Advanced Surface Engineering Division
Room: 104 - Session SE+PS-ThA

Pulsed Plasmas in Surface Engineering
Moderator: J. Patscheider, EMPA, Switzerland

2:00pm **SE+PS-ThA1 High-Power Impulse Magnetron Sputtering of WO_3 - Influence of the Pulse Parameters on the Discharge**, ***A. Hemberg***, *F. Renaux, J.P. Dauchot,* Materia Nova, Belgium, *R. Snyders, S. Konstantinidis*, UMons, Belgium

Metal oxides as WO3, SnO2 and TiO2 are widely used as active layers in gas sensor applications. The sensor performances (sensitivity, selectivity, and ageing) are strongly dependent grain size, phase constitution, and material microstructure. It is accepted that in magnetron sputtering, these properties can be modified by controlling the energy and the flux of ions impinging the growing films. The ion bombardment allows modifying the nucleation process, increasing the film density, and changing texture, stress and microstructure of the coating, and ultimately improving its performances . Compared to other techniques used for thin films deposition, HiPIMS (High Power Impulse Magnetron Sputtering) enables the sputtered material to be strongly ionized. Therefore, using HiPIMS, the film properties can be altered to a larger extend as compared to conventional DC magnetron.

In this study, WO3filmshave been synthesized using reactive HiPIMS of a metallic tungsten target in Ar/O2 mixtures. A comparison is made between results obtained in HiPIMS with those obtained with a conventional DC reactive magnetron discharge (RDCMS) at identical mean power (*PD*). We discuss the influence of the pulse duration (*t*)and the target voltage (*VD*) on both the film deposition rate (*RD*)and the hysteresis behaviour. During the HiPIMS experiments, *t* is varied between 10 and 50 µs and *VD* between 800 and 1500 V. *PD* is kept constant by adjusting the frequency. In reactive mode, for a given value of *PD*, *RD* increases as *t* and *VD* are increased. Comparing the HiPIMS data with those recorded during the RDCMS process, it is found that for t = 50 µs and VD = 1500 V, *RD* in HiPIMS is larger than for the RDCMS discharge. In order to understand this behaviour, the target current waveforms associated with these working conditions have been studied. For this particular condition (t = 50 µs, VD = 1500 V), the discharge current waveforms in metallic and reactive mode are similar. This observation wouldreveal that the target surface chemistry is identical, although the discharge is ignited either in a pure Ar or a in an Ar/O2 mixture.

The ion flux composition was also studied with a mass spectrometer located in front of the magnetron target. Time-resolved and time-averaged measurements were carried out.

2:20pm **SE+PS-ThA2 A Versatile Magnetized Pulsed Cascaded Arc Source for Surface Modifications and Efficient Material Deposition**, ***G. De Temmerman***, *J.J. Zielinski,* FOM Institute for Plasma Physics Rijnhuizen, Netherlands, *L. Marot, D. Mathys,* University of Basel, Switzerland, *W. Melissen,* FOM Institute for Plasma Physics Rijnhuizen, Netherlands, *M.C.M. van de Sanden*, FOM-Instituut for Plasma Physics Rijnhuizen & Eindhoven University of Technology, Netherlands

The interaction of low-temperature plasmas with solid surfaces is at the core of numerous applications such as thin film deposition or materials processing. On the other hand, the interaction of the confined plasma with the plasma-facing materials in a nuclear fusion device can have a serious impact on the operations of a fusion device. This is especially true during plasma instabilities where surfaces are exposed to high transient heat and particle fluxes (several MJ.m-2 for 0.2-1ms). A pulsed cascaded arc source has been developed [1] to produce fusion-relevant plasmas and study the surface modifications induced by simultaneous continuous and pulsed plasma exposure.

The cascaded arc source, extensively used for thin film deposition by PECVD is used, in the Pilot-PSI linear plasma device to reproduce the plasma conditions expected in a fusion reactor with particle and heat fluxes of 1024.m-2s-1 ~10 MW.m-2 respectively. Magnetic field of up to 1.6T is used to confine the plasma. The plasma source has been modified to allow for combined pulsed/continuous operations [1]. Parallel to the DC power supply, the plasma source is connected to a capacitor bank (5kV, 8.4mF, 100kJ), which is discharged in the source to transiently increase the input power. Peak surface heat fluxes in excess of 1 GW.m-2 have been generated with pulse duration of about 1 ms (up to 1MJ.m-2). To provide more flexibility, the shape and the duration of the pulse can be adapted to the needs. The plasma conditions during the continuous and pulsed phases can be varied independently. The source can be operated in a variety of gases (Ar, H, He, N) as well as with mixed gases. Plasma properties are studied using Thomson scattering, fast visible and infrared imaging.

We will describe how synergistic effects arising from the simultaneous exposure to continuous and pulsed plasma affect the surface of a polycrystalline tungsten surface. The field of applications of the pulsed cascaded source is however not restricted to fusion-related research. Using a slightly altered configuration, the pulsed plasma source system has also opened a new route for the efficient deposition of metallic nano-particles and nano-structured thin films. Complete coverage of the surface by 10-15nm diameter nano-particles can be obtained with only a few pulses (5-10). Under different conditions, deposition rates as high as 50nm per pulse (1ms duration) have been achieved for copper and aluminium films. With a possible repetition rate of 10Hz, the system combines unprecedented deposition rates and the possibility of in-situ surface processing in between pulses.

[1] G. De Temmerman et al., Appl. Phys. Lett. 97 (2010) 081502

2:40pm **SE+PS-ThA3 Pulsed Magnetron Sputtering Systems for Reactive Deposition of Oxide and Nitride Films**, ***J. Vlcek***, *J. Rezek, P. Steidl*, University of West Bohemia, Czech Republic **INVITED**

In recent years, novel high-power pulsed dc magnetron systems have been used for sputtering of films[1].

In the presentation, we report on discharge and deposition characteristics, and on film structure and properties for two different pulsed magnetron sputtering techniques.

High power impulse magnetron sputtering of zirconium target in argon-oxygen gas mixtures was investigated at a high average target power density in a pulse, being up to $2kWcm^{-2}$. The repetition frequency was 500Hz at duty cycles ranging from 2.5 to 10%. The total pressure of the argon-oxygen gas mixture was around 2 Pa. An effective reactive gas flow control, developed by us, was used for high-rate reactive deposition of insulating, highly optically transparent ZrO_2 films. In addition to the ZrO_2 films, high power impulse magnetron sputtering was also successfully used for high-rate reactive deposition of highly optically transparent Al_2O_3 and Ta_2O_5 films. Details of the process and measured properties of the films will be presented.

Pulsed dc magnetron sputtering of B_4C-Si (25:75%) target in an argon-nitrogen (50:50%) gas mixture at the total pressure of 0.5Pa was used for deposition of Si-B-C-N films with extremely high thermal stability (even above 1500°C). The repetition frequency was 10kHz at an 85% duty cycle to avoid microarcs at the target and thus, to produce high-quality defect-free films. Prior to the deposition, target atoms were subplanted into various substrates, being at a high negative rf potential, during their etching using pulsed magnetron sputtering of the B_4C-Si target in argon gas (the same repetition frequency and the duty cycle of 20%) to enhance adhesion of the Si-B-C-N films.

[1] K. Sarakinos, J. Alami, S. Konstantinidis, Surf. Coat. Technol. 204 (2010) 1661.

3:40pm **SE+PS-ThA6 Structure Evolution and Wear Mechanism in TiAlCN/VCN Nanoscale Multilayer Coatings Deposited by Reactive High Power Impulse Magnetron Sputtering Technology**, ***P. Hovsepian***, *A.P. Ehiasarian, G.K. Kamath,* Sheffield Hallam University, UK, *R. Haasch, I. Petrov*, University of Illinois at Urbana Champaign

2.5 µm thick TiAlCN/VCN coatings were deposited by reactive HIPIMS process. XTEM showed gradual evolution of the structure of the coating with thickness. The initial structure is nanoscale multilayer with sharp interlayer interfaces. This transforms to nanocomposite of TiAlCN and VCN nanocrystalline grains surrounded by C-rich tissue phase and finally changes to an amorphous carbon rich Me-C phase. In contrast deposition in similar conditions using standard magnetron sputtering produces a well defined nanoscale multilayer structure. Depth profiling by AES showed that the carbon content in the HIPIMS coating gradually increased from 25% at the coating substrate interface to 70% at the top thus supporting the TEM observations.

Energy-resolved mass spectrometry revealed that HIPIMS plasma is a factor of 10 richer in C^{1+} ions, and therefore more reactive, as compared to the plasma generated by standard magnetron discharge at the same conditions. The peculiar structure evolution in HIPIMS is discussed in relation to target poisoning effect and carbon outward diffusion during coating growth.

Highly abrasive AlSi9Cu1 alloy was dry machined using TiAlCN/VCN coated 25 mm diameter end mills to investigate the coating-work piece material interaction. Green (532 nm excitation) and UV (325 nm excitation) Raman spectroscopy was employed to identify the phase composition of the built up material on the cutting edge and swarf surfaces produced during machining. These analyses revealed formation of lubricious Magnèli phases namely V_2O_5 and graphitic carbon as well as highly abrasive SiO_2 and Al_2O_3 thus shedding light on the wear processes and coating tribological behaviour during machining.

4:00pm **SE+PS-ThA7 Plasma Study and Interconnect Metallization using a Modulated Pulse Power (MPP) Hollow Cathode Magnetron**, ***L. Meng***, *H. Yu, T.S. Cho, S. Jung, D.N. Ruzic*, University of Illinois at Urbana Champaign

Modulated pulse power (MPP) magnetron sputtering, as a derivative of high power pulsed magnetron sputtering (HPPMS), was applied to a 200 mm hollow cathode magnetron (HCM) with a Cu target. The aim was to develop a more advanced ionized physical vapor deposition (IPVD) tool for applications such as interconnect metallization for sub-32 nm technologies. The MPP plasma generator, featured with 1000 V maximum pulse voltage and 550 A maximum pulse current, has a unique advantage of flexibly adjusting on- and off-time for each individual pulse, so that a long pulse packet of several milliseconds with desired waveform shapes can be generated. Distinct discharge stages were normally observed in one MPP pulse packet. Time-dependent plasma parameters were investigated using a triple Langmuir probe to help understand the MPP discharge characteristics and its performances. Plasma behaviors were shown to closely depend on the pulse waveforms and various other parameters including pulse current, repetition frequency, pressure, and distance from the target. A high electron density (n_e) of 3×10^{18} m^{-3} and an electron temperature (T_e) of 5 eV during the pulse were obtained at the substrate level, with an average power less than 8 kW. Compared with the DC magnetron sputtering at the same average power, the pulsed plasma density was an order of magnitude higher, which resulted in an enhanced ionization of the sputtered flux. As measured by an electrostatic gridded energy analyzer combined with a quartz crystal microbalance, the Cu ionization fractions above 30% were easily achieved by the MPP sputtering on the substrate level, twice higher than those by the DC sputtering. Increasing the pulse duty ratio or reducing the pressure resulted in a stronger ionization. The performance of Cu deposition in narrow trenches (70-100 nm) using the MPP sputtering was further studied, which exhibited an improvement over the DC sputtering. Stronger pulses with higher duty ratios and a lower gas pressure were preferred to reduce the overhang and achieve better step coverage and bottom coverage.

4:20pm **SE+PS-ThA8 Structural and Optical Properties of Ultra-Thin Silver Films Deposited via High Power Impulse Magnetron Sputtering (HiPIMS) on Various Adhesion Layers**, ***R. Jakubiak***, Air Force Research Laboratory, *L. Sun,* General Dynamics Information Technology, *N. Murphy,* Air Force Research Laboratory, *A. Waite,* Universal Technology Corporation, *J. Jones*, Air Force Research Laboratory

Multilayer metal -dielectric stacks containing noble metals such as gold, silver, and copper have myriad applications in the areas of linear and nonlinear optics and photonics. The optical dispersion of Ag makes it particularly attractive for optical interference filters and metamaterials applications. In this regard, it is essential for the Ag layers be sufficiently thin as to not inhibit transparency in the visible spectral region yet still exhibit the favorable optical dispersion of bulk Ag. This can prove difficult due to the Volmer-Weber island growth process noble metals exhibit on dielectric materials. Island formation occurs at the initial growth stages, followed by nucleation and coalescence with increasing material deposition. Below the coalescence threshold the optical dispersion does not follow that of bulk Ag and that has a detrimental effect on the optical performance of the coating. In order to lower the thickness at which coalescence occurs we've explored highly energetic deposition techniques such as high power impulse magnetron sputtering (HiPIMS) alone or in conjunction with deposition on adhesion layers of Ti, Ge or transition metal nitrides. The adhesion layers also act as barriers to oxidation of the Ag from dielectric materials incorporated in the interference coatings. Using *in-situ* spectroscopic ellipsometry the coalescence threshold of the Ag was easily monitored by noting when during the growth process the optical dispersion of the film matched that of bulk Ag. A systematic study of the how the adhesion layers and deposition parameters affected the optical properties of the Ag films was achieved by correlating structural and compositional data gather from XPS and X-ray diffraction (XRD) to the optical transmission and optical dispersion obtained by UV-Vis spectroscopy and spectroscopic ellipsometry, respectively.

4:40pm **SE+PS-ThA9 Inductively Coupled Impulse Sputtering (ICIS): A Novel Technique for Ionised PVD**, ***A.P. Ehiasarian***, *D. Loch*, Sheffield Hallam University, UK

One limitation of magnetrons is their use of inhomogeneous magnetic fields which constrains deposition of magnetic materials to thin targets, complex (magnetic) alloys by erosion-dependent stoichiometry, and oxides by build-up of arc-prone insulating layers on the target edge. Inductively Coupled Impulse Sputtering (ICIS) is a new technology for physical vapour deposition based on sputtering without magnetic fields. A plasma is generated in front of the target via an inductively coupled coil driven with a 13.56 MHz radio frequency (RF) power supply. The target is then biased to a high voltage to initiate sputtering. In order to ionise significant fractions of the sputtered flux, the RF power density is pulsed with peak values in excess of 30 Wcm^{-2} to produce plasma density of the order of 10^{12} cm^{-3}. A low duty cycle of < 25% is used to achieve high peak powers and plasma densities at low average power. The degree of ionisation of ICIS of Cu and Ti in Ar atmosphere were evaluated using optical emission spectroscopy and atomic absorption spectroscopy and the film microstructure and coverage of vias was studied with cross sectional SEM. The effect of peak RF power density (P) was to increase metal ionisation degree hyperbolically. The rate of production of Ti^{1+} metal ions was proportional to $\sim P^{1.1\pm0.2}$ and was significantly faster than that of metal neutrals of $\sim P^{0.66\pm0.08}$ indicating enhanced ionisation of the vapour with power. The mechanisms of ionisation will be discussed. The influence of pressure on the process was studied at a constant peak RF power density of P = 30 Wcm^{-2}. The intensity of copper and argon neutral emission rose linearly for pressures of 2.95×10^{-2} - 1.2×10^{-1} mbar and saturated at higher pressures. The deposition rate was 2 nm min^{-1} for RF-power density of 30 Wcm^{-2}, average target power of 67 W and a pressure of 1.2×10^{-1} mbar. The microstructure of Cu films was globular at 2.95×10^{-2} mbar and large-grain columnar at 1.2×10^{-1} mbar. Bottom coverage of unbiased vias with width 0.36 µm and aspect ratio of 2.5:1 increased from 15 % to 20 % as pressure increased from 2.95×10^{-2} to 1.2×10^{-1} mbar. The current work has shown that the concept of combining a high powered RF coil with a magnet-free cathode is feasible and produces very stable plasma and uniform target erosion. The experiments have shown a significant influence of power and pressure on the plasma and coating microstructure. The process is suitable for Fe, Ni and FeCo alloy deposition.

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