures in atmospheric conditions. This study explores the benefit of a-BN for environmental stability of 2D TMDs, using an example of few monolayer thick exfoliated 2H-MoTe₂ capped with a PLD-grown a-BN top layer to create a 2D BN-MoTe₂ heterostructure. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements demonstrated a significant improvement in chemical stability and resistance to oxidation for BN-MoTe₂ heterostructures as compared to uncoated MoTe₂ samples when heating in air up to 300 °C. Both XPS and Raman analysis showed a rapid oxidation and structural degradation for uncapped MoTe₂ while BN-MoTe₂ demonstrated significant durability after one hour of heating at 100 °C. This was correlated with heating in air experiments with BN-MoTe₂ 2D

filed effect transistor (FET) devices. Uncapped MoTe₂ FET devices heated in air for 1 minute showed a polarity switch from n- to p-type at 150 °C, while BN-MoTe₂ devices switched only after 200 °C of heat treatment. Time dependent experiments at 100 °C in air showed that uncapped MoTe₂ FET devices exhibited the polarity switch after 15 minutes of heat treatment while the BN-capped device maintained its n-type conductivity for the 60 minutes of the heating exposure. This work demonstrates the effectiveness of an amorphous BN capping layer in preserving few-layer MoTe₂ material quality and controlling its oxidation rate at elevated temperatures in an atmospheric environment.

1. Glavin et al, Thin Solid Films, 572 (2014), 245-250.
2. Glavin et al, Adv. Funct. Mater. (2016) 26: 2640–2647.

8:40am **F3-3 A Predictive Thermokinetic Model of Friction in MoS₂**, *John Curry*, *A Hinkle*, Sandia National Laboratories, USA; *T Babuska*, *B Krick*, Lehigh University, USA; *M Dugger*, *N Argibay*, *M Chandross*, Sandia National Laboratories, USA

Building on more than a century of concerted effort to understand the friction behavior of 2D materials, we present a thermokinetic model for predicting the shear strength of MoS₂ based on energetic barriers to sliding. This model accounts for a wide range of factors underlying the interaction between molecularly thin lamellae, including defects, temperature, crystallite size and commensurability. Findings are supported by results from thermally ramped sliding experiments and molecular dynamics simulations.

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9:00am **F3-4 Supercritical Fluid Assisted Synthesis of V₂O₅/VS₂ Nanocomposites for use in Supercapacitor**, *Yen-Chun Liu*, *J Ting*, National Cheng Kung University, Taiwan

A novel one-pot Supercritical fluid (SCF) CO₂ synthesis method was used to fabricate V₂O₅/VS₂ nanocomposite. VS₂ was first synthesized using a microwave assisted hydrothermal technique. The obtained VS₂ powders were then mixed with an oxidizing agent and subject to the SCF treatment to form V₂O₅/VS₂ nanocomposites as follows. During the SCF process, the VS₂ was exfoliated to form nanosheets of VS₂ by the SCF CO₂. In the meantime, V₂O₅ nanoparticles (NPs) were formed due to the partial oxidation of the VS₂. The formed V₂O₅ NPs were intercalated into the VS₂ nanosheets also with the assistance of the SCF CO₂. The effects of the SCF condition and the strength of the oxidizing agent on the formation and characteristics of V₂O₅/VS₂ nanocomposites were investigated. Supercapacitor cells were assembled using the resulting V₂O₅/VS₂ nanocomposites as the electrodes. The cells were evaluated using cyclic voltammetry, and electrochemical impedance spectroscopy, and subjected to cycle life and charge-discharge cycling tests.

9:20am **F3-5 2D and Layered Metal Chalcogenide Semiconductors: Growth, Electronic Structure, Light-Matter Interactions**, *Peter Sutter*, University of Nebraska-Lincoln, USA

INVITED

Metal chalcogenides have received attention as layered crystals and as 2D materials beyond graphene. Semiconducting chalcogenides show promise for applications in energy conversion and next-generation low-dimensional (opto) electronics benefiting from carrier confinement and other unique characteristics, such as a thickness dependent or anisotropic electronic structure, non-charge based degrees of freedom, and strong light-matter interactions. Here, I discuss recent work using novel high spatial resolution probes to study the properties of 2D semiconductors and their variations on the nanometer scale.

Real-time microscopy provides insight into the microscopic mechanisms governing the bottom-up growth and transformation of 2D semiconductors. Local band structure measurements are used to establish the thickness dependent electronic properties, as well as other key aspects such as the interlayer coupling as a function of layer orientation. Finally, I present nanometer-scale measurements of light-matter interactions in 2D semiconductors, which offer a way to probe and manipulate optical excitations far below the diffraction limit near defects, edges, or engineered interfaces.

10:00am **F3-7 Fabrication and Photocatalytic Application of Functional group Modification of Carbon Nitride Derivatives nanosheets**, *ChunHung Chen, K Chang*, National Cheng Kung University (NCKU), Taiwan

Carbon nitride has recently attracted much attention owing to its visible-light-driven hydrogen evolution capability which is first published in 2009.^[1] Compared with 1D-structured melon, which has already been well-studied by other research groups, the melon oligomer and poly (triazine imide) (PTI/Li⁺Cl⁻) are two promising structures which show a better photocatalytic property. However, there still remains some room for improvements to be done such as increasing the amount of functional groups of carbon nitride, which are known to be active sites during a photocatalytic process. These active sites are regarded as the predominant factor in the carbon nitride series.^[2] Herein, two strategies were applied to modify the PTI & melon oligomer for the purpose of enhancing its photocatalytic ability. The first process is by using isopropanol (IPA) and ethanol in distinct heat treatment to accomplish surface functionalization. Solid NMR, FTIR, and EA were used to prove that additional functional groups are successfully linked. Also, the UV-Vis results indicated that the absorption range had a red-shift to a higher wavelength which is due to the change in powder color. For the second process, liquid exfoliation method was used to obtain ultrathin nanosheets in order to enhance its photodegradation ability due to the further increase in surface area and active sites. By considering that the enthalpy of mixing should be minimized, water is considered as the optimal solvent and was applied due to having a similar surface energy to carbon nitride nanosheet.^[3] The BET analysis showed that the surface area has significantly increased, which brought about more than five times enhancement in its photocatalytic property. Furthermore, from the photoelectrochemistry measurement, the modified carbon nitride shows the linear relationship as the sensor of Cu ion determination, indicating that our sample is a promising candidate for ion determination in water solution.

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10:20am **F3-8 Enhanced Photocatalytic Performance for g-C₃N₄ through the Addition of α -MoO₃ Nanobelts and Mesoporous TiO₂ Beads**, *Yen Duong, J Ting*, National Cheng Kung University, Taiwan

Multi-component photocatalysts based on g-C₃N₄ was synthesized to enhanced the photocatalytic performance of g-C₃N₄. Exfoliated g-C₃N₄ was fabricated by heating melamine at 550°C, followed by the use of hydrogen peroxide (H₂O₂) to exfoliate bulk g-C₃N₄. Mesoporous TiO₂ beads were prepared using a two-step process. α -MoO₃ nanobelts were made by hydrothermal method. Three groups of binary-component photocatalysts of TiO₂/g-C₃N₄, TiO₂/ α -MoO₃ and α -MoO₃ / g-C₃N₄ having various compositions were then made. Based on the performance of these binary-component photocatalysts, TiO₂/ α -MoO₃/g-C₃N₄ ternary composite photocatalysts were synthesized. The photocatalytic performance of all the single-binary and ternary component photocatalysts were evaluated by degrading methyl blue under both UV and visible light irradiations.

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10:40am **F3-9 Fabrication of Nanostructured MoS₂ Thin Films on Porous Silicon Substrate for Ammonia Gas Sensing Properties**, *S Sharma, A Kumar, Davinder Kaur*, Indian Institute of Technology Roorkee, India

In the present work, we have fabricated the molybdenum disulphide (MoS₂) nanostructure thin films on the 2×2 cm² porous Silicon (100) substrates using DC magnetron sputtering technique. Porous silicon was fabricated by the metal-assisted chemical etching of the Si (100) substrate using HF as etchant solution. The structural and surface morphological properties of MoS₂ nanostructure thin films were systematically studied using X-ray diffraction (XRD), field-emission scanning electron microscopy

(FESEM), atomic force microscopy (AFM) and Raman spectroscopy. The ammonia gas sensing properties of porous MoS₂ thin film sensor shows the remarkable response with fast response/recovery time towards the 100 ppm ammonia gas (NH₃) at the room temperature. These sensing performances suggest porous MoS₂ thin films a potential candidate for room temperature sensor devices. The sensing mechanism and response behaviour towards ammonia gas was also discussed in detail.

11:00am **F3-10 Wettability, Structural and Optical Examination of Sputtered Zirconium Oxide Thin Films**, *Uttkarsh Patel*, McMaster University, Canada; *P Dave*, Gujarat forensic science university, India; *K Chauhan*, Charotar University of Science and Technology (CHARUSAT), India; *S Rawal*, McMaster University, Canada

Zirconium oxide films were deposited by reactive magnetron sputtering at different sputtering pressure values of 0.4Pa, 0.7Pa, 1.0Pa and 1.5Pa. The effect of sputtering pressure on structural, hydrophobic and optical properties of deposited zirconium oxide thin films is reported in this research work. Due to this variation during thin film growth, it is observed that zirconium oxide thin films formed has monoclinic phase with (111) orientation. Its intensity increase with increase in sputtering pressure from 0.4Pa to 1.5Pa. The contact angle values of 96° for water and 44° for aniline were observed at 0.4Pa. The band gap of zirconium oxide films increases as sputtering pressure is increased from 0.4Pa to 1.5Pa.

11:20am **F3-11 Synthesis and Characterization of Molybdenum-based Thin Films for Flexible Electronics**, *T Jörg*, Montanuniversität Leoben, Austria; *M Cordill*, Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria; *D Music*, RWTH Aachen University, Germany; *R Franz*, Montanuniversität Leoben, Austria; *H Köstenbauer*, *J Winkler*, Plansee SE, Austria; *J Schneider*, RWTH Aachen University, Germany; **Christian Mitterer**, Montanuniversität Leoben, Austria

INVITED
Mechanical failure of thin metal films on compliant substrates presents a considerable challenge in the development of flexible electronics. In particular, this applies for sputter-deposited molybdenum thin films, which are frequently used as back electrode materials in flexible solar cells, as electrode materials in flexible piezoelectric micro- and nano-electromechanical systems, in the metallization of thin film transistors, e.g. as gate and source/drain electrodes, as adhesion promotion, diffusion barrier and ohmic contact layers due to their attractive combination of functional properties.

Within this work, different strategies for film synthesis and alloying are proposed to design Mo-based thin films on polymer substrates with enhanced fracture resistance. The fracture properties of pure Mo films can be tailored by their compressive residual stress state, enabling a considerable improvement in crack onset strain. Moreover, both fracture strength and crack onset strain of Mo thin films scale with their thickness. Since all Mo thin films exhibit a distinctly brittle fracture behavior, alloying with Re and Cu was explored as feasible concept to overcome their poor ductility. A substantial toughness improvement with rising Re content up to the solubility limit was obtained, which stems from the increased plasticity and bond strengthening in the Mo-Re solid solution. Furthermore, it was observed that Cu addition to Mo results in an increased ductility, which was rationalized by the low shear resistant bonding in the Mo-Cu solid solution. In general, both concepts proved to be promising in order to enable utilization of Mo based thin films in flexible electronics.

Thursday Afternoon Poster Sessions, April 26, 2018

New Horizons in Coatings and Thin Films

Room Grand Hall - Session FP

Symposium F Poster Session

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

Initiated by our recent works on intermetallic Al-Cr-Fe droplets [1–3], which indicate the ability to trigger the nucleation of corundum-structured $(\text{Al,Cr,Fe})_2\text{O}_3$ crystallites, the oxidation behaviour of intermetallic Fe-doped $\text{Al}_{0.70}\text{Cr}_{0.30}$ coatings and corresponding substoichiometric oxides was investigated. The structure and composition of the outermost oxide scale and the oxidation temperature at which it forms is determined by the initial microstructure. Columnar intermetallic coatings, for instance, oxidise via an outermost metastable Al_2O_3 scale, which transforms into the thermodynamically stable corundum-phase starting at 1000–1050 °C. However, nano-composite-like structures, present in substoichiometric coatings, show a more diverse oxidation at the surface and complex elemental separation within the unoxidised material. In the present work, we extend our studies on the oxidation and oxide phase formation to intermetallic and substoichiometric coatings prepared from powder-metallurgically produced $\text{Al}_{1-x}\text{Cr}_x$ cathodes with nominal compositions of $x=0.10, 0.25, 0.30, 0.50, \text{ and } 0.75$. The structural evolution of the outermost scale and coating underneath—studied by X-ray diffraction and cross-sectional electron microscopy—is related to the Cr content, oxygen flow rate during the synthesis process and the oxidation conditions.

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

ZnO is highly useful for applications such as short-wavelength optoelectronics and transparent conductive electrodes [1]. We have developed a new CVD method for ZnO film growth using a reaction between dimethylzinc and catalytically generated high-temperature H_2O . ZnO films grown on a-plane (11-20) sapphire ($\text{a-Al}_2\text{O}_3$) substrates at temperatures of 773–873 K exhibited excellent optical and electronic properties [2]. However, the electronic properties were dependent on the film thickness: ZnO films thinner than 500 nm showed inferior electrical properties, namely, a low Hall mobility ($<100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and a high residual carrier concentration ($>10^{18} \text{ cm}^{-3}$). The room-temperature electron mobility increased from 30 to $190 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ as the film thickness increased to $\sim 3 \mu\text{m}$. The mobility also increased significantly as the temperature was decreased to approximately 110–150 K, but decreased at temperatures below 100 K for films thicker than 500 nm. On the other hand, the mobility was almost independent of temperature for films thinner than 500 nm. These results suggest that a region with a high defect density exists near the film-substrate interface. To evaluate the crystal quality of the ZnO film along the growth direction, cross-sectional transmission electron microscopy was performed and the defect density was determined. The ZnO epitaxial film that was studied had a thickness of $4.5 \mu\text{m}$ and a room-temperature electron mobility of $187 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The dislocation density estimated using Ham's method [3] was found to be lower near the film surface than near the film-substrate interface. The combined density of all dislocations (edge,

screw, and mixed) in the top $1.5 \mu\text{m}$ of the film was approximately $1.1 \times 10^9 \text{ cm}^{-2}$, while in a 30-nm-thick region near the interface, it was approximately $1.6 \times 10^{11} \text{ cm}^{-2}$.

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

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

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

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

Photoluminescence (PL) spectra of the films grown at T_s of 550 and 575 °C were dominated by the near-band-edge (NBE) emission at wavelength of $\sim 380 \text{ nm}$. The PL intensity of the green band emission at wavelength of $\sim 480 \text{ nm}$ relative to that of the NBE emission increased with increasing T_s , suggesting that the film composition became more oxygen deficient.

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

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

In this work we obtain pure NiO_x thin films via sol-gel method, employing nickel acetate, citric acid and ethylene glycol as main precursors. The synthesis consist in mixing 1:1 of $\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$ and citric acid in DI water. The pH was adjusted to 8.0 and finally ethylene glycol was added. The solution was stirred vigorously at 90°C until light green colored gel was

Thursday Afternoon Poster Sessions, April 26, 2018

formed. The sol-gel solution was deposited on quartz substrate by spin-coating technique and annealed at 410°C in air atmosphere. The annealing temperature was determined previously by thermogravimetric analysis.

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

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

FP-8 Exploring the Visible Light Photocatalytic Activity of the ZnO - RGO Hybrid - Nanostructures by Sol-gel Process, Chih-Chiang Wang, National Chung Hsing University, Taiwan; *H Shih*, Chinese Culture University, Taiwan
Carbon-based material, like the graphene, exhibits the unique 2-D structures, e.g., sp²-conjugated C atoms, highly electronic conductivity, larger specific surface area, better chemical stability. Hence, it attracts various attentions in many fields, like the photocatalysts, solar cells, energy storage, etc. ZnO is an n-type semiconducting material with a wide direct band gap (3.3eV), hexagonal wurtzite structure and higher exciton binding energy (60meV), and has been applied in the field of photocatalyst, gas sensors, and solar cells. In this study, the pristine and ZnO-RGO hybrid-nanostructures were fabricated by sol-gel method at the ambient environments. Subsequent baking was conducted at the 500°C under 4x10⁻³ torr.

XRD showed that peaks of (100), (002), (101), (102) and (110) planes belonged to the pure ZnO as the wurtzite structure, but no RGO-related peaks appeared at 24° of the ZnO-RGO hybrid-nanostructures. The SEM images revealed that the sheet-structures appeared in the adding RGO samples and TEM-SAD showed the RGO patterns, suggesting that the RGO was covered by the ZnO nanoparticles which has confirmed the XRD results. Raman spectra exhibited the decreasing ratio of I_D/I_G from 1.2 to 0.8 while the ZnO combined with the RGO, meaning that ZnO fixed the defects inside the RGO and increased the sp²-carbon domain.

UV-vis. spectra revealed the characteristic peak of ZnO at 375nm, and the absorbance increased with the increasing RGO concentrations. PL spectra exhibited two emission regions at NBE and DLE, and displayed the decreasing tendency while the RGO contents increased, indicating that the recombination of electrons and holes was hindered by the adding of RGO. The specific surface area (BET) showed the increasing profile from 4 to 18.5m²/g while the RGO contents was from 0 to 6400ppm, while the grain size decreased from 31 to 26nm. The results suggested that the RGO could inhibit the grain growth of ZnO, therefore, the BET values increased. The visible light photocatalytic tests revealed that the efficiency of pristine ZnO, ZnO-RGO_{400ppm}, ZnO-RGO_{800ppm}, ZnO-RGO_{1600ppm}, ZnO-RGO_{3200ppm}, ZnO-RGO_{6400ppm} were 10%, 50%, 94%, 95%, 96%, and 94%, respectively, after 15min illuminating time. Furthermore, the rate constant was smaller than 0.012min⁻¹ while the RGO was lower than 400ppm. On the other hand, the rate constant larger than 0.04min⁻¹ while the RGO was higher than 800ppm. Both of which confirmed the results of photocatalytic efficiency. In summary, the RGO should be able to inhibit the recombination of electrons and holes, and increase the BET values, as followed by the enhancing of the photocatalytic efficiency under the visible light.

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

The effects of water absorption on the Thin Film Transistor (TFT) devices fabricated from zinc oxynitride (ZnON) films deposited by direct current magnetron sputtering (DCMS) and high-power impulse magnetron sputtering (HiPIMS) have been investigated. When exposed to moisture at room temperature, DCMS-made ZnON TFTs exhibited a smaller mobility, lower threshold voltage, increased carrier concentration and higher subthreshold slope with a deteriorated electrical stability under positive gate voltage. However, for the set of similar conditions, TFT devices made from HiPIMS-deposited ZnON films exhibited relatively stable electrical

characteristics than that of the ones made by DCMS. The enhanced performance of ZnON films deposited by HiPIMS could be attributed to the high film density and the amorphous nature which is free of crystallographic defects. Such film characteristics reduce the formation of oxygen vacancies and the bonding of zinc and nitrogen, and thus hold the efficiency of electrical behavior of the films intact.

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

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

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

One of the most important challenge of the humanity is the production of sustainable energy, the increase in energy consumption and the use of coal reserves could come several environment problems and high cost solutions. Semiconductors based on bismuth oxide present a band gap in the visible light, so is possible to use these materials in the production of hydrogen by photoelectrochemical water splitting. We report the synthesis of cuprate bismuth thin films deposited by reactive magnetron co-sputtering, metallic copper and bismuth oxide (Bi₂O₃) targets were used to deposit cuprate bismuth on FTO (fluorine doped tin oxide), glass (fused silica) and silicon substrates. For the copper target it was necessary to vary the applied power (DC) from 3 to 60 Watts finding that the best option is 10 Watts, while at the bismuth oxide target 30 Watts (RF) were applied. The coatings were grown under reactive environment with Ar: 28 sccm and O₂: 12 sccm and heating the substrates at 200 ° C. However, the as-deposited coatings were amorphous and it was necessary to perform a heat treatment at 500 ° C in static air for 2 hours to obtain the tetragonal structure. The X-ray diffraction confirmed the formation of the tetragonal phase (CuBi₂O₄) coexisting with copper oxide, the optical and electronic properties were measurement by UV-VIS spectrometry and Mott- Schottky plots, finding that the optical band gap is ~ 1.4 to 1.6 eV and the films presented an p-type conductivity with a flat band potential of 0.4 eV. The photocurrent was evaluated as a function of the thickness.

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

Zn injection is known to cause changes in composition as well as in crystalline morphology of the oxide layers, which is responsible for mitigating corrosion on the Ni-based alloys in the simulated primary water [1]. Conventionally Zn precursors such as dimethyl zinc, diethyl zinc, zinc hydroxide, zinc carbonate, and zinc acetate are used for Zn injection and this, however might cause additional problem due to the formation of other corrosive ions (OH⁻, CO₃²⁻, and CH₃COO⁻) [2].

To eliminate this problem, in this study, pure Zn nanoparticles were synthesized by atmospheric plasma discharge process in aqueous solution for the mitigation of primary water stress corrosion cracking (PWSCC). Zn nanoparticles with various sizes were synthesized using SPP and were applied for the treatment of Ni-based alloy samples at simulated primary water environment (300°C, 150 bar). The Zn treatment duration was controlled in the range from 0 to 240 hours. As-obtained oxide films after various Zn treatment durations were investigated using X-ray diffractometry (XRD) analysis. The Zn-treated and non-treated U-bend type Ni-based alloy samples were subjected to very harsh corrosion test under simulated PWR environments, in which the conditions were Na₂S of 1.0 M and NaOH of 1.0 M. To measure the corrosion behavior of Zn-treated and non-treated Ni-based alloy samples, electrochemical potential analysis was

Thursday Afternoon Poster Sessions, April 26, 2018

performed by Potentiostat/Galvanostat. Diffraction patterns exhibited that stable oxide films with a spinel structure of $ZnCr_2O_4$ would form with increasing Zn treatment duration. It is postulated that the exchange reaction between Zn and Fe/Ni cations occurred extensively so that the dense and compact Zn spinel structure responsible for the corrosion inhibition formed [1]. Zn treated Ni-based alloys exhibited a low electrochemical potential (ECP) value comparing with non-treated Ni-based alloys. In addition, the results from U-bend test showed that the PWSCC in Zn-treated Ni-based alloy samples was much retarded comparing with non-treated Ni-based alloys.

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

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

Bold page numbers indicate presenter

- A —
 Aguiar, O: F2-2-2, 3
 Ahlgren, M: F4-2-3, 10
 Alling, B: F4-2-3, 10
 Ambriz-Vargas, F: F1-9, **7**
 Amorim, C: F4-1-3, 8
 Anders, A: F2-1-4, 1
 Araujo, M: F2-2-2, 3
 Argibay, N: F3-3, 12
 — B —
 Babuska, T: F3-3, 12
 Balbaud, F: F2-2-3, 3
 Bandorf, R: F2-3-2, 5
 Batková, Š: F4-2-5, 11
 Belosludtsev, A: F2-2-4, 3
 Bianco, E: F3-1, 12
 Bilek, M: FP-9, 15
 Birch, J: F4-2-3, 10
 Bobzin, K: F2-1-5, 1; F4-2-4, 10
 Borges, J: F4-2-7, 11
 Boumaza, M: F1-6, 6
 Braeuer, G: F2-3-2, 5
 Breilmann, W: F2-1-2, 1
 Brenning, N: F2-1-1, 1
 Brögelmann, T: F2-1-5, 1; F4-2-4, 10
 — C —
 Čapek, J: F4-2-5, 11
 Castillo, J: FP-5, **14**
 Cemin, F: F2-2-8, 4
 Čerstvý, R: F2-2-4, 3; F4-1-4, 8
 Chandra, R: F4-1-7, **9**
 Chandross, M: F3-3, 12
 Chang, K: F3-7, 13
 Chauhan, K: F3-10, 13
 Chen, C: F3-7, **13**
 Chen, K: F1-10, **7**; F1-5, **6**
 Chen, Y: F2-2-6, **4**; F2-3-3, 5
 Chien, T: F2-3-3, 5
 Chiu, Y: F2-3-3, 5
 Chu, P: F1-4, 6
 Corbella, C: F2-1-3, 1
 Cordill, M: F3-11, 13
 Curiel, M: FP-5, 14
 Curry, J: F3-3, **12**
 — D —
 Dalbauer, V: F4-2-2, **10**; FP-2, **14**
 Dave, P: F3-10, 13
 Davydov, A: F3-2, 12
 de los Arcos, T: F2-1-3, 1
 Delfour-Peyrethon, B: F4-1-3, 8
 Deluca, M: F4-2-6, 11
 Depablos-Rivera, O: FP-13, 15
 Dick, K: F1-2, 6
 Dong, C: F2-3-4, 5
 Duchoň, T: F4-2-5, 11
 Dugger, M: F3-3, 12
 Duong, Y: F3-8, **13**
 — E —
 Ehasarian, A: F4-1-6, **9**
 Eklund, P: F4-2-3, 10
 Engels, M: F2-1-5, 1
 — F —
 Ferrec, A: F2-2-3, 3
 Ferreira, E: F2-2-2, 3
 Franco-Pelaez, D: FP-13, 15
 Franz, R: F2-1-4, 1; F3-11, 13
 — G —
 Gan, K: F2-3-3, 5
 Ganesan, R: FP-9, **15**
 Garcia-Farrera, B: F2-2-1, 3
 Gauthier, M: F1-9, 7
 Gerdes, H: F2-3-2, **5**
 Ghauri, F: F1-7, 7
 Glavin, N: F3-1, 12; F3-2, 12
 Göthelid, E: F4-2-3, 10
 Grosdindler, T: F2-3-4, **5**
 Gudmundsson, J: F2-1-1, **1**; FP-15, **16**
 — H —
 Hajihoseini, H: FP-15, 16
 Hashim, A: FP-3, 14
 Haviar, S: F2-2-4, 3; F4-1-4, 8; F4-2-5, 11
 Hecimovic, A: F2-1-2, 1
 Heisig, A: F4-1-6, 9
 Held, J: F2-1-2, **1**
 Helmersson, U: F2-2-9, **4**
 Hinkle, A: F3-3, 12
 Hoshida, L: F2-2-2, 3
 Houska, J: F2-2-4, 3; F4-1-4, 8; F4-2-5, 11
 Hrebik, J: F2-1-6, **2**
 Hsu, Y: F2-2-7, **4**
 Huang, M: F1-4, 6
 Hug, H: FP-9, 15
 Hultman, L: F4-2-3, 10
 — I —
 Ibe, R: FP-3, 14
 — J —
 Jaiswal, J: F4-1-7, 9
 Jörg, T: F3-11, 13
 — K —
 Kalscheuer, C: F4-2-4, 10
 Kato, A: FP-3, 14
 Kaur, D: F3-9, **13**
 Keckes, J: F4-2-6, 11
 Kelly, P: F4-1-3, **8**
 Keraudy, J: F2-2-8, 4
 Kim, J: FP-14, 15
 Kim, S: FP-14, 15
 Kindlund, H: F1-2, **6**
 Kolhatkar, G: F1-9, 7
 Koller, C: F4-2-2, 10; FP-2, 14
 Kolozsvári, S: F4-2-2, 10; FP-2, 14
 Köstenbauer, H: F3-11, 13
 Krick, B: F3-3, 12
 Kruppe, N: F2-1-5, 1
 Krylyuk, S: F3-2, 12
 Kumar, A: F3-9, 13
 Kumar, B: F4-1-7, 9
 Kuo, P: F2-3-3, 5
 — L —
 Landälv, L: F4-2-3, **10**
 Layes, V: F2-1-3, 1
 Lee, J: F2-2-5, 3; F2-3-5, **5**
 Lee, S: FP-14, **15**
 Lehmann, S: F1-2, 6
 Lertola, A: F1-3, 6
 Li, L: F1-3, **6**
 Li, W: F1-4, **6**
 Liccardo, V: F2-2-2, 3
 Lin, J: F2-2-1, 3; F2-3-1, **5**
 Lin, Y: F2-2-6, 4
 Liu, D: F1-4, 6
 Liu, L: F1-4, 6
 Liu, P: F2-3-3, 5
 Liu, Y: F3-4, **12**
 Loch, D: F4-1-6, 9
 Lomello, F: F2-2-3, 3
 Lu, J: F4-2-3, 10
 Lundin, D: F2-1-1, 1; F2-2-8, **4**
 — M —
 Malik, G: F4-1-7, 9
 Marcelino, R: F4-1-3, 8
 Maruyama, B: F3-1, 12
 Maskrot, H: F2-2-3, 3
 Maszl, C: F2-1-2, 1
 Mateos, D: FP-5, 14
 Matthews, A: F4-1-5, 8
 Mayrhofer, P: F4-2-2, 10; FP-2, 14
 McKenzie, D: FP-9, 15
 Mello, C: F2-2-2, 3
 Melo, L: FP-12, 15
 Melo-Máximo, D: F2-2-1, 3; FP-12, 15
 Melo-Máximo, L: F2-2-1, 3
 Meng, F: F4-1-8, **9**
 Michau, A: F2-2-3, 3
 Minea, T: F2-1-1, 1; F2-2-8, 4
 Mingo, B: F4-1-5, 8
 Mitterer, C: F3-11, **13**; F4-2-6, 11
 Monje, S: F2-1-3, **1**
 Mourya, S: F4-1-7, 9
 Muratore, C: F3-1, **12**; F3-2, 12
 Murillo, A: F2-2-1, **3**
 Music, D: F3-11, 13
 — N —
 Nedev, N: FP-5, 14
 Neidhardt, J: F4-1-6, 9
 Nomoto, J: FP-4, 14
 Nouar, R: F1-9, 7
 — O —
 Ochi, Y: FP-4, 14
 Oliva-Ramírez, J: F2-2-1, 3
 Oliveira, A: F2-2-2, 3
 Oliveira, R: F2-2-2, **3**
 Oseguera, J: F2-2-1, 3; FP-12, **15**
 Ostach, D: F4-2-3, 10
 Ougier, M: F2-2-3, 3
 — P —
 Patel, U: F3-10, **13**
 Peng, X: F1-4, 6
 Pérez, O: FP-5, 14
 Persson, A: F1-2, 6
 Petty, T: F2-1-1, 1
 — Q —
 Qiang, L: F4-1-5, 8
 Quenardel, A: F2-2-3, 3
 — R —
 Raadu, M: F2-1-1, 1
 Ramm, J: F4-2-2, 10; FP-2, 14
 Rao, R: F3-1, 12
 Ratova, M: F4-1-3, 8
 Rawai, K: F1-6, 6
 Rawal, S: F3-10, 13
 Raza, M: F1-7, **7**
 Rehman, Z: F1-7, 7
 Rezek, J: F4-1-4, 8
 Rodil, S: FP-13, **15**
 Rosas, N: FP-5, 14
 Rösler, J: F2-3-2, 5
 Ruan, D: F2-3-3, 5
 Ruediger, A: F1-9, 7
 — S —
 Saito, T: FP-3, 14
 Salas, O: F2-2-1, 3
 Sall, M: F2-2-3, 3
 Samih, Y: F2-3-4, 5
 Sarkissian, A: F1-9, 7
 Schalk, N: F4-2-6, **11**
 Schlegel, M: F2-2-3, 3
 Schneider, J: F3-11, 13; F4-1-11, **9**
 Schulz-von der Gathen, V: F2-1-2, 1; F2-1-3, 1
 Schuster, F: F2-2-3, **3**
 Sharma, S: F3-9, 13
 Shih, H: FP-8, 15
 Silva, M: F2-2-2, 3
 Sirota, B: F3-2, **12**
 Sloof, W: F4-1-1, **8**
 Song, M: FP-14, 15
 Stüber, M: F4-2-3, 10
 Su, Y: F2-2-5, **3**
 Sutter, P: F3-5, **12**
 Sze, S: F2-3-3, 5

Author Index

— T —

Tang, Q: F2-3-5, 5
Terasako, T: FP-4, **14**
Terziyska, V: F4-2-6, 11
Thorwarth, K: FP-9, 15
Ting, J: F1-10, 7; F1-5, 6; F3-4, 12; F3-8, 13
Tkadletz, M: F4-2-6, 11
Trant, M: FP-9, 15
Tu, C: F1-8, **7**
— V —
Valdez, B: FP-5, 14
Vaz, F: F4-2-7, **11**
Vergöhl, M: F2-3-2, 5
Vila, R: F3-1, 12
Vlček, J: F2-2-4, **3**; F4-1-4, 8

Voevodin, A: F3-2, 12
von Keudell, A: F2-1-2, 1; F2-1-3, 1
— W —
Wallenberg, R: F1-2, 6
Wang, C: FP-8, **15**
Wang, G: F1-4, 6
Wang, J: F1-4, 6; F2-2-3, 3
Wang, Z: F4-1-5, 8
Wei, R: F2-3-1, 5
Welters, M: F4-2-4, **10**
Winkler, J: F3-11, 13
Wu, M: F1-8, 7
Wu, W: F1-8, 7; F2-2-6, 4; F2-2-7, 4
Wu, Y: F2-3-5, 5

— Y —

Yaakop, N: F4-1-5, **8**
Yagi, M: FP-4, 14
Yamamoto, T: FP-4, 14
Yang, N: F1-4, 6
Yasui, K: FP-3, **14**
Yerokhin, A: F4-1-5, 8
Yu, M: F2-3-3, 5
Yu, X: F1-4, 6
— Z —
Zamani, R: F1-2, 6
Zeman, P: F4-1-4, **8**
Zoehrer, S: F2-1-4, **1**
Zuzjakova, S: F4-1-4, 8