New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F2-1

HiPIMS, Pulsed Plasmas and Energetic Deposition

Moderators: Tiberiu Minea, Université Paris-Sud, Tomas Kubart, Uppsala University, Angstrom Laboratory, Sweden

8:00am **F2-1-1 An Ionization Region Model of the Reactive Ar/O$_2$ High Power Impulse Magnetron Sputtering Discharge**, ***Jon Gudmundsson,*** University of Iceland, Iceland*; D Lundin,* CNRS, Université Paris-Sud, France*; N Brenning, M Raadu, C Huo,* KTH - Royal Institute of Technology, Sweden*; T Minea,* CNRS, Université Paris-Sud, France

In the reactive high power impulse magnetron sputtering discharge experimental findings indicate that there is a significant increase in the discharge current and this current increase appears to follow one of two paths as the discharge enters the poisoned mode. On one hand the current waveform becomes distinctly triangular in shape and on the other hand the current maintains the shape of the non-reactive waveform [1,2]. A reactive ionization region model (R-IRM) is developed to describe the reactive Ar/O$_2$ high power impulse magnetron sputtering (HiPIMS) discharge with titanium target [3]. It is then applied to study the temporal behaviour of the discharge plasma parameters such as electron density, the neutral and ion composition, the ionization fraction of the sputtered vapour and the oxygen dissociation fraction. We study and compare the discharge properties when the discharge is operated in two well established operating modes, the metal mode and the poisoned mode. Using the R-IRM we find that when the discharge is operated in the metal mode Ar$^+$ and Ti$^+$ -ions contribute most significantly (roughly equal amounts) to the discharge current while in the poisoned mode the Ar$^+$-ions contribute most significantly to the discharge current while the contribution of O$^+$ -ions and secondary electron emission is much smaller. Furthermore, we find that recycling of atoms coming from the target, and subsequently ionized, are required for the current generation in both modes of operation. In the metal mode self-sputter recycling dominates and in the poisoned mode working gas recycling dominates, and it is concluded that the dominating type of recycling determines the discharge current waveform.

[1] J. T. Gudmundsson, Plasma Phys. Contr. Fusion, 58(1) (2016) 014002

[2] F. Magnus, T. K. Tryggvason, S. Olafsson and J. T. Gudmundsson, J. Vac. Sci. Technol. A, 30(5) (2012) 050601

[3] J. T. Gudmundsson, D. Lundin, N. Brenning, M. A. Raadu, Chunqing Huo and T. M. Minea, Plasma Sources Sci. Technol. accepted for publication 2016

8:20am **F2-1-2 Residual Stress Control of Al-rich (Ti,Al)N Hard Coatings by Pulse Duration in High Power Impulse Magnetron Sputtering**, ***Tetsuhide Shimizu****, S Takahashi, H Komiya,* Tokyo Metropolitan Univeristy, Japan*; Y Teranishi, K Morikawa,* Tokyo Metropolitan Industrial Technology Research Institute, Japan*; M Yang,* Tokyo Metropolitan Univeristy, Japan*; U Helmersson,* Linköping University, IFM, Sweden

A present study demonstrates the controllability of residual stress of deposited ternary nitride films by regulating pulse duration in high power impulse magnetron sputtering (HiPIMS). Optical emission spectrum (OES) measurements were firstly performed in the plasma of Al-rich $Ti_{0.33}Al_{0.67}$ alloy sputtered in an Ar/ N$_2$ gas mixture to analyze ion and excited neutral densities at different peak current intensities and plasma compositions. Based on the OES spectra, specific pulse conditions of 100, 200 and 1000 µs with a same pulse off time of 3000 µs were chosen to deposit (Ti, Al)N films on Si (100) wafer. Residual stress of the deposited films was estimated by a deflection of 50 µm-thick thin glass sheets. Chemical composition, surface morphology and phase composition of the films were analyzed by an energy dispersive spectroscopy, an atomic force microscopy and X-ray diffraction, respectively. Mechanical properties were characterized by using nanoindentation. As results, clear gradual variation from tensile to compressive stress was demonstrated by varying pulse duration from 1000 to 100 µs. A compressive stress was found in the film grown using the shortest pulse duration of 100 µs, which also had the highest Ti ion-to-neutral ratio, while the pulse duration of 200 µs and 1000 µs showed the tensile stress. In particular, the pulse duration of 200 µs showed almost no residual stress but the highest hardness with highest crystallinity of mixed cubic and hexagonal phase. The cause of these tendencies in residual stress between different pulse duration was discussed based on the effect of ionization degree of sputtered species and compositions of the gas and metallic ions in the discharge plasma.

8:40am **F2-1-3 Energetic Deposition of Electronic Materials**, ***Jim Partridge****, B Murdoch, N McDougall, D McCulloch,* RMIT University, Australia*; R Ganesan, M Bilek, D McKenzie,* The University of Sydney, Australia*; M Tucker, N Marks,* Curtin University, Australia **INVITED**

Energetic deposition provides increased control over the micro-structural, electrical and optical properties of thin films. In our work, high power impulse magnetron sputtering (HiPIMS) and filtered cathodic vacuum arc deposition systems have been employed to form high quality metal oxide and carbonaceous materials. Electronic and optical applications for these materials including transparent thin film transistors, photo-detection and resistive memory storage devices have been explored. Process and film characteristics will be discussed for materials including ZnO, HfO$_2$, HfO$_x$N$_y$, BN and C. In particular, the plasma and target conditions during HiPIMS growth of metal oxides and carbonaceous materials will be related to microstructural, electronic and optical measurements performed on the films produced. In addition, work will be presented in which ab initio calculations and X-ray absorption spectroscopy have been employed to characterise defects in energetically grown hBN.

9:20am **F2-1-5 Controlled Reactive HiPIMS of Thermochromic VO$_2$ Films at a Low Deposition Temperature (300 °C)**, ***David Kolenaty****, J Vlcek, T Kozak, J Houška, R Čerstvý,* University of West Bohemia, Czech Republic

Vanadium dioxide (VO$_2$) is the most interesting thermochromic material due to its reversible phase transition from semiconducting IR transparent state (monoclinic structure) to metallic IR reflective state (tetragonal structure) at around 68 °C. A high IR transmittance modulation makes the VO$_2$–based films a suitable candidate for optical switching applications, such as self-tunable infrared filters, temperature sensing devices and “smart” windows regulating the solar transmission. Current drawbacks limiting the application potential of the VO$_2$ films include high deposition temperatures (> 400 °C) of the films and the necessity to use a substrate bias potential in the case of their magnetron sputter deposition.

Reactive HiPIMS with a feed-back pulsed reactive gas (oxygen) flow control and an optimized location of the oxygen gas inlets in front of the target and their orientation toward the substrate made it possible to form crystalline thermochromic VO$_2$ films at very high values of the maximum target power density of up to 5 kWcm^{-2} in a pulse. The thermochromic VO$_2$ films (80 nm thick) were deposited onto floating glass substrates without any nucleation–promoting “seed” layer at the temperature of 300 °C. The depositions were performed using a strongly unbalanced magnetron with an indirectly water-cooled planar vanadium target (50.8 mm in diameter) in argon-oxygen gas mixtures at the argon pressure of 1 Pa. The duty cycle was set to a constant value of 1%, the voltage pulse durations were 50 µs and 80 µs, and the corresponding repetition frequencies were 200 Hz and 125 Hz, respectively. The deposition-averaged target power density was approximately 13 Wcm^{-2}. The target-to-substrate distance was 150 mm.

The phase composition of the VO$_2$ films was determined by X-ray diffraction. The thermochromic behavior of the films was investigated using a spectrophotometer and spectroscopic ellipsometer equipped with custom designed heat cells to control the measurement temperature of the samples from 25 °C to 100 °C. The temperature-dependent electrical resistivity of the films was measured by a four-point probe. The time-averaged energy distributions of positive ions were measured with an energy-resolved mass spectrometer placed at the substrate position.

The VO$_2$ films prepared at the voltage pulse duration of 50 µs exhibited a high IR modulation (ΔT_{2500nm} ~ 45% between 25 °C and 90 °C), an optical transmittance of about 40 % in the visible region, a large drop in the electrical resistivity (from 5.5×10^{-3} Ωm to 1.5×10^{-5} Ωm) after the semiconductor-to-metal transition, and a lower transition temperature of 58 ˚C than the bulk VO$_2$ (68 ˚C).

9:40am **F2-1-6 High Power Impulse Plasma Magnetron Sputtering – Dawn of Industrialization**, *W Gajewski, P Rozanski, P Lesiuk, P Ozimek,* ***Rafal Bugyi***, TRUMPF Huettinger Sp. z o.o., Poland

Since the first presentation of the High Power Impulse Magnetron Sputtering (HiPIMS) idea by *Kouznetsov and co-workers* in 1999 the basic architecture of a DC-charged capacitor bank dissipating periodically its energy into the plasma in pulses evolved to a sophisticated electronic device commercially available for industry. In order to meet rigorous requirements of industrial application, engineers have proposed different modifications of HiPIMS power delivery units to make the pulse shape and duration independent on the size of the capacitor bank and time-dependent plasma impedance. Since typically pulses longer than 100 µs are required to reach metal self-sputtering regime, a precise control of voltage and current pulse shape is required during the whole pulse length. Furthermore, for tuning ionization of the plasma species and deposition rate flexibility in power delivery regulation is of a key importance.

This contribution provides a series of case-study examples where HIPIMS was tested and qualified for industrial applications. First, the examples from the hard and decorative coating applications will be discussed. Using the basic facts about the HIPIMS plasma parameters the influence of the modified rectangular-like current peak on the plasma composition and dynamics will analyzed. As next, a novel approach of a flexible and application selectable HiPIMS power delivery control will be presented: *(i)* peak current regulation, *(ii)* pulse frequency, and *(iii)* pulse length. The in-field experiments data will be used to discuss the influence of peak current regulation on the ionization degree of the sputtered species as well as the influence of frequency regulation on the deposition rate.

Finally, tests performed in reactive processes both on metallic and ceramic target materials will complete the discussion on HIPIMS industrialization demonstrating the importance of fast arc detection and suppression algorithms required for a long term stability of industrial processes.

10:00am **F2-1-7 Comparison of CrN from Planar and Rotating Target using Highly Ionized Processes***, **Holger Gerdes**, A Themelis, R Bandorf, M Vergöhl, G Braeuer,* Fraunhofer Institute for Surface Engineering and Thin Films IST, Germany

CrN is used in many industrial applications. It provides good electrical conductivity, high hardness, corrosion resistance and high temperature stability. As known from many other investigations high power impulse magnetron sputtering (HIPIMS) lead to significant improved properties.

This presentation will discuss the influence of different HIPIMS techniques on the adhesion, hardness and composition of the thin film. Therefore, the gas composition (ratio between Ar and N2), the working pressure were changed. Additionally, the influence of the sputtering plant and target geometry was investigated. Two sputtering plants were used. The first one, a lab scale one, was equipped with a planar target (132 mm x 224 mm) and the second one with a planar (130 mm x 470 mm) and a rotating (Length of 500 mm) target.

While conventional processes require temperatures in the range of 250 °C and additional biasing the presented films all showed hardness values up to 2900 HV without substrate bias or additional heating.

10:20am **F2-1-8 Molybdenum Thin Films Deposited by High Power Impulse Magnetron Sputtering***, **Arutiun P. Ehiasarian**, D Loch,* Sheffield Hallam University, UK

Molybdenum thin films used in chalcopyrite solar cells can influence the Na diffusion rates and the texture of the $Cu(InGa)Se_2$ absorber according to the microstructure and morphology. The lowest resistivity films are achieved at low working pressure and are accompanied by high residual stress and poor adhesion due to the resulting high energy of the deposited flux. High Power Impulse Magnetron Sputtering was employed to ionise the sputtered flux, achieve high adatom mobility at low energy and influence the growth of Mo back contacts. Pulse durations in the range 60 to 1000 µs, sputtering voltages between 800 and 1500 V and deposition pressures of 2×10^{-3} mbar and 4×10^{-3} mbar resulted in ten-fold variations in the flux ratios of Mo^{1+}/Mo^0 Mo^{2+}/Mo^{1+}, Ar^{2+}/Ar^{1+} and Mo^{1+}/Ar^{1+} as determined by optical emission spectroscopy and time-resolved plasma-sampling energy-resolved mass spectroscopy. The energy of metal and gas double- and single-charged ions reduced with pulse duration and increased with voltage. The microstructure of the films varied from open columnar with faceted tops to fully dense as observed by secondary electron microscopy. The reflectivity of the films improved by 20% compared to industry-standard materials. The lowest resistivity was in the range of 12 µΩ-cm as observed by four-point probe measurements of 570 nm thick films. The correlation between resistivity, microstructure, crystallographic texture and deposition flux characteristics is discussed.

10:40am **F2-1-9 Epitaxial Growth of Copper Thin Films on Si(001) by HiPIMS***, **Felipe Cemin**,* Université Paris Sud, France*; G Abadias,* Université de Poitiers, France*; D Lundin, T Minea,* Université Paris-Sud, France

The heteroepitaxial growth of metallic thin films on semiconductor substrates is usually required to provide a special growth direction for subsequent deposition of magnetic ultrathin layers or to reduce the dislocation density of lattice mismatched heterostructures. However, epitaxial relationship may be only obtained if the substrate surface is free of native oxides and contaminants, i.e., an atomic cleaning process is required. Conventional pre-treatment methods include the heating of the substrate at relatively high temperatures (800 °C) and the creation of a hydrogen-termination layer on the substrate surface through chemical etching with hydrofluoric acid. In this contribution we report a new route to grow epitaxial copper thin films at room temperature on silicon(001) wafers covered with native oxide without any prior substrate cleaning process. This method consists in a single-step deposition using high power impulse magnetron sputtering (HiPIMS) and substrate biasing. The studied Cu thin films were deposited onto Si(001) wafers by HiPIMS and conventional direct current magnetron sputtering (DCMS) at different substrate bias voltages. The stress evolution during deposition was monitored *in situ* using the real-time wafer curvature method. The as-deposited Cu films were characterized *ex situ* by X-ray diffraction, focused ion beam scanning electron microscopy, electron backscattering diffraction and atomic force microscopy. It was found that for higher bias voltages, a Cu/Si epitaxial growth is achieved following the Cu(001) [100] // Si(001) [110] orientation relationship in HiPIMS films, while polycrystalline Cu films with [111] preferred orientation are obtained using a DCMS discharge under the same deposition conditions. Detailed investigation of the film structure correlated with the intrinsic stress measurements shows that the substrate bias voltage affects the early growth stages of HiPIMS Cu films on Si, and thus their final microstructures.

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