Advanced Surface Engineering Division
Room 202C - Session SE+PS-TuM

Plasma-assisted Surface Modification and Deposition Processes

Moderators: Jolanta Klemberg-Sapieha, Ecole Polytechnique de Montreal, Canada, Matjaz Panjan, Jozef Stefan Institute, Slovenia

8:00am **SE+PS-TuM-1 Surface Modification of 304 Stainless Steel by Neutral Nitriding*, Petros Abraha,*** Meijo University, Japan

Austenitic stainless steel is the choice of material in the manufacturing industries for its corrosion resistance but lacks surface hardness leading to poor wear resistance and ultimately short lifetime. Stainless steel possesses the same microstructure at all temperatures and therefore, cannot be hardened by heat treatment. Attempts to increase the hardness of austenitic stainless steels by plasma nitriding has been successfully demonstrated in using different processes and methods. Here, we have introduced a nitriding method that improves the hardness and corrosion resistance of stainless steel while maintaining the initial surface conditions of the untreated surface.

In this research, neutral nitriding, a plasma nitriding method performed on a sample inside a cathodic grid in using an electron beam excited plasma device is presented. In this method, nitrogen ion incidence onto the sample surface is prevented by a positive bias to the sample ultimately controlling the formation of the compound layer. Further, the incidence of electrons causing an excessive rise in sample temperature is prevented by applying a negative bias to the cathodic grid. The setup creates a favorable condition that enables the neutral nitrogen species to be the primary species within the plasma to diffuse into the sub-surface of the sample and form a hardened layer.

The results obtained are as follows: (1) The S-phase without any compound layer on the surface was confirmed and the surface roughness of the untreated surface (Ra 10 nm) was maintained (Ra 15 nm). (2) The surface hardness was increased to more than two times, 550 Hv. (3) Pitting potential tests confirm Improved critical pitting potential on samples nitrided at 350 °C and 375 °C.

8:20am **SE+PS-TuM-2 Plasma Cratering and Hardening for Friction Reduction and Wear Resistance of Cast Iron*, Wei Zha,*** Univesity of Windsor, Canada*; C Zhao, X Nie,* University of Windsor, Canada

Cathodic plasma electrolysis (CPE) is used to reduce the friction and increase the wear resistance of cast iron. During the process, cast iron sample serves as a cathode where the plasma discharging occurs, increasing the surface hardness and leaving an irregular array of craters on the surface. As the applied voltage increases, the number and size of craters become larger. The areal density of craters (as reservoir) and oil retention are determined from SEM image analysis and surface profiler. Reciprocating tribotests are conducted on blank sample, CPE-treated samples and sample with crosshatched surface. The results show that the CPE-treated samples can have a lower coefficient of friction and higher wear resistance than other two kinds of samples. As for the CPE-treated samples, the friction behaviors are also discussed by considering effects from their areal density of craters, surface roughness and oil retention.

Keywords: Cathodic plasma electrolysis, Cratering, Hardening, Friction, Wear

8:40am **SE+PS-TuM-3 Area-selective Deposition by Surface Engineering for Applications in Nanoelectronics. From Blanket to Confined Dimensions*, Silvia Armini,*** IMEC, Belgium

At advanced nodes targeting 10nm feature size and below, lithography starts to dominate costs (EUV, multiple mask passes per layer, pattern placement error). Complementary techniques and materials are needed to continue 2D scaling and extend the Moore's law. Area-selective atomic layer deposition (AS-ALD) is rapidly gaining interest because of its potential application in self-aligned fabrication schemes for next-generation nanoelectronics. The strong sensitivity of ALD to the chemistry of the surface and its self-limiting nature are particularly appealing. In this talk we report two examples of AS deposition triggered by i) area activation, i.e. a H2-based plasma triggered selective placement of ALD Ru catalyst on SiCN liner with respect to amorphous carbon materials (Fig. 1) followed by AS electroless metal bottom-up deposition and ii) area deactivation by a combination of surface functionalization by molecular self-assembled organic films and ALD of metal oxides and metal nitrides. In the latter case the idea is to chemically and locally bond a molecule directly to the metal surface in order to inhibit reactive sites and then prevent further reactions between the precursor molecules and the surface. A selectivity driven benchmarking of organic passivation films deposited on copper surface from the vapor and liquid phase will be presented, both on blanket surfaces, micron-scale and nanometer-scale patterned features. Two major challanges will be investigated: i) defectivity induced by a reactive ALD process which also nucleates on the part of the surface covered with the organics and metrology; ii) understanding and control of AS ALD material shape at the boundaries between Cu and dielectrics. In Fig.2 the top-down SEM images after AS ALD Hf nitride on 240nm Si oxide/50nm Cu lines are shown. A target thickness of 10nm Hf nitride is deposited by ALD at 120˚C.

9:00am **SE+PS-TuM-4 Experimental and Numerical Evaluation of Cohesive and Adhesive Failure Modes during Indentation of TiAlN Coatings on Si(100) Deposited by MPPMS*, Z.T. Jiang*,** *M Lei,* Dalian University of Technology, China

The mechanical behavior of TiAlN coatings was studied by Indentation test and FEM modeling. The TiAlN coatings were deposited by modulated pulse power (MPP) magnetron sputtering. The peak power was used from 21 kW to 50 kW with the gas flow ratio of Ar/N_2=4:1. The microstructure of the indented regions was observed by focused ion beam (FIB), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). XRD with grazing angle of incidence reveals that the coatings consisted with c-TiAlN. The achieved hardness and modulus for the coatings show significant increase from 23.6 GPa to 46.7 GPa and 396 GPa to 461 GPa. The eXtended Finite Element Method (XFEM) was applied to study the cohesive cracks through the coatings, while the Cohesive Zone Model (CZM) was to evaluate the coating/substrate interfacial crack. The stress transfer from the coating to the substrate was dependent on the elastic and elastic/plastic properties of the coating and substrate. The energy release rate of the coating and the cohesive zone parameters were investigated by the fracture toughness of the coatings. Compared with the experimental results, the simulation results were able to accurately observe the deformation as well as the fracture behavior of the coatings. Under indentation loading, the crack initiation tended to begin at the outer surface and to propagate along the coating in thickness direction until the cracks reached the substrate.

9:20am **SE+PS-TuM-5 Growth of TiB_x Thin Films by DC Magnetron Sputtering and High-Power Impulse Magnetron Sputtering: Effect of Pressure and Substrate Temperature*, Niklas Hellgren,*** Messiah College*; J Thörnberg, I Zhirkov,* Linköping University, Sweden*; G Greczynski,* Linköping University, Sweden*; J Palisaitis,* Linköping University, Sweden*; M Sortica,* Uppsala University, Sweden*; P Persson,* Linköping University, Sweden*; I Petrov, J Greene,* University of Illinois at Urbana-Champaign*; L Hultman, J Rosen,* Linköping University, Sweden

We report on titanium boride, TiB_x, thin films grown by both direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) from a compound TiB_2 target, in an attempt to grow high-quality stoichiometric TiB_2 films. The composition, microstructure, and texture was analyzed as a function of deposition temperature (room temperature – 900 °C) and pressure (5 – 20 mTorr). Films deposited by DCMS at low pressure, regardless of temperature, result in over-stoichiometric films (B/Ti ≈ 3), while high pressure gives close to stoichiometric films. This can be explained by differences in angular distribution of sputtered B and Ti atoms, as well as differences in gas scattering [1]. These high-pressure films, however, are under-dense and have a mixed 100/101 preferred crystal orientation.

The composition of the HiPIMS-deposited films show a more complex dependence on pressure and temperature: At low temperatures, the trend vs pressure is opposite to DCMS, with the higher pressure resulting in higher B/Ti ratio. At higher temperatures, the effect of pressure is smaller, and even reverses slightly, with higher pressure giving lower B/Ti ratio.

We attribute these trends to a combination of several factors: (1) The much higher degree of ionization in HiPIMS, and the different transport of the ionized sputtered particles in the presence of a magnetic field, (2) gas density decrease at higher temperature resulting in less scattering, and (3) more sublimation, primarily of boron, at higher substrate temperatures. The highest quality stoichiometric TiB_2 films, with 001-textured nano-columnar structure, form by HiPIMS at 5 mTorr and 500-700 °C.

[1] J. Neidhardt et al., Appl. Phys. 104, 063304 (2008).

9:40am **SE+PS-TuM-6 Time-resolved Analysis of the Cathodic Arc Plasma from Nb-Al Cathodes***, S Zöhrer,* Montanuniversität Leoben, Austria*; A Anders,* Lawrence Berkeley National Laboratory, Leibniz Institute of Surface Engineering (IOM), Leipzig, Germany*; D Holec,* ***Robert Franz,*** Montanuniversität Leoben, Austria

Cathodic arc deposition has been established as one of the standard techniques for the physical vapour deposition of thin films and coatings as it allows the synthesis of a wide variety of materials including metallic films, but also nitrides, carbides and oxides if a reactive background gas is used. In addition, the highly ionised plasma and the achievable high deposition rates allow a variety of control mechanisms to influence the film growth while the manufacturing costs remain rather low due to the short deposition times. With the advent of multifunctional thin films and coatings, the use of multi-element cathodes providing the non-gaseous elements during the synthesis has become an industrial standard. However, a detailed understanding of the discharge properties is vital for the further optimisation of the deposition processes to enable synthesising thin films or coatings with improved properties.

By using a time-resolved method in combination with pulsed arcs and a comprehensive Nb-Al cathode model system in this work, we investigate the influence of cathode composition on the plasma, while making the influence of neutrals visible for the observed time frame. This model system consists out of three different Nb-Al compositions with the atomic ratios 75/25, 67/33 and 25/75, as well as pure Nb and Al cathodes. The results visualize ion detections of 600 µs plasma pulses, extracted 0.27 m from the cathode, resolved in mass-per-charge, energy-per-charge and time. In addition to high vacuum at a base pressure of 10^{-4} Pa, the measurements were carried out at three elevated Ar gas pressures: 0.04 Pa, 0.20 Pa and 0.40 Pa. Ion properties were generally found to be strongly dependent on the cathode material in a way that cannot be deduced by simple linear extrapolation. For high vacuum, current hypotheses in cathodic vacuum arc physics applying to multielement cathodes, like the so called “velocity rule” or the “cohesive energy rule”, are tested for early and late stages of the pulse. In addition, the influence of an inert background gas is analysed by comparing the results with those at increased pressure, which show reduced ion charge states, up to a state where mostly Nb^{2+} and Al^{1+} ions are detected. Beside Nb and Al ions, time-resolved energy and charge distributions of Ar ions are taken into account, providing further insights on the processes involved.

11:00am **SE+PS-TuM-10 Dedicated Experiments to Challenge a Model for Reactive Magnetron Sputtering***,* ***Diederik Depla,*** Ghent University, Belgium **INVITED**

Reactive magnetron sputter deposition is conceptual easy technique which can be explained in a few lines. Behind this apparent simplicity there is a complex interplay between different plasma and surface related processes. To get a better understanding of the impact of the different process parameters, modelling is inevitable. Therefore, the paper will first focus on the RSD (Reactive Sputter Deposition) model. As this code is freely downloadable and it has a GUI, it permits not only the research team to investigate this fascinating deposition technique, but also you. Important target processes such as sputtering, chemisorption, direct and knock-on reactive ion implantation will be discussed. With the model as a guide, some important fundamental questions will be tackled. Experiments related to the transition from metallic to poisoned mode, the deposition rate during reactive sputtering, the presence of parameter hysteresis will be presented. The confrontation between model and experiment will highlight not only the success of the RSD model, but also the further challenges to improve this model, and our understanding of reactive magnetron sputtering.

11:40am **SE+PS-TuM-12 Current-voltage-time Characteristics of HiPIMS Discharges Revisited***,* ***André Anders,*** Leibniz Institute of Surface Engineering (IOM), Germany

Continuous discharges can be characterized by their current-voltage (*I-V*) characteristics, which expresses the quasi-steady-state plasma impedance for slowly varying parameters of the driving circuit. For fast and strongly changing conditions, the plasma impedance may become a strong function of time and therefore one needs to explicitly add time as a parameter, leading to current-voltage-time (*I-V-t*) characteristics .

This general approach is applicable to magnetron sputtering, where the magnetron’s *I-V* characteristic is a power law, $I = K V^n$, with K being a device-specific constant and the power exponent n typically in the range from 6 to 10. For HiPIMS, the current is a strong function of time, and one needs to consider *I-V-t* characteristics [1]. In the special case when HiPIMS pulses have similar pulse shapes *I(t)* at various voltages, one may reduce the description to *peak* current - voltage characteristics and arrive again at a power law $I_p = K V^n$, this time with n in the range between 1 and 2. Most interesting, however, is the case when the *I(t)* curves are more complicated because they contain additional information. Since the appearance of publication [1] more than a decade ago we have learned a lot about HiPIMS, such as the relative importance of self-sputtering and gas recycling [2], leading to a more unified model [3]. In this contribution, *I-V-t* characteristics are revisited in light of today’s knowledge.

Acknowledgments: The experimental data for this work were primarily generated during the tenure of the author at Lawrence Berkeley National Laboratory, Berkeley, California.

[1] A. Anders, J. Andersson, A. Ehiasarian, J. Appl. Phys. 102 (2007) 113303.

[2] A. Anders, J. Čapek, M. Hála, L. Martinu, J. Phys. D: Appl. Phys. 45 (2012) 012003.

[3] N. Brenning, J.T. Gudmundsson, M.A. Raadu, T.J. Petty, T. Minea, D. Lundin, Plasma Sources Sci. Technol. 26 (2017) 125003.

12:00pm **SE+PS-TuM-13 Advantages Associated with Applying a Positive Pulse Option to a HIPIMS Power Supply***,* ***Jason Hrebik,*** Kurt J. Lesker Company

HIPIMS is an ionized PVC technique that produces a high density, high performance films. The extreme power densities in HIPIMS create a higher ionized plasma that creates a very high energy of material being deposited onto the substrate.

Many advanced techniques have been found to further enhance the quality of HIPIMS films, creating more ideal process and applications for utilizing this technique.

We will show advantages of integrating a positive “kick” pulse into a HIPIMS application. The “kick” pulse is an ideal feature for reactive sputtering applications due to its ability to carry out the HIPIMS plasma for extended period of time, minimizing the disapperating anode effect and repelling metal ions from the plasma toward the substrate resulting in higher sputtering rates.

Author Index

Bold page numbers indicate presenter