Advanced Surface Engineering
Room: 302 - Session SE+PS+TF-MoA

Pulsed Plasmas in Surface Engineering
Moderator: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Michael Stueber, Karlsruhe Institute of Technology

2:00pm **SE+PS+TF-MoA1 Complex Magnetic Systems for High Power Pulsed Magnetron Sputtering**, ***Priya Raman****, *I.A. Shchelkanov, J. McLain,* University of Illinois at Urbana Champaign, *S. Armstrong,* Kurt J. Lesker Company, *B. Zhang, M. Schilling,* DEXTER Magnetic Technologies, *D.N. Ruzic*, University of Illinois at Urbana Champaign

High Power Pulsed Magnetron Sputtering (HPPMS) is a type of magnetron sputtering technique where high peak power pulses reaching tens of kilowatts are applied to the sputter magnetron target keeping the average power equal to that of direct current magnetron discharges by using low duty cycles. Due to very high power densities, HPPMS discharge leads to high degree of ionization of the sputtered material. These ionized sputtered materials assist in film growth leading to more adhesive, dense, and smoother films. Therefore, HPPMS is considered an ideal candidate for the next generation magnetron sputtering systems, however these techniques suffer from low deposition rate due to "return effect" of the ionized sputter material [1]. One way to solve this problem is to have a magnetic field configuration that is optimized for HPPMS discharges. Magnetic pack design is critical as it helps in achieving full-face target erosion and higher deposition rate in HPPMS. Magnet pack design is generally selected by experimental observation. It has been confirmed from our previous work on HPPMS that a spiral-shaped magnetic field design on 14 inch (36 cm) diameter copper target was able to produce superior plasma uniformity on the substrate in addition to improved target utilization without the need for magnet rotation [2]. Commercial 4 inch (10cm) magnetron sputter guns function with a variety of power supplies like DC, Pulsed-DC, Modulated Pulsed Power Magnetron sputtering (MPP) and HPPMS. These 4 inch magnetron sputter guns typically have a conventional circular magnetic field configuration and suffer from low deposition rate in HPPMS discharges. To optimize the magnet field configuration in HPPMS for the 4 inch magnetron sputter gun, the spiral design from the 14 inch target was scaled down and modified to fit into 4 inch magnetron sputter gun. A new "ε" design magnet pack with enhanced discharge parameters was developed by modifying the spiral magnet pack in COMSOL Multiphysics, which leads to higher deposition rate and better target utilization in HPPMS compared to the conventional magnet pack. The influence of "ε" design magnet pack configuration on deposition rate, plasma parameters, and discharge stability with HPPMS (Huettinger's HiPIMS), MPP(zPulser), DC and pulsed DC power supplies were investigated. The deposition rate for "ε" pack is 2.1±0.2 times the conventional pack for an average discharge power of 500W with zPulser power supply.

1. Papa F *et al* 2011 *Thin Solid Films* 520.5 1559-1563.

2. He Yu *et al* 2013 *Plasma Sources Sci. Technol.*22 045012.

2:20pm **SE+PS+TF-MoA2 Triple Langmuir Probe and Ion Fraction Measurements in an Industrial PVD Deposition System**, ***YuiLun Wu****, S.S. Ma, I.A. Shchelkanov, D.N. Ruzic*, University of Illinois at Urbana-Champaign

High Power Pulsed Magnetron Sputtering (HPPMS) discharges are an ideal candidate for the next generation PVD magnetron sputtering systems. Compared with traditional DC sputtering, HPPMS discharges offer high degree of ionization of the sputtered material with very high peak power on the target. An industrial size chamber will be used to investigate the HPPMS discharge operation in full scale production environments utilizing different power supplies. Plasma was observed to be originated from the race track region then expanded downward afterwards. Plasma density was very high (~10^{19}-10^{20} m^{-3}) when generated then decreases as it expanded [1] In order to understand the temporal evolution of the plasma between the target and the wafer plane, a time resolved triple Langmuir probe was employed to measure the plasma parameters such as electron temperate and density and scanning in a three dimensional map. Plasma parameters between traditional DC discharge and HPPMS discharge will be compared. Quartz crystal microbalance and 2 inch gridded energy analyzer will be designed to determine fluxes of metal ions, metal atoms and argon ions. The setup will be able to tilt around 10 degrees about the wafer plane in 1 degree intervals and measure the angular distribution of the ion and neutral fluxes generated by the HPPMS discharge.

Reference:

[1] H.Yu, L. Meng, M. Szott, J. McLain, T.S. Cho, D.N. Ruzic, Investigation and optimization of the magnetic field configuration in high-power impulse magnetron sputtering, Plasma Sources Sci. Technol. 22 045012, 2013

2:40pm **SE+PS+TF-MoA3 Understanding the Physics of Magnetron Discharges: Ionization Zones and Their Role in Transport of Charged Particles**, ***Matjaž Panjan****, R. Franz, A. Anders*, Lawrence Berkeley National Laboratory **INVITED**

Magnetron sputtering is one of most commonly used techniques for the deposition of thin films. The physics of magnetron discharges has been intensively studied, however, recent investigations revealed that our understanding is rather incomplete. To the naked eye the ionization process appears to be homogeneously distributed along the racetrack – i.e. the region of strongest target erosion caused by sputtering. Imaging of the magnetron discharges with intensified CCD cameras using short exposure times revealed differently, namely, the plasma is concentrated in several zones along the racetrack [1-3]. These so-called ionization zones or spokes are organized in periodic or quasi-periodic patterns that move in the **E** × **B** direction with approximately 1/10 of the electron drift speed (where **E** and **B** are the electric field and magnetic field vectors). Recent experiments further revealed that ionization zones are a fundamental feature of magnetron discharges run in pulsed and continuous mode [4]. In this talk, recent advances in understanding the ionization zone phenomenon will be reviewed. The interpretation of the formation, drift, self-sustainability, and self-organization of ionization zones will be presented with emphasis on potential, electric field and ionization rate distributions. It will be shown that ionization zones play a critical role in the transport of both electrons and ions [4-6].

[1] A. Kozyrev et al., Plasma Physics Reports 37 (2011) 621

[2] A. Anders et al., J. Appl. Phys., 111 (2012) 053304

[3] A.P. Ehiasarian et al., Appl. Phys. Lett. 100 (2012) 114101

[4] M. Panjan et al., Plasma Sources Sci. Technol., 23 (2014) 025007

[5] A. Anders et al., Appl. Phys. Lett., 103 (2013) 144103

[6] P.A. Ni et al., Appl. Phys. Lett., 101 (2012) 224102

3:40pm **SE+PS+TF-MoA6 Properties of Ionization Zones in Magnetron Sputtering Observed in the Transition Region between dc and HiPIMS**, ***André Anders****, Y. Yang, J. Liu, Y. Qiu*, Lawrence Berkeley National Laboratory

Research in the last years revealed that the plasma in high power impulse magnetron sputtering (HiPIMS) is rich in structure, featuring self-organized patterns [1], plasma flares [2], and azimuthally asymmetric particle jets [3]. Most prominent are drifting regions of enhanced excitation and ionization, which are called ionization zones but sometimes also labeled spokes in analogy to similar phenomena seen in other **E** x **B** devices such as Hall thrusters. Fast imaging of ionization zones in HiPIMS revealed the presence of several distinct ionization zones, for example 3-5 zones in the case of sputtering with a 3-inch magnetron at peak currents of the order 100 A. The zone drift velocity is several 1000 m/s, up to 10^4 m/s, yet much slower than the **E** x **B** drift of electrons, which is of the order of 10^5 m/s. In contrast, when sputtering continuously (dc) at very low current (less than 1 A), and at low pressure (less than 1 Pa), we find only one ionization zone moving at low velocity in the reverse, i.e. the – **E** x **B** direction. Increasing the current and pressure tends to split the zone into two and occasionally three zones. The appearance of each zone depends on current and other factors such as the pressure of the process gas. In this contribution, we explore the transition regime between dc operation at low current and HiPIMS operation with high peak currents. Using fast streak and frame imaging cameras we detect even more structures and structure changes than anticipated. We conclude that the discharge and its particle transport is governed by zone-related instabilities and turbulence.

[1] A. Anders, et al., J. Appl. Phys. 111 (2012) 053304.

[2] P.A. Ni, et al., Appl. Phys. Lett. 101 (2012) 224102.

[3] M. Panjan, et al., Plasma Sources Sci. Technol. 23 (2014) 025007.

*** Coburn & Winters Student Award Finalist**

4:00pm **SE+PS+TF-MoA7 Observation of Multiple Charge States and High Ion Energies in High-Power Impulse Magnetron Sputtering (HiPIMS) and Burst HiPIMS using a LaB_6 Target**, ***Robert Franz,*** Montanuniversität Leoben, Austria, *C. Clavero,* Lawrence Berkeley National Laboratory, *R. Bolat,* Nazarbayev University, Kazakhstan, *R. Mendelsberg, A. Anders*, Lawrence Berkeley National Laboratory

In high-power impulse magnetron sputtering (HiPIMS), a variation of pulsed magnetron sputtering, short high-voltage pulses are utilized to create discharges with high current densities and a high degree of ionization of the target atoms. In recent years, more complex pulse patterns than the single pulses used in the original or conventional HiPIMS have been developed, e.g. burst-HiPIMS where a series of very short (few µs) pulses are bunched to form bursts.

In the present work, the charge-state-resolved ion energies of HiPIMS discharges were measured, using a LaB_6 target, as a function of charging voltage, pulse length, pulse frequency and on/off time ratio within applied HiPIMS bursts [1]. The highest charge states can reach +2 and +3 for boron and lanthanum ions, respectively. At high discharge powers, the B/La ion ratio can exceed the respective atom ratio in the target producing B-rich plasma with up to 98% boron ions. In the case of two-segmented bursts with high on/off time ratios, La^{3+} is the dominating lanthanum ion species and the ion energy distribution of B^+ shows a pronounced high-energy tail extending up to 750 eV. The measured plasma compositions, ion charge states and ion energies are discussed within the established framework of HiPIMS discharges and the recent postulation that potential humps are associated with drifting ionization zones. The recorded high B/La ion ratios are a result of complex effects related to particle fluxes in the HiPIMS plasma of compound targets, as explained with the help of an expanded schematic representation of self-sputtering and gas atom recycling. The high energies of the B^+ ions are based on a combination of the self-sputtering of boron, backscattering of incident boron ions on lanthanum atoms in the target and acceleration by localized potential humps [2]. Further evidence for potential humps is provided by the observed charge-state dependence of ion energies and features between the thermal peak and high-energy tail of the ion energy distribution functions.

[1] R. Franz, C. Clavero, R. Bolat, R. Mendelsberg, A. Anders, Plasma Sources Sci. Technol. 23 (2014) 035001.

[2] A. Anders, M. Panjan, R. Franz, J. Andersson, P. Ni, Appl. Phys. Lett. 103 (2013) 144103.

4:20pm **SE+PS+TF-MoA8 Pulsed Magnetron Sputtering of Novel Multifunctional Films**, ***Jaroslav Vlcek,*** *J. Rezek, J. Kohout*, University of West Bohemia, Czech Republic

High-power impulse magnetron sputtering with a pulsed reactive gas flow control was used for the reactive deposition of Ta-O-N films with tunable composition and properties [1]. The depositions were performed using a strongly unbalanced magnetron with a planar directly water-cooled Ta target in Ar-O_2-N_2 gas mixtures at an average target power density of up to 2.4 $kWcm^{-2}$ in a pulse. The repetition frequency of pulses was 500 Hz at a fixed 50 µs voltage pulse length and the total pressure close to 2 Pa. An effective reactive gas flow control made it possible to adjust the film composition from Ta_2O_5 to a mixture of Ta_3N_5 and TaN. We prepared Ta-O-N films possessing appropriate band-edge levels for water splitting and a narrow optical band gap of 2.5 eV that permits a visible light absorption up to 500 nm.

Pulsed dc magnetron co-sputtering of a single target (B_4C-Si, B_4C-Zr or B_4C-Hf-Si) in Ar-N_2 gas mixtures was used for deposition of different multifunctional films. The repetition frequency of pulses was 10 kHz at a fixed 85 µs voltage pulse length and the total pressure of 0.5 Pa. We present the results obtained for amorphous Si-B-C-N films with an exceptionally high thermal stability (above 1500°C) and very high optical transparency [2], for nanostructured Zr-B-C-N films with a high hardness (37 GPa) and high electrical conductivity [3], and for nanostructured Hf-B-Si-C films with a high hardness (34-37 GPa), high electrical conductivity and significantly improved oxidation resistance in air up to 800°C [4].

[1] J.Rezek, J.Vlcek, J.Houska, R.Cerstvy, Thin Solid Films (submitted).

[2] J.Vlcek, P.Calta, P.Steidl, P.Zeman, R.Cerstvy, J.Houska, J.Kohout, Surf. Coat. Technol.

226 (2013) 34.

[3] J.Vlcek, P.Steidl, J.Kohout, R.Cerstvy, P.Zeman, S.Proksova, V.Perina, Surf. Coat. Technol. 215 (2013) 186.

[4] J.Kohout, J.Vlcek, J.Houska, P.Mares, R.Cerstvy, P.Zeman, M. Zhang, J.Jiang, E.I. Meletis, S. Zuzjakova, Surf. Coat. Technol. (submitted).

4:40pm **SE+PS+TF-MoA9 Surface Engineering of Magnesium and Magnesium Alloys for Improved Corrosion Resistance**, ***Michael Melia,*** *J.R. Scully, J.M. Fitz-Gerald*, University of Virginia

Due to the need for significant weight reduction of structural components, the development of Mg alloys has been ongoing over the last 100 years. One long-standing obstacle regarding the use of Mg alloys for widespread field application is their intrinsically poor corrosion resistance and lack of surface films or oxides that enable "self-healing" or active scratch protection. Micro-galvanic induced "self-corrosion" due to alloy heterogeneity is a key concern. The effects of Excimer laser surface modification and electric arc surface processing on the corrosion resistance of commercially pure Mg (99.8 wt% Mg) and Mg alloy (AZ31B) is investigated. Non-equilibrium processing is being investigated to control surface chemistry, microstructure, and phase formation in order to mitigate the micro-galvanic corrosion with the initial goal of microstructural and composition homogenization. In an attempt to achieve surface homogenization and control Mg evaporation, a range of operating parameters (energy density, dwell time, and processing atmosphere) were explored.

Surface morphology, composition, and local phase imaging were performed with scanning electron microscopy in secondary and backscattered electron imaging modes. X-ray diffraction was used to examine phase and surface regions in grazing incidence mode. Corrosion characterization was performed in a standard three electrode corrosion cell with an aerated 0.6 M NaCl solution. Electrochemical Impedance Spectroscopy (EIS) (10,000 to 0.001Hz) and potentiodynamic polarization scans (0.1 mV/s) were used to determine corrosion resistance, anodic/cathodic behavior, pitting potential and open circuit potential (OCP).

Preliminary results confirm that a measured level of surface homogenization was achieved irrespective of process gasses used (Ar, N_2, He). Moreover, in the case of N_2 processed 99.8% purity Mg samples, the formation of Mg_3N_2 was found to have a significant impact on the corrosion resistance. The AZ31B samples processed in Ar exhibited a similar corrosion response to the N_2 processed surfaces, suggesting homogenization was a larger factor than nitriding. The cathodic behavior consistently exhibited a significant reduction in the rate of the H_2 evolution reaction, more apparent in 99.8% purity Mg. Furthermore, the OCP was reduced by 100-350 mV. Impedance results support these findings with a significant improvement in polarization resistance after treatment. However, processed samples exhibited a minimal change in anodic behavior besides minor fluctuations in pitting potential. Possible mechanisms for the inhibition of the cathodic reaction rate will be presented and discussed.

5:00pm **SE+PS+TF-MoA10 Designing a Precious Metal-Free Catalyst for Purification of Automotive Exhausts: NO Reduction and CO Oxidation on CuO(110) Surface**, *H. Kasai, J. Moreno, A.A. Padama,* Osaka University, Japan, *C. Matsuda, K. Naito, M. Uenishi, H. Tanaka,* Daihatsu Motor Co., Ltd, Japan, *Y. Nishihata,* Japan Atomic Energy Agency, Japan, ***Mamoru Sakaue***, Osaka University, Japan

Nitrogen oxide (NO_x) and carbon monoxide (CO) are known by-products of fossil fuel combustion, which greatly contribute to atmospheric pollution. Thus, understanding the conversion process of NO_x and CO into less hazardous gases is of utmost importance. It is well known that precious metals (such as Rh, Pd and Pt) work well to reduce these pollutant gases, but their high cost is a road block to a more prevalent use. Therefore, a more readily available and inexpensive material with comparable, if not better, catalytic performance is needed. Our group has investigated the role of surfaces as a foundation to realizing designer materials, in this case for exhaust purification [1]. In particular, we have previously studied the dissociation of nitric oxide (NO) on $Cu_2O(111)$ surface [2-4]. In this work, we look at the possibility of using a CuO catalyst for NO reduction and CO oxidation. Using density functional theory, we first investigated the dissociation process of NO on CuO(110) surface [5]. We found that NO is molecularly adsorbed perpendicular to the surface on the active hollow site between the surface Cu-atoms with an N-end configuration. An energy barrier of 1.1 eV was obtained for NO dissociation. The dissociated state was found to be most stable when the coadsorbed N and O atoms are on adjacent hollow sites. In comparison with the Rh(111) surface, the CuO(110) provides lower activation barrier for NO dissociation and lower adsorption energies for coadsorbed N and O atoms. To further investigate the oxidation of CO after the NO dissocation process, CO was adsorbed on the CuO(110) surface with coadsorbed N and O atoms. In this case, CO was molecularly adsorbed on top of a surface Cu atom while attracting the adsorbed O atom. An energy barrier of 0.9 eV was obtained for the CO oxidation process. This barrier was lower than the case of CO oxidation on Rh(111) surface with adsorbed oxygen atoms. The resulting CO_2 molecule was stably adsorbed with its center on top of a surface Cu atom. The results obtained in this study are in agreement with our experimental findings. In conclusion, we believe that CuO is a very promising catalyst for the purification of automotive exhausts.

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