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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