New Horizons in Coatings and Thin Films
Room San Diego - Session F2-2

HiPIMS, Pulsed Plasmas and Energetic Deposition

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

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

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

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

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

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

The rise of low carbon energy, in particular nuclear energy, requires the development of new materials resistant to extreme environments with very often combined stresses: high-temperature oxidation, irradiation, wear and corrosion, frequently in concentrated media. During the last years and especially due to the development of HiPIMS (High Power Impulse Magnetron Sputtering) technologies, industrial developments that could not be considered in the past are now possible thanks to the progresses made by PVD (Physical Vapor Deposition) processes. Applications for protective coatings concern the whole nuclear fuel cycle, specifically the development of EATFs (Enhanced Accident Tolerant Fuels) in order to increase the resistance in loss of coolant accidental conditions. The protection of components operating in concentrated nitric acid in case of reprocessing plants is also of particular interest to increase drastically their lifespan, as wear-resistant components for valves and the protection against corrosion of nuclear waste storage steel containers.

To address these issues, various studies led CEA to develop over the last few years a wide range of HiPIMS coatings, from simple monolithic metals, metallic alloys, self-healing Cr/Ta nanometric multilayers, to more complex nanocomposites compositions in Cr-Si-N and Ti-Si-N ternary systems but also simple and mixed oxides such as ZrO_2 and $ZrSiO_4$.

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

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

2:30pm **F2-2-4 Reactive High-power Impulse Magnetron Sputtering of Al-O-N Films with Tunable Composition and Properties***, **Jaroslav Vlček**, A Belosludtsev, J Houska, R Čerstvý, S Haviar,* University of West Bohemia, Czech Republic

Oxynitrides are a class of materials with yet unexplored physical, chemical and functional properties, and a great potential for industrial applications [1,2].

In this work, a modified version of HiPIMS, called Deep Oscillation Magnetron Sputtering, with a feedback pulsed reactive gas (oxygen and nitrogen) flow control and an optimized location (high-density plasma) of the reactive gas inlets in front of the target and their orientation toward the substrate made it possible to produce high-quality Al-O-N films with a tunable elemental composition, structure and properties. We give the basic principles of this method, maximizing the degree of dissociation of both O_2 and N_2 molecules in a discharge plasma, which leads to a replacement of very different reactivities of the O_2 and N_2 molecules with metal atoms on the surface of growing films by similar (high) reactivities of atomic O and N.

The depositions were performed using a strongly unbalanced magnetron with a planar aluminium target of 100 mm diameter in argon-oxygen-nitrogen gas mixtures at the argon pressure of 2 Pa. The nitrogen fractions in the reactive gas flow were in the range from 0 % to 100 %. Voltage macro-pulses, composed of 10 voltage micro-pulses (pulse-on time of 20 µs and pulse-off time of 30µs), with a total length of 500 µs and repetition frequency of 350 Hz were used for all depositions with a maximum target power density up to 675 Wcm^{-2} during pulses at a deposition-averaged target power density of 8.5 Wcm^{-2}. The substrate temperatures were less than 120°C (no external heater) during the depositions of films on a floating substrate at the distance of 100 mm from the target. A pulsed reactive gas (O_2 and N_2) flow control made it possible to produce hard (11–19 GPa) and highly optically transparent (extinction coefficient ≤ 1 x 10^{-4} at 550 nm) Al-O-N films with gradually changed elemental compositions from Al_2O_3 into AlN.

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

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

Films 566 (2014) 70–77.

[2] A. Belosludtsev, J. Houska, J. Vlcek, S. Haviar, R. Cerstvy, J. Rezek, M. Kettner,

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

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

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

Recently, the TiBCN hard coating has attracted lots of attentions owing to its wide range of hardness and coefficient of friction values, which are caused by adjusting the chemical composition of N and C and resulting phases. Meanwhile, the superimposed high power impulse magnetron sputtering (HiPIMS) and middle frequency (MF) power system has been developed to improve the low deposition rate of traditional HiPIMS without sacrificing its high target peak power density. In this study, a superimposed HiPIMS and MF power system was used to grow TiBCN coatings. The pure Ti and TiB_2 targets were adopted during deposition. The reactive gas mixture consisted of nitrogen and acetylene. A plasma emission monitoring system was employed to grow coatings under different Ti target poisoning regime. Various acetylene gas flow rates were added during deposition. The phase of each coating was studied using the X-ray diffractometer. The microstructures of thin films were examined by the field-emission scanning electron microscopy and transmission electron microscopy. Atomic force microscopy was employed to analyze the surface roughness of films. The nanoindentation, scratch and pin-on-disk wear tests were used to evaluate the hardness, adhesion and tribological properties of thin films, respectively. Effects of the Ti target poisoning status and flow rates of acetylene on the microstructure, chemical composition, phase, deposition rate and mechanical properties of TiBCN were studied in this work.

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

The improvement in the performance and durability of medical implants and surgical tools is an important issue. Therefore, various surface coatings have been applied onto these implants and tools to enhance their functional properties and lifetime. It is known that several metal ions (Cu^{2+}, Ag^{+}, Zn^{+}) exhibit antibacterial effect which fit such a purpose. Among these metal ions, Cu represents a very promising one because of its lower toxicity and higher cytocompatibility. However, the hardness and the adhesion of Cu thin film to the Ti6Al4V substrates require further improvement. As a result, an asymmetric bipolar high-power magnetron sputtering (HiPIMS) technique was used to deposition Ti-Cu thin films using two different targets of Ti and Cu due to Ti can provide a better mechanical property. The peak currents of the Ti and Cu targets were individually varied from 80 to 200A. The thin films were deposited on different substrates, including Si wafer, Ti6Al4V, and a flexible substrate. The microstructure, composition, mechanical properties, antibacterial effect, and biocompatibility of the resulting Ti-Cu thin films were then investigated and reported.

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

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

3:50pm **F2-2-8 Preparation of Anatase TiO_2 Thin Films by Reactive HiPIMS***, F Cemin,* Université Paris-Sud, France*; J Keraudy,* Linköping University, Sweden*; T Minea,* Université Paris-Sud, France*; **Daniel Lundin**,* Université Paris-Sud/CNRS, France

Titanium dioxide (TiO_2) is one of the most investigated semiconducting materials for a wide range of applications, *e.g.*, in photocatalysis (for water splitting, decomposition of pollutants, self-cleaning windows), memory capacitors and transistors (dielectric material), lithium-ion batteries (as anode material), gas and humidity sensors, anti-reflective coatings, etc. Compared to the rutile phase, the anatase phase possesses the highest photocatalytic activity and the best properties for lithium-ion intercalation, which are critical factors for the performance of energy-related devices/applications. Although most HiPIMS studies on TiO_2 phase formation are focused on the rutile phase, there is some evidence that anatase (or a mixture of anatase-rutile) grows preferentially under conditions of relatively weak ion bombardment of the growing film. However, the reported deposition conditions are often contradictory with no obvious choice of pulse parameters, gas pressure, substrate-to-target distance, etc. In this contribution we have therefore investigated the HiPIMS growth conditions required specifically for anatase TiO_2 and systematically studied the phase formation, microstructure and chemical composition as a function of mode of target operation (metal-transition-compound modes) as well as of external process parameters (substrate temperature, working pressure, and peak current density). Phase pure anatase films were deposited at power normalized deposition rates of more than a factor 10 higher compared to what has previously been reported. Also the crystal quality was improved by using ion bombardment of weak to moderate intensity. Furthermore, the reactive HiPIMS process of TiO_2 was characterized using a new reactive ionization region model (R-IRM). The model provided insight into the temporal behavior of the discharge plasma parameters such as electron density, the neutral and ion composition, the ionization fraction of the sputtered vapor, the oxygen dissociation fraction, and the composition of the discharge current for various discharge conditions.

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

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

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

New York (1999)

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

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

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