New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F1-TuM

Nanomaterials and Nanofabrication

Moderators: Ulf Helmersson, Linköping University, **Vitezslav Stranak**, University of South Bohemia

8:00am **F1-TuM-1 Single and Multi-component Nanomaterials Prepared by Means of Cluster Beam Deposition**, ***Ondrej Kylian***, Charles University, Czech Republic; *A Shelemin, D Nikitin,* Charles University, Czech Republic, Czechia; *P Pleskunov, J Hanus, P Solar, A Choukourov, A Kuzminova, M Cieslar, H Biederman,* Charles University, Czech Republic **INVITED**

Cluster beam deposition by means of gas aggregation sources (GAS) based either on magnetron sputtering or plasma polymerization become very attractive tool for the production of metal, metal-oxide or plasma polymer nanoparticles (NPs). The increasing popularity of GAS systems is caused by many advantageous features that these sources offer such as their relative simplicity, high efficiency, no or only limited use of potentially harmful solvents and precursors, cleanness of produced NPs as well as the possibility to combine gas aggregation sources with another vacuum-based deposition methods that in turn enables production of functional nanocomposite or nanostructured materials. Furthermore, recent studies showed that not only single material NPs, but also more complex multi-component NPs may be produced by GAS systems including dumbbell-like, janus-like or core@shell nanoparticles.

In this study we introduce and compare three different strategies that allow producing multi-component heterogeneous metal/plasma polymer NPs. The first one is based on the use of a composite metal/polymer target. An example of this approach is the use of Cu/nylon target mounted onto a planar magnetron introduced into the aggregation chamber of GAS. As it was found this system makes it possible to produce metal/plasma polymer nanoparticles with multiple small metallic cores embedded in a plasma polymer shell. Similar multi-core@shell structure of created NPs was observed also when the second approach was used, in which a high amount of precursor (HMDSO) was introduced into the aggregation chamber of the GAS equipped with planar magnetron used for metal sputtering (Ag in our case). The formation of multi-core@shell NPs in both of these arrangements may be explained by the competitive growth of metal NPs and plasma polymerization process and phase segregation of metals and polymers caused by the differences between the cohesive forces of metal atoms and interaction energies of metals and organics. In order to achieve single-core@shell NPs, the third strategy was developed. This is based on the in-flight coating of metallic NPs by a thin plasma polymer shell. This is realized by an auxiliary plasma deposition source positioned in between the output orifice of the GAS and substrate. It is shown that this approach enables to fully decouple the core production from the shell deposition and it is suitable for effective production of metal/plasma polymer single-core@shell NPs.

Acknowledgments: This work was supported by the grant GACR 17-22016S from the Czech Science Foundation

8:40am **F1-TuM-3 Preparation of High Activity and Stability of Cobalt Carbide Nanoparticles for Hydrogen Evolution Reaction**, ***Yi-Heng Lin***, National Cheng Kung University, Taiwan; *S Wang,* Southern Taiwan University of Science and Technology, Taiwan; *J Huang,* National Cheng Kung University, Taiwan

Hydrogen is one of the promising renewable energy in substitution for petroleum energy. The hydrogen produced by splitting water using renewable energy is the key to becoming a sustainable and environmentally friendly green energy. The catalyst plays an important role in hydrogen evolution reaction (HER) to enhance the efficiency. Among the transition metal carbides (TMCs), cobalt carbide is considered to be a potentially active catalyst from theoretical calculations and literature reports. However, the common syntheses are solid phase or chemical vapor deposition processed at high temperature. Here we report two wet-chemistry synthesis methods to prepare nano-sized transition metal carbide. For the first process, $Co(CHOCOO)_2$ and triethylene glycol (TEG) are used as cobalt and carbon source precursor, respectively. With increasing temperature and time of the reaction, TEG decomposes and Co^2+ becomes carbonized. By controlling the amount of NaOH addition, we can adjust the ratio of Co_2C and Co_3C in the product. In the other process we use TEG and oleylamine (OLA) as precursor and without participation of NaOH, and the product will be only Co_2C. The X-ray diffraction pattern peaks show that there is the presence of Co_3C in the former process, and Co_2C dominate in the latter process. The detailed analysis of the product such as TEM, SEM, FT-IR and electrochemical properties on HER will be reported in future.

9:00am **F1-TuM-4 Nanocluster-Based Metal Oxide Films for Hydrogen Gas Sensing**, ***Stanislav Haviar***, *J Čapek, Š Batková, N Kumar,* University of West Bohemia, Czech Republic

Advances in the field of hydrogen-based technologies bring new challenges for material researchers working in the field of gas sensors.

Metal oxide semiconductors (MOSs) are well established as active materials in gas sensor assemblies. Especially nanostructured MOSs attract the attention because of the unique electronic properties of nanomaterials and a high reactive area. Here, we present the study of nanostructured MOS films prepared by use of a gas aggregation cluster source (GAS).

To assemble a functional hydrogen gas sensor we combined sputter-deposited thin film of tungsten oxide with cupric oxide nanoclusters prepared by GAS. Sputtering conditions were tuned to vary the chemical composition and structure of the prepared films. Various architectures were examined for their sensorial response when assembled into a hydrogen gas sensor. The specimens were tested for the response to a time-varied hydrogen concentration in synthetic air at various temperatures. The sensitivity and the response time were evaluated. It is shown that optimization of the structure, architecture and/or composition results in enhanced sensorial properties.

The prepared materials were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and Raman spectroscopy. The chemical composition was studied using X-Ray Photoemission Spectrometry (XPS) and Near Ambient Pressure XPS (NAP).

With further expansion of mobile and portable hydrogen-based technologies the demand on miniaturization of gas sensor rises. That is why it is of a key importance that both the magnetron sputtering and deposition of clusters are techniques compatible with industrial microcircuit technologies. Moreover, in contrary to commonly used wet-techniques the GAS process provides nanoparticles which are clean and ready to use for catalytic purposes in the “as-deposited” condition.

Therefore the technique is very attractive for the research of new catalytic materials.

9:20am **F1-TuM-5 Depostion of Magnetic Thin Films by High Power Impulse Magnetron Sputtering**, ***Jon Tomas Gudmundsson***, *H Hajihoseini, M Kateb, S Ingvarsson,* University of Iceland, Iceland

We study the microstructure and magnetic properties of Ni and $Ni_{80}Fe_{20}$ thin films grown by high power impulse magnetron sputtering (HiPIMS), and compare with films grown by dc magnetron sputtering (dcMS). The nickel films were grown under tilt angles ranging from 0 (substrate faces to the target) to 70 degrees. The magnetic hysteresis was characterized using a home-made high sensitivity magneto-optical Kerr effect (MOKE) looper. It is shown that both deposition methods exhibit in-plane biaxial anisotropy when deposited at small tilt angles while larger tilt angles result in uniaxial anisotropy. However, the angle of transition for anisotropy type is different when depositing with dcMS (35 degrees) compared to HiPIMS deposition (60 degrees). The $Ni_{80}Fe_{20}$ films were grown under a tilt angle of 35 degrees to identical thickness of 37 nm using both dcMS and HiPIMS [1]. All the films exhibit effective in-plane uniaxial anisotropy with square easy axis and linear hard axis magnetization traces. X-ray diffraction reveals that there is very little change in grain size within the pressure and temperature ranges explored. However, variations in film density, obtained by x-ray reflectivity measurements, with pressure have a significant effect on magnetic properties such as anisotropy field (Hk) and coercivity (Hc). We find that HiPIMS deposition results in dense films with low H_k and H_c. For epitaxial growth of $Ni_{80}Fe_{20}$ film on MgO (001) we find the film deposited with HiPIMS has very well defined in-plane uniaxial anisotropy along the <100> direction while the dcMS deposited film presents biaxial anisotropy in-plane, the easy directions are along the [110], indicating that crystalline anisotropy is dominant in that case.

[1] Kateb et al., J. Phys. D: Appl. Phys. 51 (2018) 285005

9:40am **F1-TuM-6 Fluorination of the Magnesium Particle Surface: Enhancing the Reactivity of Magnesium**, *M Pantoya,* ***Shancita Islam***, Texas Tech University, USA

Most metal fuel particles are inherently passivated with their native metal oxide to prevent the pyrophoric metal core from spontaneous reaction with the surrounding environment. The metal oxide is typically a heat sink

and barrier to diffusion limited oxidation reactions. One strategy for increasing the energy release rate of nanoparticle fuels is to activate surface reactions that promote faster and more complete main oxidation reactions. Recent work with aluminum (Al) nanoparticles has shown that the native oxide shell can be used to exothermically contribute to the overall energy generated. The goal of this study was to assess reactivity spurred from surface exothermic reactions to other fuels, namely magnesium, Mg. The objective was to examine surface reactions of Mg particles including nano and micron scale particles coated with a liquid fluorinated perfluoro-polyether (PFPE) polymer. To closely observe the properties of the exothermic surface reaction, magnesium-oxide (MgO) nanoparticles were also examined. Many experimental techniques including differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD) and transmission electron microscopy (TEM) are used to characterize the Mg-PFPE and MgO-PFPE reactions. The results showed that all samples generate a pre-ignition reaction (PIR) including micron Mg particles, and the PIR enthalpy increases with decreasing particle size. The XRD results confirm MgF_2 in all product samples. Further, activation of surface exothermic reactions was shown to affect the overall reactivity of Mg particles by combining the Mg-PFPE coated particles with another solid oxidizer, polytetrafluoroethylene (PTFE) and measuring the flame speed compared with uncoated Mg particles. Results from this study extend previous work promoting surface reactions on Al to other fuels that also benefit from this strategy.

New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F3-TuA

2D Materials: Synthesis, Characterization, and Applications

Moderator: Eli Sutter, University of Nebraska-Lincoln, USA

1:40pm **F3-TuA-1 Roll-to-roll Plasma Chemical Vapor Deposition for Scalable Graphene Production**, ***Timothy Fisher***, UCLA, USA; *M Alrefae,* Purdue University, USA **INVITED**

Recently, roll-to-roll (R2R) chemical vapor deposition (CVD) processes have been implemented to produce graphene with substrate feed rates ranging from 5-100 mm/min. However, this production rate must increase much further to make graphene a feasible product in semiconductor and materials manufacturing industries. Plasma sources can be applied to increase the graphene deposition rate, and additionally, to decrease energy input. This work will describe the implementation of a radio frequency plasma R2R CVD process to deposit graphene on copper and nickel foils, and carbon fibers. The growth process takes advantage of the high-temperature plasma gas that produces active carbon species to accelerate growth kinetics. Thus, supplemental heating of the substrate is unnecessary when using plasma, in contrast to thermal CVD systems that consume energy to heat the substrate and to decompose the carbon gas source. *In situ* temperature measurements of the substrate in the plasma region confirm the plasma's ability to heat the substrate to the 1200-1500 K range depending on the plasma power. From these real-time temperature measurements, a heat transfer model is developed and validated to determine the substrate temperature profile during R2R graphene growth. The effects of plasma power and web speed on substrate temperature are explored and correlated to graphene quality. The results indicate that graphene growth on Cu foil is most significantly influenced by the in-plasma substrate temperature, whereas growth on Ni foil is controlled by the substrate cooling rate, which is evaluated from the heat transfer model. Furthermore, the plasma environment is characterized by optical emission spectroscopy (OES) to optimize graphene growth and assess the impact of ion bombardment. The OES results suggest that the quality of graphene deposited on Cu foil is enhanced with increased CH emission and decreased emission from O, H, Ar^+, C_2, and CN. The process characterization techniques aid in controlling and optimizing graphene growth in a large-scale setup, including graphene quality as a function of reactor pressure and nitrogen mole fraction with associated uncertainties obtained from statistical analysis. The talk will include a discussion of applications of the resulting materials in energy and biosensing technologies, as well as plans for a new MHz plasma R2R system supplemented by solar heating.

2:20pm **F3-TuA-3 Magnetron Sputtered MoS_2/C Nanocomposites as Highly Efficient Electrocatalyst in Hydrogen Evolution Reaction**, *S Rowley-Neale, M Ratova,* Manchester Metropolitan University, UK; *L Fugita,* University of Sao Paulo, Brazil; *G Smith,* University of Chester, UK; *A Gaffar,* ***Justyna Kulczyk-Malecka***, *P Kelly, C Banks,* Manchester Metropolitan University, UK

The design and fabrication of an inexpensive and highly efficient electrocatalyst for the hydrogen evolution reaction (HER), were performed by the route of magnetron sputtering. Molybdenum disulfide (MoS_2) was coated directly onto the nanocarbon (C) powder support. Sputtering time was explored as a function of physiochemical composition of MoS_2/C nanocomposites, and its performance in HER. Increased sputtering time gave rise to materials with different compositions and oxidation states of Mo ions, Mo^{4+} and Mo^{6+}, associated with sulfur anions (sulfide, elemental and sulfate) and improved HER outputs. The physiochemical characterisation of the MoS_2/C nancomposites as a function of sputtering time was evaluated using scanning electron microscope (SEM) equipped with an energy-dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and Raman Spectroscopy. An optimised sputtering time of 45 minutes was used to fabricate MoS_2/C nanocomposites. This gave rise to an optimal HER performance in regards to its onset potential (-0.44 mV vs saturated calomel electrode (SCE)), achievable current (-1.45 mVs^{-1}) and Tafel value (43 $mVdec^{-1}$) for the compositions rich in Mo^{4+} and sulfide (MoS_2). This bespoke fabricated MoS_2/C nanocomposites were incorporated into the bulk ink utilised in the fabrication of screen-printed electrodes (SPEs) to allow improved electrical wiring to the MoS_2/C and to produce scalable and reproducible electrocatalytic platforms. The MoS_2/C-SPEs displayed far greater HER catalysis with a 450 mV reduction in the HER onset potential and a 1.70 mA cm^{-2} increase in the achievable current density (recorded at − 0.75 V vs SCE), compared to a bare/unmodified graphitic SPE. The approach of using magnetron sputtering to modify carbon with MoS_2 facilitates the mass production of stable and effective electrode materials for possible use in electrolysers, which are cost competitive to platinum (Pt) and mitigate the need to use time consuming and low-yield exfoliation techniques, typically used to fabricate pristine MoS_2.

2:40pm **F3-TuA-4 HIPIMS Graphene on Copper for Heat Spreading**, *C Chen, E Liao,* ***Ping-Yen Hsieh***, *Y Chen, J He,* Feng Chia University, Taiwan

The heat generated from electronic devices such as light emitting diodes, batteries, and highly integrated transistors is one of the major causes limiting their performance and reliability. The extraordinarily high thermal conductivity of graphene has let intensive studies for use as a heat spreader. A strategy of further enhancing the thermal conductivity by growing graphene layer on copper will thus proposed in this study. Based on our previous study, it is able to grow graphene layer on copper foil at relative low temperature by using high power impulse magnetron sputtering (HIPIMS) equipped with synchronized substrate bias. The thermal conductivity of the graphene-on-copper (GOC) layer structure was measured, here in this study, based on Angstrom's method. The thermal conductivity of GOC was significantly enhanced as compared to bare copper foil alone. This is due to epitaxial graphene on copper generated low interfacial thermal resistance, and intrinsic high thermal conductivity of graphene. Finally, a strong correlation between graphene layer thickness and thermal conductivity was reported.

3:00pm **F3-TuA-5 Tailoring Optical Properties of Two-Dimensional Transition Metal Dichalcogenides Via Photonic Annealing**, ***Rachel Rai***, *K Gleibe,* University of Dayton, Air Force Research Laboratory, USA; *N Glavin,* Air Force Research Laboratory, Wright-Patterson AFB, USA; *R Wheeler,* UES, Inc., Air Force Research Laboratory, USA; *R Kim,* Air Force Research Laboratory, Wright-Patterson AFB, USA; *A Jawaid,* UES, Inc., Air Force Research Laboratory, USA; *L Bissell,* Air Force Research Laboratory, Wright-Patterson AFB, USA; *C Muratore,* University of Dayton, USA

Semiconducting transition metal dicahlogenides (TMDs) exhibit unique combinations of physical properties at thicknesses of less than 5 molecular layers. For example, mechanical flexibility and photoluminescence (PL) in the visible to near infrared (NIR) frequencies are not properties that are commonly observed in a single material, but are routinely measured for materials such as 2D MoS_2 and WSe_2. Such properties make TMDs attractive candidates for the next generation of flexible and wearable opto-electronic technologies. Incorporation of TMDs into commercial applications is currently limited, however, by challenges associated with synthesis of large area, device-quality films with tunable properties. Our work encompasses diverse innovative techniques to tailor optical properties of TMD thin films by controlling their area, thickness, crystalline domain size, defect density and uniformity during and after processing. We begin by application of thin amorphous films of WSe_2 and other TMDs on both flexible and rigid substrates via vapor phase and liquid phase application over large areas. We then illuminate the amorphous film with diverse light sources, including lasers (visible-IR), broad-band xenon lamps, and nanoscale electron beams. WSe_2 was selected as a model material due to high quantum yield at room temperature. Tailoring the 'structure' of the amorphous material via modulation of the energy flux during magnetron sputtering provides an opportunity to model homogeneous or heterogeneous crystallization during illumination by controlling the density of pre-existing nuclei. Crystallization kinetics were examined by *in situ* analysis of real-time images and electron diffraction patterns. The amorphous-crystalline conversion is correlated to 2D growth theory and contrasting elements of 2D versus 3D growth are highlighted. A significant increase in photoluminescence intensity is accompanied by a change in crystal edge density, consistent with observations that PL originates preferentially from defective regions of 2D WSe_2. Furthermore, we examine quantum confinement effects on photoluminescence yield in nanoscale crystalline areas (~10 nm) via electron beam irradiation .

4:00pm **F3-TuA-8 Mechanism of Formation of Nitrogenated Doped Graphene Films, Investigated by In situ XPS During Thermal Annealing in Vacuum**, ***Yannick Bleu,*** Univ. Lyon, Université Jean Monnet, France*; V Barnier, F Christien,* Laboratoire Georges Friedel, Ecole Nationale Supérieure des Mines, France*; F Bourquard,* Univ. Lyon, Laboratoire Hubert Curien, Université Jean Monnet, France*; J Avila,* Synchrotron SOLEIL & Université Paris-Saclay, France*; F Garrelie,* Univ. Lyon, Université Jean Monnet, France*; M Asensio,* Synchrotron SOLEIL & Université Paris-Saclay, France*; C Donnet,* Université de Lyon, Université Jean Monnet, France

The introduction of dopants, such as nitrogen, into the graphene network, is paramount for many applications such as nanoelectronics, nanophotonics, sensor devices and green energy technology. One way consists in thermal heating of a doped solid carbon source, such as an amorphous a-C:N film, in the presence of a metal catalyst, to obtain nitrogenated graphene (NG) layers. The control of such a process requires to investigate diffusion and segregation mechanisms of the graphene precursor through the metal catalyst.

In the present study, the mechanism of atomic diffusion and NG film growth through a nickel catalyst thin film was investigated using in situ X-ray photoelectron spectroscopy (XPS) performed during thermal heating responsible for NG synthesis. Amorphous a-C:N films, containing 16%at. nitrogen, 10 nm thick, were synthetized by femtosecond pulsed laser ablation on fused silica substrates. A 150 nm thick nickel film was subsequently deposited by thermal evaporation on the a-C:N films. Thermal annealing at various temperatures (200, 300, 500 and 650°C), with different time durations, were performed in ultra-high vacuum during *in situ* XPS analysis, to carry out the top surface genesis of the NG film onto the nickel catalyst. FEG-SEM, Raman and X-ray absorption (XAS) spectroscopies were also performed to elucidate the nature and chemical composition of NG films. The diffusion of carbon and nitrogen through the nickel film towards the surface from 300°C was observed, without any graphene signature. Graphene films are formed at the highest temperatures, with a final 3%at. nitrogen content, in both pyrrolic and pyridinic configurations. In addition, the kinetics of carbon surface enrichment observed using in-situ XPS is discussed in the frame of the interface segregation theory and modelled using the Du Plessis approach. The solid-state transformation mechanism responsible for the formation of few-layer NG films is thus investigated.

4:20pm **F3-TuA-9 Engineering Point and Extended Defects in Transition Metal Dichalcogenides**, ***Hannu-Pekka Komsa,*** Aalto University, Finland
INVITED

Two-dimensional (2D) materials such as graphene, hexagonal boron nitride, and transition metal dichalcogenides have recently received lots of attention due to their unique material properties and numerous potential applications. The 2D atomic structure can also facilitate distinct defect formation mechanisms and offer new possibilities for defect engineering.

In my talk, I will present the results from layered molybdenum dichalcogenides (MoS_2, $MoSe_2$, and $MoTe_2$), where vacancy, substitutional, interstitial, and grain boundary defects are introduced by electron irradiation or by various chemical treatments. Due to the 2D nature, transmission electron microscopy and scanning tunneling microscopy imaging allows direct monitoring of formation and agglomeration of defects as well as of larger structural changes. First-principles calculations are used to provide microscopic insight into the energetics and kinetics of these processes. The gained understanding together with the computationally predicted defect properties can be used to guide future efforts in tailoring the 2D material properties via defect engineering.

5:00pm **F3-TuA-11 Physicochemical and Mechanical Performance of Nylon 6.6 Coated Thin Free-standing Boron-doped Diamond Nanosheets**, ***Robert Bogdanowicz,*** *M Ficek,* Gdansk University of Technology, Poland*; V Stranak, J Kratochvil,* University of South Bohemia, Czech Republic*; M Szkodo, J Ryl, M Sobaszek,* Gdansk University of Technology, Poland

In the following work, we describe studies on the fabrication and the physicochemical performance of thin and free-standing heavy boron-doped diamond (BDD) nanosheets coated by thin nylon 6.6. First, the diamond nanosheets with less than 400 nm of thickness were grown and doped by boron on Ta substrate by using microwave plasma-enhanced chemical vapor deposition technique (MPECVD) [1]. Then, the BDD/Ta samples where covered by 6.6 nylon to improve their stability in harsh environments.

The plasma polymer films, the thickness in the range 500-1000 nm, with different surface energies were obtained by magnetron sputtering of a bulk target. The hydrophilic nitrogen-rich C:H:N :O were prepared by sputtering of nylon 6.6. C:H:N :O as films with high surface energy improves adhesion at ambient condition. However, their disadvantage lays in a natural swelling increasing its volume about of 15% after immersion into an aqueous liquid. This behavior influences diamond-C:H:N :O structure in a wet environment.

The C:H:N :O coated diamond nanosheets were delaminated from Ta substrate creating free-standing nanostructures (Diamond-on-Nylon). The C:H:N :O film fixtures the thin polycrystalline diamond sheets enhancing its mechanical stability and enabling transfer and integration with microelectronic systems.

We have manifested that investigated Diamond-on-Nylon nanostructures possess altered morphology and physicochemical properties, revealed by electron microscopy and Raman spectroscopy. Moreover, the electrical response of investigated nanostructures as conductive electrodes is time-stable and indicates the high activity of the sheets with higher dopant concentrations.

Moreover, the Diamond-on-Nylon is characterized with altered mechanical properties like Young modulus or internal stress. These properties varied strongly with the thickness and density of nylon coverage.

In summary, the Diamond-on-Nylon nanostructures show excellent electrical and thermal conductivity along with high mechanical strength. Composite diamond-on-polymer structures could be further developed for flexible and robust electronic devices or thermal heat spreaders.

Acknowledgments

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[1]. Bogdanowicz, Robert, et al. *Advanced Functional Materials* (2018): 1805242.

[2]. Ryl, Jacek, et al. *Carbon* 96 (2016): 1093-1105.

New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F4-1-WeM

Functional Oxide and Oxynitride Coatings I

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

8:00am **F4-1-WeM-1 Microstructure and Piezoelectric Properties of Hexagonal $Mg_xZn_{1-x}O$ and $Mg_xZn_{1-x}O$/ZnO Films at Lower Mg Compositions**, ***Hsin Hung Chen***, *C Liu, J Huang,* National Cheng Kung University, Taiwan

We investigate the piezoelectric coefficient(d33) of MgxZn1-xO and MgxZn1-xO/ZnO with various Mg content. The films were grown on Si (111) substrate using MgO and ZnO targets by radio frequency magnetron sputtering. Thickness of all films are fixed at around 600nm for MgxZn1-xO and 300/300nm for MgxZn1-xO/ZnO. There shows high crystallinity with preferred orientation along c-axis in XRD pattern, and columnar structures are clearly observed in SEM images, indicating that the films still remain wurtzite structures. Besides, XRD pattern, PL and XPS spectra proved that substitution of smaller magnesium ions at zinc sites causes lattice distortion and therefore enhance the d33 at maximum 48.7pm/V of MgxZn1-xO and 39.1pm/V of MgxZn1-xO/ZnO (x=0.17 for both) by PFM measurement. These values are nearly four and three times larger than pure ZnO films. We consider these films as a promising candidate for nanogenerators(NGs) and ultraviolet photodetectors(UV-PDs).

8:20am **F4-1-WeM-2 Structure Optimization of Ta-O-N Films Prepared by Reactive HiPIMS for More Effective Water Splitting**, ***Šárka Batková***, Department of Physics and NTIS - European Centre of Excellence, University of West Bohemia, Czech Republic*; J Čapek, S Haviar, J Houška, R Čerstvý,* University of West Bohemia, Czech Republic*; M Krbal,* University of Pardubice, Czech Republic*; T Duchoň,* Charles University, Czech Republic

The TaON material is a promising candidate for application as a visible-light-driven photocatalyst splitting water into H_2 and O_2 and thus converting solar energy into chemical energy. The photo-generated electron-hole pairs act here as the active water splitting species. In order to work as a water splitting photocatalyst, the material must satisfy certain conditions: (i) band gap of proper width (preferably corresponding to visible light absorption) and (ii) suitable alignment of the band gap with respect to the water splitting redox potentials. The subsequent transport of the charge carriers through the material (particularly across the films thickness) plays an important role in the effectivity of the process.

In this work we first demonstrate that using reactive high-power impulse magnetron sputtering (HiPIMS) as the deposition technique followed by post-annealing of the amorphous as-deposited film at 900°C in a vacuum furnace allows us to prepare a polycrystalline film exhibiting a pure TaON phase. Such film satisfies the above mentioned conditions for a water splitting photocatalyst (band gap of ~2.6 eV). However, as it is desirable to prepare the TaON phase in situ, we investigate the possibilities of substrate heating and biasing during deposition while focusing on fine-tuning of the elemental composition. Additionally, as the monoclinic TaON phase exhibits anisotropic charge carrier conductivity, tailoring of the texture of the film can further improve the charge carrier transport in a desired direction. In this work, we therefore also investigate the possibilities of deposition at high power densities in a pulse (up to 4 kW/cm^2) and/or deposition onto suitable substrates providing proper seeding layers (e.g., Pt, ZrO_2) to prepare textured TaON film allowing enhanced charge carrier mobility across the film thickness.

8:40am **F4-1-WeM-3 A Sustainable and Viable Alternative to Low Cost Electronics based on Metal Oxides**, ***Elvira Fortunato***, *R Martins,* New University of Lisbon, Portugal **INVITED**

In the last 50 years we observed a drastic change in our daily life since society was never before so efficient and interconnected. This provides a collaborative environment that is essential for economic growth and progress like: Silicon Valley for microelectronic technology and Boston for biotechnology. This breakneck development has been in part dictated by an empirical technologically and economically driven rule know as “Moore’s law”. Indeed today a microprocessor has more than 7 billion integrated transistors in an area of 350 mm2. This unbelievable integration capability with higher processing speeds, memory capacity and functionality gives rise to what we call today: ubiquitous electronics. Despite the importance of silicon technology there are applications where it is impossible, either technically or economically use it. Displays are the most notorious example, more if we want them to be flexible and conformable. On the other hand, 10 years ago it was pure science fiction the notion of fully transparent, flexible and conformable displays, like those used by T. Cruise in the Minority Report movie fully based on materials away from silicon! Thanks to the Hollywood vision and the hard work of scientists this is now a reality. After the huge success and revolution of transparent electronics where we must highlight the low process temperatures that turn possible the use of low cost eco-friendly materials and substrates such biopolymer or paper, where CENIMAT is pioneer and with the worldwide interest in displays/smart interfaces where metal oxide thin films have proved to be truly semiconductors, display backplanes have already gone commercial due to the huge investment of several high profile companies such: SAMSUNG, SHARP, LG, BOE, in a very short period of time. Recently IDTechEx estimated that 8 km sqr of metal oxide-based backplanes will be used in the OLED and LCD industry by 2024, enabling a 16 billion USD market at the display module level alone. We can anticipate that the metal oxide based industry will be in the near future a so-called multi billion euro market similar to what is observed with the pharmaceutical industry, due to the number of different applications that can serve, ranging from information technology, biotechnology/life sciences and energy to food/consumer products. In this talk we will present results on recent new technologies developed at CENIMAT|i3N where it is possible to have the use of sustainable materials used in disruptive applications.

9:20am **F4-1-WeM-5 Photocatalytic Study for Indium Tantalum Oxide Thin Film in Visible Light**, ***Chuan Li***, National Yang Ming University, Taiwan*; J Hsieh,* Ming Chi University of Technology, Taiwan*; P Hsueh,* National Central University, Taiwan

Indium tantalum oxide thin film was deposited by sputtering using three different designs: 5-7 and 10-14 nm alternative layers of Ta_2O_5 and In_2O_3, and co-sputtering of In_2O_3 and Ta_2O_5. Then as-deposited films were rapid annealed at different temperatures to assess the thermal effects on microstructures and photocatalytic functions. Results from XRD and EDS indicates that crystalline $InTaO_4$ emerges in 5-7 and 10-14 nm stacks of films but absent in the co-sputtered films. Since crystalline $InTaO_4$ is capable of photocatalysis under both ultraviolet and visible light, we particularly tested the annealed films in water to degrade methylene blue under visible light. The photo-induced degradation on methylene blue by 5-7 and 10-14 nm stacks can reach 45% after 6-hour continuous exposure. Using UV-Visible-NIR spectroscopy, we can estimate the optical band gaps in these annealed films and from these estimations, a mechanism for the photocatalysis is discussed following. This mechanism is similar to other electron-hole separation and transfer across the heterogeneous junctions in semiconductors.

9:40am **F4-1-WeM-6 Tailoring the Microstructure of ZnO Thin Films for Antimicrobial Applications**, *P Pereira-Silva, J Borges, A Costa-Barbosa, D Costa, M Rodrigues,* ***Filipe Vaz***, *P Sampaio,* University of Minho, Portugal

Nosocomial infections are microbial infectious diseases that are acquired in healthcare settings, and are a worldwide health problem. The surfaces are involved in the spread of these infections, thus there is an urgent need to eliminate this route of transmission. Nanotechnology allows the production of materials with improved properties and effective action against pathogens. Zinc oxide (ZnO) is frequently used due to its excellent antimicrobial properties.

This work focused on the evaluation of the antimicrobial activity of ZnO thin films. All the samples were produced by reactive DC magnetron sputtering and tested against the fungus *Candida albicans*. A first set of thin films were produced with different O_2 flows, which affected the thin films’ chemical composition and morphology. Additionally, some of the thin films were subjected to an annealing treatment, which promoted the crystallization of the ZnO matrix. A second set of thin films was produced modifying the deposition angle, using the Glancing Angle Deposition technique, GLAD, with a fixed O_2 flow. These changes were performed to increase the porosity and roughness of the thin films, which may allow the tailoring of the film’s biological response. To evaluate the ZnO thin films surface antimicrobial properties, a direct contact assay was performed, and the results revealed no significant cell growth after five hours of incubation. Analysing possible molecular mechanisms responsible for the antimicrobial activity, it was observed that the loss of membrane integrity and the increase of Reactive Oxygen Species (ROS) within *C.albicans* cells was correlated with the incapacity of the cells to grow.

As a general conclusion, one may claim that all the thin films showed a significant antifungal activity, and the observed differences among them can be correlated with the evolution of the (micro)structural features.

11:00am **F4-1-WeM-10 Exploring Thin Film Zn-Sn-O (ZTO) Composition Spreads Using Combinatorial Sputtering***, **Siang-Yun Li**, Y Shen, K Chang, J Ting,* National Cheng Kung University, Taiwan

Transparent conducting oxide (TCO) films are extensively applied as electrodes in the fields of solar cells and displays, due to their high transparency and excellent electrical conductivity. Multicomponent oxides such as Zn-Sn-O (ZTO) have attracted much attention due to the low cost elements of indium (In). In addition, thermal stability and mechanical strength of ZTO can be tailored by varying its stoichiometry. However, making compounds having different ratios of Zn/Sn systematically is not trivial.

Combinatorial methodology has been proven its validity in such an application. This approach allows the Zn/Sn ratio continuously to change across a single sample area and a feasible intimate mix of Zn and Sn. Therefore, a single ZTO composition spread sample essentially includes a full spectrum of properties to be investigated. A Zn-Sn-O (ZTO) composition spread, consisting of thickness wedges of SnO and ZnO, was prepared using a state-of-the-art combinatorial sputtering system, equipped with a moving shutter and two RF guns for the targets of Zn and Sn, respectively. The thickness gradient was determined using SEM, α-step and SIMS. It was found a smooth thickness variation across the sample area for both ZnO and SnO with the coefficient of determination (R2) ≅ 0.99, indicating a good control of the ZTO composition spread. Structure evolution was characterized using XRD. We found in-situ 500 ºC annealing resulted in crystallization of the samples, where ZnO, Zn_2SnO_4, $ZnSnO_3$, and SnO_2 phases were observed, depending upon the ZnO/SnO ratios on the ZTO composition spread. The resistivity was characterized using a four-point probe on different substrates, which revealed lower resistivity near ZnO-rich. Morphology and optical characteristics were studied as well using AFM, SEM and UV-Vis spectrometry. A clear variation trend of both properties was observed. A systematic study of physical properties of ZTO has been successfully demonstrated.

11:20am **F4-1-WeM-11 Can Thin-Film Technology Help to Realize The Einstein Gravity Quantum Computer?***, **Norbert Schwarzer**,* SIO, Germany

After it became clear that quantum computers are more powerful than originally thought [1], we were asked by the industry to find the most fundamental form of a Turing machine based on Quantum Theory. Do this job in a very comprehensive manner, we found that the deepest layer for the Quantum Computer was not to be found inside the theoretical apparatus of Quantum Theory. Surprising as this may be, it is the General Theory of Relativity which “contained it all”. We found that an extremely simple solution of the Einstein-Field-Equations, using pairwise dimensional entanglement, sports the principle structural elements of computers [2]. We will derive these structural elements and show that the classical computer technology of today and even the quantum computers are just degenerated derivatives of this general solution. In the talk we will discuss thin-film technology- and smart material-options potentially helping us to one day realize the general computer concept.

[1] J. Aron, “Quantum computers are weirder and more powerful than we thought”, www.newscientist.com/article/2170746

[2] N. Schwarzer, “Einstein had it, but he did not see it – Part XXXIX: EQ or The Einstein Quantum Computer”, www.amzon.com, ASIN: B07D9MBRS3

Keywords— Quantum Computer, Smart Materials, Quantum Dots, Quantum Gravity

New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F4-2-WeA

Functional Oxide and Oxynitride Coatings II

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

3:00pm **F4-2-WeA-4 Structural, Optical and Electrochromic Properties of Nanocrystalline WO_3 Thin Films**, ***Madhuri Venkat Kalapala***, VFSTR University, India

In the present work, WO_3 thin films were coated onto well cleaned corning 7059 glass, Silicon and ITO coated glass substrates by electron beam evaporation (EBE) technique under an oxygen partial pressure of $2x10^{-4}$ mbar by maintaining the substrate temperature at 6-8 °C and room temperature (RT). The deposited films were subsequently annealed at 400 °C in air at about 2 hours and the films were systematically characterised to analyse the electrochromic properties which are useful in emerging chromogenic technology. The structural, morphological, vibrational, optical and electrochromic properties of WO_3 films were studied by XRD, AFM, Raman, UV-VIS spectroscopy and Cyclic voltammetry respectively. XRD studies reveal that the prepared WO_3 films are completely monoclinic structure with different orientations. The AFM images and the grain sizes are comparable with the XRD data. The optical transmission and energy bandgap of the films increases with the lowering of temperatures to 6-8 °C. Finally it is found that, the coloration efficiency at the wavelength of 550 nm for the annealed films deposited at 6-8 °C is maximum 72.60 cm^2C^{-1}.

3:20pm **F4-2-WeA-5 Structure, Mechanical Characteristics and Thermal Stability of HS-PVD $(Al,Cr)_2O_3$ Coatings**, *K Bobzin, T Brögelmann, C Kalscheuer,* ***Martin Welters,*** Surface Engineering Institute - RWTH Aachen University, Germany

Alumina coatings with corundum structure, α-Al_2O_3, bear great potential concerning the application under harsh conditions even at temperatures above T ≥ 900 °C and in corrosive or oxidative environments. Typically, α-Al_2O_3 is used on cutting and molding tools. However, the industrial deposition of α-alumina coatings is typically performed by chemical vapor deposition (CVD) at temperatures between 800 °C ≤ T ≤ 1,100 °C, which limits the choice of base materials. In the last decades $(Al,Cr)_2O_3$ coatings deposited by physical vapor deposition (PVD) attract great interest as an alternative to CVD α-Al_2O_3, due to their potential to form corundum-type structure at lower process temperatures. $(Al,Cr)_2O_3$ coatings with high Al content promise similar characteristics to α-alumina. However, the deposition of crystalline α-$(Al,Cr)_2O_3$ by PVD technology with high alumina content, x_{Al} > 70 at.%, is still one of the greatest challenges. So far, various PVD technologies, such as cathodic arc deposition and magnetron sputtering, were investigated concerning the deposition of α-$(Al,Cr)_2O_3$. The investigations showed that low deposition temperatures, T ≤ 650 °C, and high aluminum contents, x_{Al} > 70 at.%, frequently led to the formation of metastable amorphous or crystalline alumina phases. Further drawbacks are low coating thicknesses and deposition rates for the deposition of oxide coatings as well as challenges regarding the coating of complex geometries. A promising technology to overcome these challenges is the high speed (HS)- PVD technology, basing on a hollow cathode discharge. Owing to the promising technology characteristics, the potential of HS-PVD concerning the deposition of α-$(Al,Cr)_2O_3$ was fundamentally investigated. After successful process adjustment, the deposition of crystalline tetragonal $(Al,Cr)_2O_3$ coatings and semi-crystalline α-$(Al,Cr)_2O_3$ coatings with high Al content, x_{Al} ≥ 70 at.%, was possible by HS-PVD at a substrate temperature of T_s = 570 °C. The analyses regarding structural characteristics confirm that the deposition of thick, s ≥ 20 µm, oxide coatings with high deposition rates above 35 µm/h is possible by HS-PVD. Furthermore, nanoindentation shows that an indentation hardness of H_{IT} = 24 GPa can be achieved for the crystalline $(Al,Cr)_2O_3$ coatings. Moreover, the oxidation and diffusion behavior of the thick $(Al,Cr)_2O_3$ coatings was investigated by thermal annealing up to T = 1,300 °C in ambient air. Thereby, the annealing tests were evaluated by scanning electron microscopy, X-ray diffraction and nanoindentation. Analog annealing tests in vacuum confirmed the stability of the α-$(Al,Cr)_2O_3$ phase up to T = 1,300 °C.

3:40pm **F4-2-WeA-6 Reactive HiPIMS Deposition of γ -Al_2O_3 Thin Films using Transition Metal Doped Al Targets**, ***Stefan Kagerer***, *L Zauner,* TU Wien, Institute of Materials Science, Austria; *S Koloszvári,* Plansee Composite Materials GmbH, Germany; *J Čapek, T Kozák, P Zeman,* University of West Bohemia, Czech Republic; *H Riedl,* TU Wien, Institute of Materials Science, Austria; *P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

The outstanding oxidation resistance, thermo-mechanical stability, and chemical inertness of alumina attracts particular attention in academia and industry. Especially, in the field of hard protective coatings there are many research activities focusing on the synthesis of the different polymorphs α- and γ-Al_2O_3 (corundum and cubic), respectively. To overcome the thermodynamic barrier stabilizing these structure types, extremely high deposition temperatures are crucial during film growth (either in CVD or PVD). Apart from this fact, the formation of isolating Al_2O_3 layers on the target surface may lead to massive arc events, and hence destabilizes PVD based deposition process.

Therefore, alternative concepts involving PVD based synthesis at low temperatures are extremely interesting. Within this study, we investigated in detail the influence of small amounts of transition metals such as M = Cr or W on the process stability and phase formation of DC as well as high power impulse magnetron sputtered $(Al_{1-x}M_x)_2O_3$ thin films in reactive gas atmospheres (Ar/O_2 mixtures). Through the introduction of high amplitude impulses at relatively low duty cycles, the amount of ionized species, either for the target-near gas or sputtered target-atoms, can be increased drastically. To gain an in-depth understanding on the influence of small amounts of tungsten compared to pure Al targets but also on different HiPIMS parameters (e.g. frequency, pulse length, power density, or synchronized bias signals), the ionization of e.g. Al^+, Al^{++} or O_2^+ was investigated by ion mass spectroscopy methodically. In addition, the obtained coating structures were analyzed with respect to phase formation and morphology applying X-ray diffraction combined with electron imaging techniques (SEM and HR-TEM).

4:00pm **F4-2-WeA-7 Influence of V Content on Phase Evolution and Thermal Stability of Reactive Pulsed DC Magnetron Sputtered $(Al,V)_2O_3$**, ***Ludvig Landälv***, Linköping Univ., IFM, Thin Film Physics Div. and Sandvik Coromant R&D, Sweden; *C Carlström,* Sandvik Coromant R&D, Sweden; *J Lu,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *M Johansson-Jõesaar,* SECO tools AB, Sweden; *M Ahlgren, E Göthelid,* Sandvik Coromant R&D, Sweden; *B Alling, L Hultman, P Eklund,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Physical vapor deposited corundum structured α-Al_2O_3 coatings have been a long sought goal for the cutting tool industry. Various PVD synthesis routes have been evaluated comprising, e.g., Cr alloying in $(Al,Cr)_2O_3$ to stabilize the corundum phase [1, 2]. Correspondingly, based on V_2O_3 crystallization in the corundum structure, similar possibilities are indicated for phase stabilization in $(Al,V)_2O_3$ alloys, although this material system has not yet been studied as much.

This work aims to investigate the influence of V concentration in reactive co-sputtered $(Al,V)_2O_3$ coatings on phase stabilization and phase evolution, correlated to its mechanical properties by nanoindentation. XRD and SEM characterization of the as-deposited coatings reveal three different phase-regions as a function of V content in the coating with a solid solution γ-$(Al,V)_2O_3$ for low V content, a defect spinel at around 50 at % metal fraction V and a corundum phase at large V content.

The phase stability and mechanical properties of $(Al,V)_2O_3$ coatings were studied after annealing in air at different temperatures up to a maximum of 1100 °C. SEM, XRD and nanoindentation was performed after each temperature step. The annealing resulted in formation of vanadiumoxide phases, predominantly V_2O_5, at the coating surface with an onset temperature correlated to the amount of V in the coating. A higher V-content resulting in a lower onset temperature. The effect of the oxidation behavior of the coatings with respect to mechanical properties will be discussed.

[1] Ramm, J., et al., Surf. Coat. Technol., 2007, **202**(4–7): p. 876-883.

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

4:20pm **F4-2-WeA-8 Al Vacancies in Wurtzite Al-(Si-)(O-)N: Theory and Experimental Assessment**, ***Maria Fischer***, *M Trant, K Thorwarth, D Scopece, C Pignedoli, D Passerone, H Hug,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Transparent hard films can be fabricated from Al, Si, O and N by reactive direct current magnetron sputter (R-DCMS) deposition. Al-Si-N and Al-O-N

are two possible ternary combinations. Up to 6% Si / 8% O, the coatings can maintain the crystalline structure of wurtzite AlN and incorporate Si / O in the form of a solid solution. As Si is an electron donor like Al, it will substitute the latter on a cationic lattice site. O, in contrast, is an electron acceptor like N, and thus replaces the latter on an anionic lattice site.

These two contrary substitutions induce the same microstructural evolution in wurtzite. The reason for this was found in the formation of cationic Al vacancies (V(Al)) in both cases, because both Si and O impose an electron excess onto the crystal system. The presence of V(Al) in Al-Si-N and Al-O-N has previously been supported by X-ray diffraction measurements, *ab initio* calculations and entropic considerations. With the present study, further experimental evidence for V(Al)s has been provided through Positron Annihilation Spectroscopy (PAS) and Lifetime (PALS) measurements of the latter. To corroborate the hypothesis on vacancy formation, PA(L)S has also been performed on a complementary material system containing anionic vacancies.

4:40pm **F4-2-WeA-9 Thermal Atomic Layer Etching of Oxide and Nitride Thin Films***, **Steven M. George**,* University of Colorado at Boulder, USA **INVITED**

Nanofabrication requires atomic layer control over both material deposition and removal. Thermal atomic layer etching (ALE) is based on sequential, self-limiting surface reactions. Thermal ALE is the reverse of atomic layer deposition (ALD). Thermal ALE yields isotropic etching. Thermal Si ALE complements plasma ALE processes that utilize directional ions and produce anisotropic etching. This talk will focus on the thermal ALE of oxide and nitride thin films.

Thermal Al_2O_3 will be described using sequential fluorination and ligand-exchange reactions [1]. During these reactions, HF is utilized to fluorinate the Al_2O_3 surface and produce an AlF_3 surface layer. Trimethylaluminum (TMA) is then used to remove the AlF_3 surface layer through a ligand-exchange reaction. During this ligand-exchange, fluorine transfers from AlF_3 to TMA and, concurrently, methyl groups transfer from TMA to AlF_3. This ligand-exchange process yields volatile $AlF(CH_3)_2$ products. Al_2O_3 etch rates of 0.51 Å/cycle are observed at 300°C [1].

Thermal SiO_2 ALE will also be demonstrated using a "conversion-etch" mechanism with TMA and HF as the reactants [2]. During SiO_2 ALE, the TMA is able to convert the SiO_2 surface to an Al_2O_3 surface layer. The Al_2O_3 surface layer is then removed by thermal Al_2O_3 ALE as described above. The conversion of SiO_2 to Al_2O_3 requires higher TMA pressures. Larger SiO_2 etch rates are observed at higher TMA pressures [2]. In addition, thermal TiN ALE will be presented using oxidation of TiN to TiO_2 and then the removal of the TiO_2 surface layer by fluorination to a volatile fluoride [3]. TiN ALE at 250°C using O_3 and HF as the reactants yields a TiN etch rate of 0.2 Å/cycle.

[1] Y. Lee, J.W. DuMont and S.M. George, *Chem. Mater.***28**, 2994 (2016).

[2] J.W. DuMont et al., *ACS Appl. Mater. & Interfaces***9**, 10296 (2017).

[3] Y. Lee and S.M. George, *Chem. Mater.***29**, 8202 (2017).

5:20pm **F4-2-WeA-11 Growth and Characterization ALD Films with a new Continuous Flow Process***, **Birol Kuyel**, A Alphonse, K Hong,* Nano-Master, Inc., USA

Growth and film deposition characteristic in a downstream ICP PEALD reactor are studied using a unique new process called Continuous Flow Process* that cuts the cycle time in half. This process is implemented in an PEALD reactor where uniform variable density O_2 and N_2 or H_2 plasmas is produced but any contact of the plasma with the substrate is prevented. Precursors are not allowed to enter the plasma production region making it possible to obtain repeatable operation free of deposits or instabilities. Design features will be discussed and application of this Continuous Flow Process in depositing PEALD GaN, Al_2O_3, AlN, SiO_2 and Si_3N_4 films on Si substrates will be shown. Examples of Continuous Flow process is presented showing ultra-smooth and uniform films with thickness linearly proportional to the number of cycles are deposited. Future applications will also be discussed.

*US Patent # 9,972,501 B1 May 15, 2018

New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F2-1-ThM

HiPIMS, Pulsed Plasmas and Energetic Deposition I

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

8:40am **F2-1-ThM-3 Recent Insights into HiPIMS Physics via Coherent and Incoherent Thomson Scattering**, ***Sedina Tsikata,*** CNRS, ICARE, France*; T Minea,* Université Paris-Sud/CNRS, France*; B Vincent,* CNRS, France*; A Revel,* Université Paris-Sud/CNRS, France **INVITED**

The emergence of the HiPIMS operating regime for planar magnetrons offers new possibilities for the generation of thin films. HiPIMS operation, characterized by high-current, short-duration plasma pulsing, produces high plasma densities which can favor improved mechanical properties of thin films. For HiPIMS plasmas to be fully exploited and for their adoption to become commonplace in industry, it is necessary to understand the basic physical processes associated with this operation.

HiPIMS operation involves complex, transient plasma states and processes which are much more challenging to model than conventional DC operation. Although a consensus has emerged that fully kinetic, three-dimensional models offer the best chance at capturing the physics of this state, such codes are in their infancy and cannot be feasibly applied to large-scale industrial development. A key missing ingredient for such codes remains the knowledge of the particle dynamics and properties.

In this talk, we report on recent new approaches to understanding the HiPIMS plasma using a combination of advanced laser diagnostics. With coherent Thomson scattering, we have recently obtained for the first time information on the nature of microturbulence affecting the confinement of electrons in the planar magnetron magnetic trap [1]. Studies with this experimental technique show that large-scale and small-scale behavior are inextricably linked. With incoherent Thomson scattering [2], we have also obtained time-resolved measurements of electron density and temperature during the evolution of a HiPIMS pulse, establishing the link between these properties and the current characteristics. The implementation of these diagnostics gives access to information on electron dynamics and properties which was previously inaccessible. We discuss the import of these experimental findings in the context of recent numerical models [3], and explain our current understanding of the physics of the HiPIMS state.

[1] S. Tsikata and T. Minea. Phys. Rev. Lett. 114, 185001 (2015)

[2] B. Vincent, S. Tsikata, S. Mazouffre, T. Minea and J. Fils. Plasma Sources Sci. Technol. 27, 055002 (2018)

[3] A. Revel, T. Minea and S. Tsikata. Phys. Plasmas 23, 100701 (2016)

9:20am **F2-1-ThM-5 Process Gas Rarefaction and Other Transport Phenomena in High Power Impulse Magnetron Sputtering Discharges Studied by Particle Simulations**, ***Tomas Kozák,*** University of West Bohemia, Czech Republic

The high power impulse magnetron sputtering (HiPIMS) technique has recently been increasingly used in the coating industry. For tailoring film properties, it is necessary to know and control the energy delivered to the film by process gas and film-forming particles. Computer simulations can help understand the relations between discharge process parameters and fluxes of particles onto the substrate. Due to the complexity of the HiPIMS discharge, it is not feasible to simulate the deposition process self-consistently. Various modelling approaches have been used to give simplified predictions of the HiPIMS plasma parameters.

A fully three-dimensional simulation using the Direct Simulation Monte Carlo (DSMC) method was developed to model the transport of neutral and ion species in a vacuum chamber of realistic size, to improve upon the existing volume-average [1,2] or Monte Carlo [3] models. The time-dependent evolution of gas and target material species densities in the discharge chamber during sputtering pulses as well as the fluxes of particles onto the substrate and their energy distributions were studied under various conditions.

First, the effect of process gas rarefaction by momentum transfer from sputtered target material atoms (Zr, Al and C) was systematically investigated. The effect of target material mass and the target current amplitude is reported. The argon density decreases during the pulse-on time to 50% of its initial value for the current density of sputtered Al atoms of around 0.5 Acm^{-2}. For Zr and C, the minimum argon density is 43% and 57%, respectively. Thus, the dependence on the mass of the target material was found to be rather weak. During the pulse-off time, argon density returns back to equilibrium within 1 ms after the pulse end.

Second, ionization of sputtered target material atoms and the transport of ions in a given electrostatic potential is further investigated. This will help us understand the complex dynamics of HiPIMS discharges and the energies of ions incident onto the substrate observed in diagnostic experiments.

References

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[3] S. Kadlec, *Plasma Process. Polym.* **4** (2007) S419–23

9:40am **F2-1-ThM-6 Insight on the Sputtered Material in HiPIMS by 2D PIC-MCC Modeling**, ***Adrien Revel,*** Université Paris-Sud/CNRS, France*; T Minea,* Université Paris-Sud, Université Paris-Saclay, France

The development of High Power Impulse Magnetron Sputtering (HiPIMS) since the early 2000 has boosted the research much beyond the Conventional Magnetron Sputtering (CMS), worldwide used in industries. In HiPIMS regime, the quantity of sputtered material from the target is greatly improved during the on time compared to the DC regime. Combined with the higher plasma density, the fraction of the sputtered material being ionized is considerably increased reaching a value between 10% and 80% depending on the discharge parameters and target characteristics. An important part of these ionized particles come back to target leading to the self-sputtering effect.

Beyond this, the plasma behavior in magnetron discharge involves complex phenomena such as ExB gradient, curvature and drift coupled with kinetic reactions and plasma-surface interactions. Hence, the motion of individual particles and the whole plasma is subject to intricate phenomena difficult to apprehend and not completely understood yet. The presence of important quantities of sputtered particles complicate even more the study of magnetron plasma, especially when focusing on their spatial distribution and evolution and not only on the global balance of plasma species.

Over the past few years, the OHiPIC model (Orsay High density Particle-in-Cell) has been developed at the LPGP (Laboratoire de Physique des Gaz et des Plasmas) for the modeling of magnetron plasma. OHiPIC code has been used in DC and in HiPIMS regime. It now takes into account the sputtered particles and their ionization. The results provided by OHiPIC are insightful and give a better understanding of the process involved in magnetron discharges. The OHiPIC and its latest improvements will be presented. The 2D density map of the different species and their evolution will be presented and discussed.

10:00am **F2-1-ThM-7 Spoke Formation in Large Scale Rectangular Magnetrons**, ***Arutiun P. Ehiasarian,*** Sheffield Hallam University, UK

Rectangular magnetron cathodes are widely used in the sputter deposition industry, however spokes have been studied mainly in the circular target geometry. The variation in magnetic field strength between the corners and straight sections of the cathode as well as the smaller spoke-to-cathode size ratio influence the motion and formation of the spokes. Fast camera imaging was used to study High Power Impulse Magnetron Sputtering (HIPIMS) discharges on 200×600 mm cathodes in a Hauzer HTC 1000/4 system. Spokes were observed at peak current densities as low as 0.6 Acm^{-2}. Spoke number (mode) was found to decrease and the velocity increase with magnetic field. Spokes were triangular for strong fields and diffusive for weaker fields for the same peak current of 1 Acm^{-2}. The splitting of spokes due to acceleration of a portion was observed. At low pressure the spoke shape was a diffuse triangle which widened and advanced in the **E×B** direction. The spokes turned diffusive at the corners and narrow sections of the magnetron and reformed upon re-entry into the straight sections. The shape of the spokes is generally triangular due to the sequential processes of build-up of ionisation to a critical value, rupture of the field and restoration of confinement. In strong confinement fields these processes are faster and produce triangular spokes. In weaker fields the triangle is stretched out resulting in larger volumes of escaping plasma. The behaviour of spokes in the corners is discussed in terms of electron dynamics and the weaker magnetic fields. At low pressures the spokes may be dominated by metal sputtering and ionisation which are initiated in the centre of the racetrack and spread across.

It is argued that spoke formation could be linked to the ratio of plasma density and magnetic field (beta, β).Spokes are associated with localised rupture in confinement and ejection of intense particle beams. Thus spokes

are a route for the escape of plasma from the confinement field which leads to a greater degree of freedom, greater number of accessible states and greater entropy. It is suggested that the increase in entropy is the driving force for the creation of zones of intense ionisation which leads to high plasma pressure and localised rupture of the confinement field.

10:20am **F2-1-ThM-8 The Use of Bipolar-HiPIMS for the Design of Ion Energies in Thin Film Growth**, ***Ulf Helmersson***, *J Keraudy, R Viloan,* Linköping University, Sweden*; N Brenning, M Raadu,* KTH Royal Institute of Technology, Sweden*; D Lundin,* Université Paris-Sud, Université Paris-Saclay, France*; I Petrov,* University of Illinois, USA, Linköping University, Sweden, USA*; J Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan*; J Gudmundsson,* University of Iceland, Iceland

The effect of a positive pulse following a high-power impulse magnetron sputtering (HiPIMS) pulse are studied using energy- and time-resolved mass spectrometry. This includes exploring the influence of a 200 µs long positive voltage pulse (U_{rev} = 10-150 V) following a typical HiPIMS pulse on the ion-energy distribution function (IEDF) of the various ions. We find that, a portion of the Ti^+ flux is affected by gaining energy which corresponds to the acceleration over the full potential U_{rev}. The Ar^+ IEDF on the other hand illustrates that a large fraction of the Ar^+accelerated, gain energy only to a portion of U_{rev}. The Ti^+ IEDFs are consistent with the assumption that practically all the Ti^+ that become accelerated during the reverse pulse come from a region adjacent to the target, in which the potential is uniformly increased with the applied potential U_{rev}, while much of the Ar^+ come from a region further away from the target that contains a boundary with a drop in potential from U_{rev} to a lower potential consistent with the plasma potential achieved without the application of U_{rev}. The deposition rate is only slightly affected and decreases with U_{rev} to ~90% at U_{rev}= 150 V. Both the Ti^+ IEDF and the small deposition rate change indicate that the potential increase in the region close to the target is uniform and essentially free of electric fields, with the consequence that the motion of the ions inside it are not much influenced by the application of U_{rev}. In this situation, Ti^+ will flow towards the outer boundary of the target-adjacent region, due to their momentum achieved during the HiPIMS discharge pulse, independent whether the positive pulse is applied or not. The metal ions that cross the boundary in the direction towards the substrate, and do this during the positive pulse, all gain an energy corresponding to the full positive applied potential U_{rev}.

10:40am **F2-1-ThM-9 Latest Developments in HIPIMS with Positive Pulsing**, ***Ivan Fernandez***, Nano4Energy, Spain*; A Wennberg,* Nano4Energy SL, Spain*; F Papa,* GP Plasma, Spain

Recently, it has been demonstrated for highly ionized discharges that the application of a positive voltage reversal pulse adjacent to the negative sputtering pulse gives rise to the generation of high fluxes of energetic ions. This effect allowed unprecedented benefits for the coating industry, where the key factor is the ability to tailor both the energy and flux of the high fraction of ionized material present in a HiPIMS discharge. Now, this can also be achieved by controlling the amplitude of the positive voltage reversal. A description of this technology as well as the experimental results obtained in different coating systems from a wide variety of industrial sectors (hard metal nitrides, optical coatings, semiconductor trench filling, roll-to-roll applications…) will be presented in this paper.

11:00am **F2-1-ThM-10 HIPIMS- Advantages of a Positive Kick Pulse**, ***Jason Hrebik***, Kurt J. Lesker Company, USA

HIPIMS is an ionized PVD technique that produces a high density, high performance films. The extreme power densities in HIPIMS create a higher ionized plasma that creates a very high energy of material being deposited onto the substrate.

A key feature to the maturing HIPIMS technology is the ability to apply a positive kick pulse. Having a full range of control over this kick pulse is key in the ability to dial out stress, build thicker deposition layers, increase rate, and tune for specific film morphology and or crystallinity and microstructures. This presentation will share examples of applications and performance data to support the many advantages of the IMPULSE power supply. The available configurations and examples of ideal operating parameters will be shared.

11:20am **F2-1-ThM-11 Plasma Parameter Determination in a HiPIMS Discharge Using Laser Thomson Scattering**, *P Ryan,* ***James Bradley***, *M Bowden,* University of Liverpool, UK

The temporal evolution of the electron density and temperature in a HiPIMS discharge has been measured using laser Thomson scattering and Langmuir probing as comparative techniques. Measurements were performed (non-simultaneously) at two positions within the plasma; in the low magnetic field region on the discharge centreline and in the high magnetic field region of the magnetic trap above the racetrack, for peak power densities of 450 Wcm^{-2} and 900 Wcm^{-2} respectively. The maximum plasma densities and temperatures were found to be 6.9×10^{19} m^{-3} and 3.7 eV in the pulse-on time, decaying to values of 4.5×10^{17} m^{-3} and 0.1 eV some 300 µs into the afterglow. The results indicate that although intrusive, the Langmuir probe can provide a good indication of electron properties in regions of different electron magnetization in the HiPIMS discharge.

New Horizons in Coatings and Thin Films
Room Pacific Salon 6-7 - Session F2-2-ThA

HiPIMS, Pulsed Plasmas and Energetic Deposition II

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

2:00pm **F2-2-ThA-3 HiPIMS Deposition of W Thin Films**, ***Alison Engwall***, *S Shin, Y Wang,* Lawrence Livermore National Laboratory, USA

High power impulse magnetron sputtering (HiPIMS) has been shown to deposit W films with desirable physical characteristics including higher strength and uniformity than films deposited with traditional direct current magnetron sputtering (DCMS) under similar processing conditions. In-situ stress measurements paired with ex-situ film characterization and Langmuir probe plasma measurements were used to investigate the fundamental differences between DCMS and HiPIMS film deposition over a range of chamber pressures with and without applied substrate biasing.

LLNL-ABS-758580

This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. Support was provided by LDRD program 17-ERD-048 at LLNL.

2:20pm **F2-2-ThA-4 Study and Development of Thermochromic VO_2 Thin Films Deposited by HiPIMS**, ***Jean-Louis Victor***, *C Marcel,* CEA Le Ripault, France*; A Rougier,* CNRS, France*; L Sauques,* DGA, France

Vanadium dioxide (VO_2) has attracted a great interest for smart coating applications because of its promising thermochromic properties. Its main characteristic is to transit from a semiconductive state to a metallic state at a phase transition temperature (Tc) of 341 K which is closer to room temperature (300 K) than any other thermochromic material. Nevertheless, the fabrication of high-quality VO_2 films by conventional direct current or radio-frequency Magnetron sputtering (DCMS or RFMS) requires an annealing step over 450°C which limits its compatibility with temperature-sensitive substrates. High power impulse magnetron sputtering (HiPIMS) is a novel sputtering method, developed recently for the deposition of VO_2 films. It is characterized by its high ionization degree of the sputtered species, which allows the control of film microstructure through ion bombardment. Due to this additional energy, the annealing temperature can be reduced for the development of functional VO_2. In this work, we show that HiPIMS supply permits to deposit dense stoichiometric crystalline VO_2 thin films at lower temperature.

2:40pm **F2-2-ThA-5 A Paradigm Shift in Thin Film Growth by Magnetron Sputtering: from Gas-ion to Metal-ion-controlled Irradiation**, ***Grzegorz Greczynski***, Department of Physics, Linköping Univ., Sweden*; I Petrov,* University of Illinois, USA, Linköping University, Sweden, USA*; J Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan*; L Hultman,* Department of Physics, Linköping Univ., Sweden **INVITED**

Traditionally, growth of dense refractory thin films by means of dc magnetron sputtering employs gas-ion bombardment to ensure sufficient adatom mobility during deposition at lower temperatures $T_s/T_m < 0.3$ (T_s and T_m: growth and melting temperature in K). This approach often results in significant concentrations of trapped inert gas atoms with accompanying high film stresses leading to cohesive failure and film/substrate delamination. A possible remedy is offered by metal-ion-synchronized bias durings high-power pulsed magnetron sputtering (HIPIMS). The inherent separation of metal- and gas-ion fluxes that stems from gas rarefaction, provides the ability to separate, in both time and energy domains, metal ions and gas ions incident at the substrate. In this approach, a substrate bias potential is synchronized with the metal-ion-rich portion of the HIPIMS pulse. Metal-ions, as opposed to noble-gas ions, are primarily incorporated at lattice sites. This, together with dramatically-reduced concentrations of trapped gas ions, results in lower compressive stresses. Moreover, the metal-ion mass, incident flux, and impact energy can be independently controlled to optimize momentum transfer and provide the recoil density and energy necessary to eliminate film porosity at low deposition temperatures. This novel approach expands the PVD process envelope to allow the use of temperature-sensitive substrates as well as synthesis of supersaturated alloys.

In the first part of the talk, results of time-resolved ion mass spectrometry analyses performed at the substrate plane during HIPIMS sputtering of TM targets in Ar and Ar/N_2 atmospheres are reviewed. Detailed knowledge of the time evolution of metal- and gas-ion fluxes incident at the growing film surface is essential for precise choice of synchronous bias pulse, and, hence, control over the incident metal-ion energy, while minimizing the role of gas-ion irradiation. In the second part of the talk, several examples of metal-ion-synchronized HIPIMS will be discussed including the growth of (i) nanostructured N-doped *bcc*-$CrN_{0.05}$ films possessing atomically-smooth surfaces with unique properties which are characteristic of both metals (*bcc*-Cr crystal structure, electrical resistivity, and toughness) *and* ceramics (high hardness); (ii) fully-dense, hard, and stress-free $Ti_{0.39}Al_{0.61}N$; (iii) single-phase cubic $Ti_{1-x}Si_xN$ with record-high SiN concentrations; (iv) single-phase NaCl-structure $V_{1-x}Al_xN$ layers with unprecedented AlN supersaturation; and (v) dense and hard dilute $Ti_{0.92}Ta_{0.08}N$ alloys deposited with no external heating ($T_s/T_m < 0.15$) .

3:20pm **F2-2-ThA-7 In Vitro and In Vivo Biocompatibility Evaluation of Zr-Ti-Si and Fe-Zr-Nb Thin Film Metallic Glasses**, ***Ai Ju Chen***, *J Wang, Y Yang,* National Taipei University of Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

Thin film metallic glass (TFMG) has been considered in the biomedical applications due to its better corrosion resistance, which attracts lots of attention from academic and industry. In this study, a co-deposition system consisting of a high power impulse magnetron sputtering (HiPIMS) and a radio frequency (RF) power supply was used to prepare Zr-Ti-Si and Fe-Zr-Nb TFMGs on the surface of 316 L stainless steel specimen.

The chemical composition, microstructure and surface roughness of Zr-Ti-Si, Fe-Zr-Nb TFMGs were analyzed by a FE-EPMA, FE-SEM and AFM respectively. The nanoindentation, scratch test and HRC-DB adhesion test were employed to evaluate the mechanical and adhesion properties of TFMGs. The corrosion resistance of TFMGs in 3.5 wt. % NaCl aqueous solution was conducted by a potentiodynamic polarization test. The MG-63 cell line (human osteosarcoma) was used to investigate the biocompatibility of coatings. Finally, the animal tests were executed to examine any allergy, poisoning or carcinogenic reaction was brought by the TFMGs to the rats.

Through the in-vitro cell test and in-vivo animal tests, both Zr-Ti-Si and Fe-Zr-Nb TFMGs exhibited better biocompatibility because of their good corrosion resistance, good hydrophilic properties and improved adhesion on the 316L surface. We can conclude that Zr-Ti-Si and Fe-Zr-Nb TFMGs have very excellent potential application in the biomedical field.

3:40pm **F2-2-ThA-8 Microstructural and Tribological Properties of Sputtered AlCrSiWN Films Deposited with Segmented Powder Metallurgic Target Materials**, *W Tillmann,* ***Alexander Fehr***, *D Stangier,* TU Dortmund University, Germany

When synthesizing magnetron sputtered films with a complex stoichiometry, integrating the desired coating constituents in one target material is favorable to avoid a nanolaminar film depositions and to enable a homogenous film growth. In contrast to alloyed targets, segmented plug targets allow to merge elements with different physical properties in one target material. Two targets, amalgamating 20 and 48 hot-pressed 80Cr5Si15W (wt. %) plugs, respectively, into a monolithic aluminum target were fabricated and employed in a direct current magnetron sputtering process to deposit AlCrSiWN films on high-speed steel (AISI M3:2, 1.3344). Furthermore, an AlCrSiN film, which served as a reference, was deposited using Cr, Si, and AlCr24 targets. The cathode powers for the Al(CrSiW)20 and Al(CrSiW)48 targets were varied between 3 and 7 kW to analyze how differently composed targets and various cathode powers affect the microstructure and tribological properties of the sputtered films.

The results revealed that the chemical composition as well as the thickness of the films are strongly dependent on the target setup. For all AlCrSiWN films, the Cr and Al contents predominated (19–29 at%), while the Si and W contents varied between 2–3 at. %. This indicates that chromium is preferentially sputtered from the alloyed CrSiW plugs. The film, which was deposited by applying 7 kW to the Al(CrSiW)20 and 3 kW to the Al(CrSiW)48 targets had the highest hardness (27.66 ± 1.87 GPa due to a dense coating growth and a finer crystalline structure. All AlCrSiWN films had a preferred (111)–(CrN/WN) orientation, which exhibited a finer crystalline growth with an increasing cathode power. Analyses of the tribological behavior of the AlCrSiWN films further revealed a significantly lower friction coefficient ($\leq 0.4 \pm 0.04 * 10^{-5}$ mm³/Nm) when sliding against Al_2O_3 balls when compared to the AlCrSiN reference system.

4:00pm **F2-2-ThA-9 Linking an Atmospheric-pressured Arc Reactor to a Magnetron Sputter Device to Synthesize Novel Nanostructured Thin Films**, *W Tillmann,* ***David Kokalj****, D Stangier,* TU Dortmund University, Germany*; Q Fu, E Kruis,* University of Duisburg-Essen, Germany

Due to their properties, nanocomposite coatings offer outstanding advantages compared to single-phase coatings. However, the choice of materials to produce such nanocomposite coatings is severely limited. Basically, there are only three mechanisms that lead to the formation of nanocomposite structures. One possibility is the use of two metals which, in certain compositions, reveal a miscibility gap and form mixed crystals with different structures. Alternatively, metals with strongly different nitrogen affinities also form the desired nanocomposite structure. The third mechanism is based on the use of a nitride-forming transition metal, which is nanocrystalline embedded in an amorphous matrix.

To allow an unrestricted combination of materials, the approach in this project is a decentralized production of nanoparticles and the thin film, whereby the films growth of both phases is combined on the substrate material. For this attempt, an atmospheric pressured arc reactor is used to generate the TiN nanoparticles with mean primary particle sizes of 7 nm to 20 nm agglomerated to clusters of about 120 nm. To inject these nanoparticles in-situ into the vacuum PVD process, an aerodynamic lens is utilized. The purpose of the aerodynamic lens is to separate the process gas from the nanoparticles to only introduce the nanoparticles into the PVD process. Thus, depending on the coating materials used, nanostructured thin films of type nc-MeN / nc-MeN or nc-MeN / nc-Me can be produced in addition to already existing systems, such as nc-MeN/a-nitride and nc-MeC/a-C, synthesized by conventional PVD processes. Within this context, the metal (Me) can also be nitrogen-affine in the new approach.

In this project, TiN nanoparticles are employed and embedded into magnetron sputtered CrN thin films. Initially, the influence of selected PVD deposition parameters, such as the temperature, chamber pressure, and bias voltage, is examined on the morphology and crystallite size of the TiN nanoparticles. Additionally, the influence on the particle distribution on the substrate is discussed. The nanoparticles were successfully deposited on silicon wafer and it was found out that the particle distribution is affected more by the deposition parameters than the particle properties mentioned. This enables the production of nanostructured PVD thin films by means of external nanoparticle injection without the particle properties being subsequently influenced by the deposition parameters during the coating process.

New Horizons in Coatings and Thin Films
Room Grand Hall - Session FP-ThP

New Horizons in Coatings and Thin Films (Symposium F) Poster Session

FP-ThP-3 Influencing the Cubic to Wurtzite Phase Transition in Ti-Al-N by Reactive HiPIMS Deposition, *L Zauner,* TU Wien, CDL AOS at the Institute of Materials Science, Austria; ***Helmut Riedl,*** TU Wien, Institute of Materials Science, Austria; *T Kozák, J Čapek,* University of West Bohemia, Czech Republic; *T Wojcik,* TU Wien, Institute of Materials Science, Austria; *H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *S Koloszvári,* Plansee Composite Materials GmbH, Germany; *P Mayrhofer,* TU Wien, Institute of Materials Science, Austria

High power impulse magnetron sputtering (HiPIMS) is often seen as one key-technology in the deposition of future hard and multifunctional coating materials. Through the introduction of high amplitude impulses at relatively low duty cycles, the amount of ionized species, either target near gas atoms or sputtered target atoms, can be increased drastically. These highly dense plasmas have various consequences on the film growth and hence coating properties, as well as on the sputter behavior of the target material itself. Applying reactive gas mixtures such as N_2/Ar atmospheres, e.g. for the deposition of TiN coatings, lead to further complex effects within the plasmas. However, several studies clearly highlighted the outstanding coating properties as well as metastable phases accessible, using HiPIMS compared to conventional DC magnetron sputtering, whereas a majority of these investigations concentrate on the plasma physics itself. Therefore, we focused in this study on the reactive HiPIMS deposition of Ti-Al-N coatings using $Ti_{1-x}Al_x$ compound targets (x = 0.40 between 0.70) in mixed Ar/N_2 atmospheres. The influence of the HiPIMS parameters such as frequency, pulse length, or synchronized bias potentials, but also of the deposition parameters like partial pressure, deposition temperature, or total pressure were investigated methodically. The so obtained coating structures were analyzed with respect to phase stability, thermomechanical properties, and morphology applying nanoindentation, X-ray diffraction combined with electron imaging techniques (SEM and HR-TEM). In addition, to correlate the observed phase stabilizing effects in relation to the deposition parameters various plasma analysis methods have been applied. Especially, the amount and type of ionized species was quantified for specific parameter settings utilizing mass spectroscopy.

FP-ThP-5 e-Poster Presentation: Vacancies to Compensate for Electronic Imbalances in Crystals, ***Maria Fischer***, *D Scopece, M Trant, C Pignedoli, K Thorwarth, D Passerone, H Hug,* Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The elements Al, Si, O and N can be combined to yield hard and transparent thin coatings. The binary combination AlN readily adopts the hexagonal crystal structure of wurtzite in thin films deposited by reactive direct current magnetron sputtering (R-DCMS). Si and O can be added to form the ternary combinations Al-Si-N and Al-O-N. Si up to 6% and O up to 8% integrate into wurtzite crystallites in the form of a solid solution. For 6-30% Si and 8-35% O, a nanocomposite forms, and higher Si / O contents lead to a fully amorphous coating.

In the crystalline solid solution regime, Si replaces Al on cationic lattice sites, while O replaces N on anionic lattice sites. Despite the different nature of these two substitutions, they induce the same microstructural evolution in the thin films. The underlying mechanism is hypothesized to be the formation of Al vacancies (V(Al)) in both cases. A model explaining this mechanism has been developed and corroborated theoretically and experimentally with *ab initio* calculations, entropic considerations, X-ray diffraction and positron annihilation lifetime spectroscopy.

FP-ThP-6 Role of the Thermalized Ions in the Reduction of the Atomic Shadowing Effect in HiPIMS, ***João Oliveira***, *F Ferreira,* University of Coimbra, Portugal; *A Anders,* Leibniz Institute of Surface Engineering, Germany; *A Cavaleiro,* University of Coimbra, Portugal

Traditionally, the most influential deposition parameters regarding both bombardment and shadowing effect in magnetron sputtering-based deposition processes are the deposition pressure and substrate biasing. In constant power mode, decreasing the process pressure results in an increased discharge voltage and less collisions with gas atoms and molecules and thus it increases the average energy of the sputtered species. On the other hand, the high-angle component of the angular distribution of the impinging species, as measured relatively to the substrate normal, also decreases thus weakening of the shadowing effect. Substrate biasing allows us to bombard the growing film with ions extracted from the plasma with an energy proportional to the applied voltage (and ion charge state). This triggers re-sputtering if a high enough voltage is used. However, the vast majority of the sputtered species in magnetron sputtering are neutrals, not ions, and thus mostly Ar ions are involved in re-sputtering.

Additional control of the bombarding flux can be obtained by ionizing the sputtered flux because ions can be controlled with respect to their energy and impinging direction. In the last decade, High-Power Impulse Magnetron Sputtering (HiPIMS) has been popularized for this purpose. In a previous paper it was shown that Deep Oscillation Magnetron Sputtering (DOMS), a variant of HiPIMS, allowed us to overcome the shadowing effect and, thus, to deposit Cr thin films with much smoother surfaces and densely packet columns even at relatively high pressure (up to 1 Pa). The main objective of the present work is to identify the mechanisms which effectively decreases the shadowing effect in DOMS. For this purpose, the deposition conditions and properties of two Cr films deposited by DOMS at higher pressure and DCMS at lower pressure were studied and compared. In both cases the energy distributions of the energetic particles bombarding the substrate during film growth were evaluated by energy-resolved mass analysis (ERMS) and the angular distribution of the Cr species impinging on the substrate was simulated using Monte Carlo-based programs. The microstructure, structure and mechanical properties of the deposited Cr films were characterized by SEM and AFM, X-Ray diffraction and nano-indentation.

FP-ThP-7 Study of the Self-organizing Structures in Magnetron Plasma by a Pseudo 3D Model, ***Adrien Revel,*** Université Paris-Sud/CNRS, France; *T Minea,* Université Paris-Sud, Université Paris-Saclay, France; *M George, B Vincent,* CNRS, France; *S Tsikata,* CNRS, ICARE, France

Magnetron plasma and Hall thrusters are magnetized plasma which presents common feature such as the formation of self-organizing structures rotating over the central axis. The, so called, spokes appear both in direct current (DC) and high power impulse magnetron sputtering (HiPIMS) and they can be at the origin of the abnormal electron transport. The spokes are only visible using fast camera (100 ns), the plasma appearing homogeneous otherwise.

Because this phenomenon is intrinsically 3D, the numerical modeling of the spokes needs to take into account all the three space dimensions. However, a straight 3D Particle-in-Cell modeling of the magnetron discharge is not feasible due to the computation cost. Hence, we developed a *pseudo* 3D approach which allows to follow the spoke formation and behavior in the three dimensions with a reasonable computation time. The results undoubtedly show high frequency instabilities lying in the range of MHz, in addition to centimetric space structured plasma as previously observed by other groups.

In addition, Incoherent and Coherent Thomson Scattering (ITS and CTS) experimental techniques have been successfully used to measure the electron density, temperature and its fluctuations in the magnetized region without disturbing the plasma. The measurements found the same MHz fluctuations as the modeling for plasma electrons, which is compatible with the electron cyclotron drift instabilities.

Particle modeling results show the microscopic information missing from almost all experiments, particularly on the electron energy distribution function, the ionization region of the spoke, the trajectories of confined electrons, the space distribution of the electric field, etc. Also, macroscopic information can be obtained, such as spoke velocity that is in good agreement with the experiments reported in the literature. Moreover, the variation of this velocity during the pulse (current rise) is presented and commented.

FP-ThP-9 Point Ion Beam Sputtering for Novel Applications, ***Victor Bellido-Gonzalez***, *D Monaghan, R Brown,* Gencoa Ltd, UK; *D Perry,* Quorum Technologies, UK; *J Brindley, A Azzopardi,* Gencoa Ltd, UK

Sputtering (magnetron sputtering and ion beam sputtering) is widely used to deposit coatings onto substrates. Ion beam sputtering utilizes an ion source to generate an ion beam which sputters the target. This work will show a grid/filament-less point ion source recently developed for ion beam sputtering of small targets. The point ion source being small in size together with the low target material cost makes it suitable for research and development. It also has a number of novel applications, including high quality biological specimen preparations for electron microscope examination, multilayer or multicomponent coating deposition using

rotating targets, integrated into minimal fab systems for revolutionary microelectronics, etc. In this work, point beam sputtering for microscope specimen preparations will be addressed. Metal and compound coatings will be deposited onto silicon and latex nanoballs at varied conditions. Optimal coating conditions for fine coating structures will be obtained. The coatings will be assessed by atomic force microscopy and scanning electron microscope, and will be compared with those prepared by magnetron sputtering in terms of surface morphology.

FP-ThP-10 Reducing the Intrinsic Stress of TiN Films in HiPIMS, *F Cemin,* LPGP, Université Paris-Sud, Orsay, France; ***Grégory Abadias,*** Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; *T Minea, D Lundin,* LPGP, Université Paris-Sud, Orsay, France

TiN is one of the most common hard coatings with applications in high-speed steel cutting tools and drill bits due to its high hardness and high wear resistance. It is also used in semiconductor devices as a diffusion barrier as well as anti-reflective or adhesion-promoting layers. It is well known that the stress levels acquired during TiN growth by ionized physical vapor deposition (IPVD) often lead to premature failure and delamination of the coated tool or device. Hence, the stress can drastically limit the industrial appeal of deposition technologies such as high power impulse magnetron sputtering (HiPIMS). Moreover, reducing stress through structure modification is required to enhance the performance and lifetime of components coated with compound-based films. Therefore, the purpose of this work is to identify HiPIMS process conditions for reduced intrinsic stress of TiN films by controlling the quantity, energy, charge state, and chemical nature of the incident ions, *i.e.*, inert gas *vs.* metal, which are impinging on the substrate during film growth.

Different discharge conditions comprising high and low energy ion bombardment as well as different substrate bias configurations (DC or pulsed bias synchronized or delayed with respect to the HiPIMS discharge pulse) were investigated. The intrinsic stress evolution during TiN growth was monitored *in situ* by wafer curvature measurement using a multi-beam optical stress sensor (MOSS). The results show that for standard HiPIMS discharges and biased substrates, the energetic metal ion irradiation during film growth results in dense but highly stressed TiN films (–11 GPa), which is not unexpected for refractory films. On the other hand, when using less energetic HiPIMS discharges and pulsed-biased substrates synchronized to the HiPIMS pulse, the compressive stress was considerably reduced (between 0 and –1 GPa). Although slightly less dense structures are observed in this latter case, the films are still significantly denser than TiN films deposited by direct-current magnetron sputtering (DCMS) under similar conditions.

FP-ThP-11 Study on Tribological Behavior of ZrB_2-Zr Coatings Deposited on Ti6Al4V and CoCrMo Alloys by HiPIMS, ***Luis Flores-Cova***, *O Jiménez, M Flores, J Pérez-Alvarez,* Universidad de Guadalajara, Mexico

CoCrMo alloys are used due to their high wear and relatively high oxidation resistance, whereas Ti6AL4V is widely used in orthopedic and dental implants due to their excellent corrosion resistance and biocompatibility . Nevertheless, the main disadvantage of titanium alloys is their poor wear resistance. Consequently, many coating systems have been deposited on these alloys in order to improve their wear resistance. In this study ZrB_2-Zr coatings were deposited by High Power Impulse Magnetron Sputtering (HiPIMS) under a selection of parameters. The thickness and the growth morphology of the films were studied from cross-sectional SEM images. The structure of the coatings was analyzed by XRD technique. The mechanical properties (hardness and Elastic Modulus) were studied through nanoindentation techniques. The adhesion of coatings to the substrate was measured by means of scratch tests. Wear tests were performed using a tribometer with a reciprocating sliding motion, using a 10 mm diameter Al_2O_3 ball, frequency of 1 Hz, a stroke length of 10 mm, sliding time of 30 minutes and at different normal loads (0.5, 1 and 1.5 N). The wear tracks were analyzed by optical profilometry. In general, the thickness of the coatings resulted between 1 and 2 µm. Hardness on the other hand, was found to be above 20 GPa and wear results showed a better resistance of coatings in comparison to substrates.

FP-ThP-16 Detecting the Direction of a Magnetic Field with a Nanocrystallited Carbon Film by Using its Anisotropic Magnetoresistance and Hall Effect, ***Chao Wang***, *T Huang, W Zhang, J Guo, X Dai,* Institute of Nanosurface Science and Engineering, College of Mechatronics and Control Engineering, Shenzhen University, China

The graphene nanocrystallited carbon film has been found not only with low friction performance and fast run-in behavior , but also with unique magnetic properties and room temperature magnetoresistance (RT-MR). Compared to magnetic alloys and rare earth semiconductors which are mostly used as magnetic sensitive materials, nanocrystallited carbon films are much lighter, cheaper, and possess better mechanical properties such as higher hardness, better flexibility and less friction coefficient, which make it an ideal candidate for next generating magnetic sensors in morco/nano-electromechanical systems and wearable devices. Therefore it is of great significance to explore carbon films with better RT-MR behaviors. In recent study, it has been found that the RT-MR performance of graphene nanocrystallited film is originated from its self-magnetism enhancement, and is highly related to the relative angles between the orientations of graphene layers inside the film and the external magnetic field. This gives us an inspiration that the graphene nanocrystallied carbon film can be utilized to detect the direction of magnetic field, which may lead to its further applications as an carbon based angle sensor or spin rate sensor.

In this study, graphene nanocrystallited carbon films were deposited with plasma assisted PVD method, and the orientation of nanocrstallites were demonstrated with high resolution TEM images. The TEM results showed thath the graphene nanocrystallites alligned perpendicular to the growing direction of the film, which is vertical to the substrate plane. The hall effect and magnetoresistance were measured under different directions of magnetic field with respect to the film surface. The results showed that the hall voltage and film resistance varied periodically as the film rotated along its surface axial, exhibiting a sinusoidal trend for hall voltage, and absolute value of a sinusoidal trend for magnetoresistance. In room temperature, the angle resolution of the film was better than 2 degree, and the largest changing rate of the film resistance can reach 200%. The mechanism of this performance was invesigated through electrical transport measurement and magnetic Raman spectra, as well as magnetic hystersis loops, which revealed the spin-enhanced magnetism of the nanocrystalltes were the main origin of this anisotropic magnetic response behaviors.

FP-ThP-17 Effect of Synchronized Bias on the Oxygen Content in r-HiPIMS Deposited γ-Al_2O_3 Thin Films, ***Stefan Kagerer,*** TU Wien, Institute of Materials Science, Austria; *S Koloszvári,* Plansee Composite Materials GmbH, Germany; *T Kozák, J Čapek, P Zeman,* University of West Bohemia, Czech Republic; *H Riedl,* TU Wien, Institute of Materials Science and Technology, Austria; *P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Österreich, Austria

Reactive high-power impulse magnetron sputtering (r-HiPIMS) is a highly complex but also versatile PVD based deposition technique establishing a broad field of parameters influencing thin film growth in general. Especially, for the synthesis of alumina-based polymorphs, such as cubic (γ) or corundum (α) type crystals, r-HiPIMS allows for novel approaches to overcome the thermodynamic barrier stabilizing α- or γ-Al_2O_3 crystals at feasible deposition temperatures. During conventional magnetron sputtering, the excellent properties of γ-Al_2O_3, such as thermomechanical resistance or chemical inertness, are usually unattainable due to the formation of nano crystalline or even amorphous structures. In addition, target poisoning and hence instable process accompanied by the formation of non-stoichiometric Al_2O_3 strongly limits the deposition of alumina-based coatings.

Therefore, within this study we combine two novel approaches depositing highly crystalline and stoichiometric γ-Al_2O_3 thin films by means of r-HiPIMS depositions. One of the key issues during HiPIMS is the ionization of ejected target species leading especially in reactive atmospheres to specific time resolved mass spectra. Here, the separation of metal and gas ions is most important, allowing for targeted species selection by specific synchronized bias impulses. Based on time resolved mass spectroscopy, a promising time window could be established, suggesting for a maximum amount of ionized oxygen compared to all other species – e.g. Ar^+ and Al^+. To validate the positive effect of synchronized bias impulses four different target to bias on-time variations have been deposited. B ased on former studies, we additionally utilized transition metal alloyed $Al_{1-x}TM_x$ targets (x = 2 at.% TM = Cr or W) – retarding the poisoning behaviour in oxygen rich atmospheres – for specific on-time variations. The so obtained coatings have been analyzed with respect to phase formation and chemistry applying X-ray diffraction combined with electron imaging techniques (SEM, EDS and HR-TEM).

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