Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B7

Plasma Diagnostics and Growth Processes

Moderators: Ante Hecimovic, Ruhr-Universität Bochum, Peter Bruggeman, University of Minnesota, USA

8:00am **B7-1 Plasma Surface Interaction Model for Titanium Nitride Thin Film Growth***,* ***Tobias Gergs****, J Trieschmann,* Ruhr University Bochum, Germany*; M Hans, D Music, J Schneider,* RWTH Aachen University, Germany*; T Mussenbrock,* Ruhr University Bochum, Germany

Reliable correlations between a set of plasma parameters and corresponding surface phenomena on the atomistic scale are scarce. The main reason being the complex physics of the two different states of matter, where at least one of which - the plasma - is far from an equilibrium state. In this contribution, we provide an initial step towards a consistent plasma surface interaction model, which covers the combination of generic materials as well as plasma discharges. As a proof of concept, we present a model which couples a direct current magnetron sputtering discharge with the resulting deposition of a titanium nitride thin film. In particular, the nucleation of cubic titanium nitride is studied at various substrate temperatures and fluxes starting from the amorphous state. Initially, the desired plasma parameter range is found by the extrapolation of classical molecular dynamics findings, validated by density functional theory calculations. This *a priori* knowledge is employed as a starting point for test particle simulations taking consistently into account the plasma and its global parameters. The resulting heavy particle fluxes and corresponding distribution functions are then again input to molecular dynamics simulations. Finally, the outcome of these simulations are compared to experimental results for the respective plasma discharge. In conclusion, it is argued that the proposed plasma surface interaction model is applicable to various plasma and material systems as well as surface modification phenomena.

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8:20am **B7-2 Correlation of the Debye Sheath Thickness and (Cr,Al)N Coating Properties for HPPMS, dcMS and PCAE Processes***, K Bobzin, T Brögelmann, N Kruppe, M Arghavani,* ***Martin Engels****,* Surface Engineering Institute - RWTH Aachen University, Germany

Physical vapor deposited (PVD) coatings are widely-used in tool applications such as the plastics processing. Predominant aims of the PVD coating application on the tools are the enhancement of the tool lifetime and an improvement of economic efficiency. The achievement of these aims amongst others strongly depends on a homogeneous distribution of the coating properties with respect to the entire functional surface, in particular on complex shaped tools. In many cases, due to the line-of-sight characteristics in PVD processes this homogeneity is hard to achieve. Besides the commonly used rotation of the tools or extensive mounting concepts, another possibility to overcome this issue is the choice of a suitable PVD technology such as the high power pulsed/impulse magnetron sputtering (HPPMS/HiPIMS), or the pulsed cathodic arc evaporation (PCAE). In order to characterize the influence of the different technologies on the coating homogeneity, the corresponding plasma properties, especially the Debye sheath thickness, can be used. Due to the positive charge in this area, the transport of positive charged ions of the coating material to the tool surface is strongly influenced. Therefore, it can be expected that a decreasing thickness increases the homogeneity of the coating, especially on complex surfaces with sharp edges, since the shielding of the surface is reduced. In the present work measurements on plasma properties as well as on coating properties using the high performance plasma processes HPPMS and PCEA with varying process parameters average power P, pulse length t_{on} and frequency f were carried out. In addition, the investigations were carried out as reference with a direct current magnetron sputtering (dcMS) process. In order to determine the Debye sheath thickness and the correlating homogeneity of coatings, the coating system (Cr,Al)N was chosen, as it is widely used as protective coating for plastics processing tools. In a first step, the plasma was analyzed using a Langmuir probe system. From the results of the U-I curves the plasma properties, especially the Debye sheath thickness, were determined. In a second step, (Cr,Al)N coatings were deposited with selected promising process parameters on structured substrates to determine the coating homogeneity. The coatings were analyzed regarding the morphology by scanning electron microscopy, the chemical composition by means of glow discharge optical emission spectroscopy as well as the universal hardness and the indentation modulus by nanoindentation. In summary, significant correlations between the processes and parameters, the Debye sheath thickness and the coating homogeneity were identified.

8:40am **B7-3 The Study of Spoke Merging and Splitting in HiPIMS Plasma***,* ***Jaroslav Hnilica****, P Klein,* Masaryk University, Czech Republic*; F Lockwood-Estrin,* University of Liverpool, UK*; P Vašina,* Masaryk University, Czech Republic*; J Bradley,* University of Liverpool, UK

High power impulse magnetron sputtering (HiPIMS) discharges demonstrate plasma self-organization, in which distinct ionization zones (often called spokes) can be seen to rotate in the ExB direction. Recently, a phenomena of spoke splitting and merging was observed in HiPIMS plasma using an array of phase correlated azimuthally arranged Langmuir probes around the discharge perimeter.

In our experiments, to gain more information on the temporal and spatial behaviour of self-organized spoke structures in HiPIMS plasmas, a correlation between the broadband 2-D optical image of an individual spoke and the current it delivers to the target has been made for a wide range of magnetron operating conditions. As a spoke passes over a set of embedded and isolated strip probes in the niobium cathode target, a distinct modulation in the local current density is observed, typically up to twice the average value associated with the spoke, as it delivers more current that the background plasma between spokes. It matching very well the radially integrated optical emission intensities obtained using 200 nanosecond time-resolved remote ICCD camera imaging. This allows us to relate the shape of spokes seen optically to their "electrical" footprint on the target.

The dual diagnostic system allows us to study the merging and splitting of a set of rotating spokes. It is found that during the merging process the trailing spoke retains its velocity. However, it is unclear whether during the merging process the leading spoke has decreased its velocity or the merging spokes have increased their azimuthal lengths. In the merged spoke both the plasma emission intensity and current collected by the embedded probes is redistributed to have their maximum at a trailing edge. In the spoke splitting process, the total charge collected by an embedded probe is conserved. Merged or split spokes are not always stable in time. Often the spoke system reverses to its former state a short time later.

A simple phenomenological model is developed to describe a stable spoke configuration. Assuming that argon presence is essential for spoke sustainment and based on spoke dimensions, spoke velocity and background gas atom velocity a stable amount of spokes can be predicted. The model provides realistic estimates for particular spoke and plasma conditions.

9:00am **B7-4 Al_2O_3- ZrO_2 Composite Coatings on Aluminum through a Hybrid Plasma Electrolytic- Electrophoretic Process***,* ***Nastaran Barati****, E Meletis,* University of Texas at Arlington, USA

Alumina-zirconia nanostructured layers were coated on 7075 Al alloy through a Plasma Electrolytic based technique in DC potentiostatic mode in the range of 540- 600 V. The layers were coated in an electrolyte containing nano ZrO_2 powder as the zirconia source. The microstructure and phase composition of the coatings were studied along with their tribological properties as a function of processing voltage.

The results showed formation of alumina- zirconia composites with different properties for the layers treated at different voltages. It was found that at higher processing voltage, the composite layers consist of high temperature phases (tetragonal zirconia and a-alumina) in addition to monoclinic zirconia. Also higher voltages introduced larger amounts of zirconia to the coated layers due to higher applied energies to the nanoparticles in electrolyte. The layers coated at 540 V and 580 V showed the lowest friction coefficient (0.14) compared to untreated Al alloy (0.69) in addition to better wear resistance (about 100 times higher in comparison to bare Al alloy). These improvements can be attributed to the formation of hard phases at high processing voltage. Furthermore, formation of tetragonal zirconia with better toughness and mechanical properties can result in improved wear resistance. The results revealed a hybrid of plasma electrolytic oxidation (PEO) and electrophoretic process as an effective coating method. In this regard, PEO was responsible for the formation of transformed tetragonal zirconia, while deposition of unchanged monoclinic zirconia from the electrolyte resulted from the electrophoretic process.

9:20am **B7-5 Low-temperature Atmospheric Pressure Plasma Processing and its Diagnostics for a Healthcare Device***, **Masaru Hori,*** Institute of Innovation for Future Society, Nagoya University, Japan **INVITED**

The healthcare has attracted much attentions from viewpoints of the innovation of industries and medicine. Technologies for the healthcare which is available everywhere and anytime has made a rapid progress by integrating various kinds of cutting edge multidisciplinary technologies in semiconductor manufacturing, plasma processing and bio fields. In recent years, microfluidic devices have received significant attention for a healthcare devices involving single cell trapping and analysis. We have been developing the non-equilibrium atmospheric pressure plasma for the fabrication of healthcare devices. The plasma is excited by a high-voltage alternating current (AC) power supply that provides a half peak voltage of 7 kV_{0-P} for a sinusoidal waveform with a frequency of 60 Hz. Argon (Ar) gas was supplied. The electron density and gas temperature were measured by the laser Thomson scattering method and optical emission spectroscopy.

The spatial distribution of absolute densities of O and N atoms were measured by the vacuum ultraviolet absorption spectroscopy (VUVAS). NO and OH were measured by laser induced fluorescence (LIF). Based these diagnostics results, the spatial distribution of radicals was systematically discussed.

The atmospheric pressure plasma was applied to the surface modification and the deposition of SiCHx films on the glass substrate. The surface wettability of micro-sized holes in glass substrates that are similar to those used as flow channels in glass microfiltration devices was drastically changed by the plasma treatment. As a result, the liquid transport flows were driven by internal Laplace pressure differences based on the surface tensions of droplets placed on the front and back sides of the tested substrates and thus cells were successfully trapped in the holes. The non-equilibrium atmospheric pressure plasma was also applied for the direct and indirect treatment of cells.

Using the multiplex coherent anti-Stokes Raman scattering (CARS) microscope, the dynamics of living cells during plasma treatments was observed. The multiplex CARS microscope enabled to obtain label-free information of the plasma-induced effects on the nature of chemical vibrations by probing signals of lipids and mitochondria from living cells

On the basis of these results of plasma diagnostics and plasma processing, plasma processes for the future healthcare are introduced.

10:00am **B7-7 Effects of Incident Particle Fluxes on the Growth and Properties of Ga-doped ZnO Films Deposited by Ion-plating with dc Arc Discharge***, **Hisashi Kitami,*** Sumitomo Heavy Industries, Ltd., Japan*; J Nomoto,* Kochi University of Technology, Japan*; T Sakemi,* Sumitomo Heavy Industries, Ltd., Japan*; H Makino,* Kochi University of Technology, Japan*; Y Aoki,* Sumitomo Heavy Industries, Ltd., Japan*; T Yamamoto,* Kochi University of Technology, Japan

We have investigated the influences of incident particle fluxes during film growth on the growth and properties of gallium-doped zinc oxide (GZO) films on glass substrates (@200 °C) deposited by ion-plating with dc arc discharge. The Ga_2O_3 contents in the pellets was 4.0 wt.%. Deposition conditions were as follows: the oxygen (O_2) gas flow rates (OFRs) and discharge current (I_D) were varied from 0 to 20 sccm and from 100 to 140 A, respectively.

We measured the incident particle flux of the neutral atoms and ions for each species quantitatively at the substrate level using a mass-energy analyzer (Hiden, EQP300), a Langumuir probe and a diaphragm gauge during the deposition. To clarify the factors limiting the growth rate, carrier density (N), hall mobility (μ_H) and optical mobility (μ_{opt}) of GZO films, we investigated the relationship between the growth rates, N, μ_H, μ_{opt} and incident flux (IF) properties of Zn species such as neutral Zn atoms and Zn^+ ions and O species such as neutral O atoms, O^+ and O_2^+ ions.

We found that an increase in the sum of IFs of O, O^+ and O_2^+ during the film growth increased the growth rates of GZO films. For lower OFR values of 0 to 10 sccm, we found that N slowly decreased and μ_H rapidly increased with increasing the neutral O ratio (= $O/(O+O^++2O_2^+)$), regardless of I_D. With further increasing OFR up to 20 sccm, N decreases rapidly and μ_H increases slowly, regardless of I_D. On the other hand, we found that μ_{opt} increased linearly with increasing the neutral O ratio. The above findings imply the strong relationships among growth rates, a microstructure with point defects associated with O species and electrical properties of GZO films. We will discuss it in more detail.

10:20am **B7-8 Mapping Potential of an Ionization Zone in Magnetron Plasma***, **Matjaz Panjan,*** Jozef Stefan Institute, Slovenia*; A Anders,* Lawrence Berkeley National Laboratory, USA

Investigations over the last few years have shown that plasma in continuous and pulsed magnetron discharges is not azimuthally uniform rather it is organized in dense structures called ionization zones or spokes [1-2]. In this work we present measurements of the plasma potential of moving ionization zone in a direct current magnetron sputtering [3]. Measurements were recorded in a space and time resolved manner using movable emissive and floating probes. This allowed us to make a three-dimensional representations of the plasma potential and derive the related electric field, space charge and electron heating distributions. The data reveal the existence of strong electric fields parallel and perpendicular to the target surface. The largest **E**-fields result from a double layer structure at the leading edge of the ionization zone. Measurements imply that the double layer plays a crucial role in the energization of electrons since electrons can gain several tens of electronvolts from azimuthal **E**-field. As electrons drift over the magnetron there is a sustained coupling between the potential structure, electron heating, and ionization processes. The ionization zone moves in the $-\mathbf{E}_z\times\mathbf{B}$ direction from which the to-be-heated electrons arrive and into which the heating region expands. The motion of the zone is dictated by the force of the local electric field on the ions at the leading edge of the ionization zone. We postulate that electron heating caused by the potential jump and physical processes associated with the double layer also apply to high power impulse magnetron sputtering.

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

[2] M. Panjan *et al.*, *Plasma Sources Sci. Technol.***24** (2015) 065010

[3] M. Panjan and A. Anders, *J. Appl. Phys.***121**, 063302 (2017)

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