Monday Afternoon, October 15, 2007

Advanced Surface Engineering

Room: 617 - Session SE+PS-MoA

Pulsed Plasmas in Surface Engineering

Moderator: J. Patscheider, EMPA, Switzerland

2:00pm **SE+PS-MoA1 Modulated Pulse Power Deposition of Nanometer-Scale Multilayered Coatings**, *R. Chistyakov, B. Abraham,* Zond, Inc./Zpulser, LLC, ***W.D. Sproul***, Reactive Sputtering, Inc., *J.J. Moore, J. Lin*, Colorado School of Mines

Modulated pulse power (MPP) sputtering is a variation of high power pulse magnetron sputtering that overcomes the rate loss issue through modulation of the pulse shape, intensity, and duration. In MPP, the pulse shape and duration and plasma perturbations directly affect the degree of ionization of the sputtered material. In this study, the MPP plasma generator was controlled by a special electronic device that allowed the generation of two different plasma discharges within the same deposition cycle. Nanometer scale layers of material deposited under the two different plasma condition were alternately deposited, and the thickness and structure of each nanolayer was controlled by varying the output voltage pulse shape of the MPP plasma generator. Films of carbon and reactively deposited titanium nitride and chromium nitride were sputtered, and the film structure, orientation, and mechanical properties were analyzed and measured. These variations in the plasma conditions directly affect the film properties, and results of the film property measurements will be presented.

2:20pm **SE+PS-MoA2 Reactive High Power Impulse Magnetron Sputter Deposition of Alumina**, *E. Wallin, S. Swedin, M. Lattemann,* ***U. Helmersson***, Linköping University, Sweden

Alumina, Al_2O_3, is one of the technologically most important ceramic materials. Due to the existence of a variety of different polymorphs, it finds use in a wide range of applications. In the present work, alumina thin films have been deposited using high power impulse magnetron sputtering (HIPIMS) of an Al target in Ar/O_2 gas mixtures. HIPIMS is a new and promising technique for ionized physical vapor deposition (I-PVD), in which a high degree of ionization of the deposition flux as well as an inherently high energy of the depositing species can be achieved at relatively low average power, by applying high power pulses with a low duty factor (typically around 1 %) to a conventional sputtering target (see, e.g., Helmersson et al., Thin Solid Films 513, 1 (2006)). Stoichiometric alumina films could be grown in a stable and essentially arc free process at rates which are high compared to the deposition rate for pure Al metal and comparable to, or even higher than, what can be achieved with traditional DC deposition methods. A model qualitatively describing and giving explanations for this behavior of the reactive process will be presented. The resulting films were investigated by x-ray diffraction, as well as scanning and transmission electron microscopy. Films deposited directly onto Si substrates at a substrate temperature of 400 °C were found to have a microstructure consisting of small, equiaxed grains with a diameter of the order of 10 nm, and with γ-alumina as the only detectable crystalline polymorph. The results demonstrate the potential of depositing dielectric films at relatively high rates using HIPIMS. In addition, HIPIMS deposition of such films opens the possibility of utilizing the ionized deposition flux to improve the film quality and affect the structure of the coatings, also at reduced substrate temperatures.

2:40pm **SE+PS-MoA3 Effect of Sub-Surface Reactions on the Growth of Nano-Structured Functional Thin Films Deposited under Energetic Ion Bombardment**, *A. Amassian, M. Dudek, P. Jedrzejowski, R. Vernhes, O. Zabeida, P. Desjardins, J.E. Klemberg-Sapieha,* ***L. Martinu***, Ecole Polytechnique, Canada **INVITED**

Recent advances in science and technology stimulate the development of new coating materials, surface and interface engineering processes and thin film systems that provide an ever increasing performance in numerous areas ranging from optical and optoelectronic to aerospace, automotive, biomedical, microelectronic, and other applications. Many successful solutions in these particular fields have been identified when using ion-assisted deposition of thin films and thin film systems with tailored functional characteristics including the complex refractive index, the mechanical properties such as stress, hardness, friction coefficient and wear, the electrical conductivity, the gas and vapour permeation, and many others. In this context, we have recently investigated ion-surface interactions in a plasma environment (biased-controlled PECVD and PVD) using a methodology combining in situ real-time spectroscopic ellipsometry (RTSE), dynamic Monte-Carlo simulations, and different complementary methods such as ERD, HRTEM, SEM, AFM and others. These have the capability to detect and simulate subplantation-related processes, such as sub-surface structural and compositional modifications, and interface broadening, on time and depth scales relevant to functional coatings deposition. The ion-induced effects result in (i) rapid structural (<< 1 s) and compositional (< 2 s) changes as deep as ?10 nm below film or substrate surfaces, as well as (ii) significant ion mixing and interface broadening, and (iii) relocation of a large proportion of deposited atoms below the growth surface. Specifically, following a description of the principal physical processes, we will show examples when the above-mentioned methodology helped to enhance our understanding of the film growth and interface evolution for numerous single and multilayer functional coatings comprising TiO2, SiO2, Si3N4, ITO and the nanocomposite superhard TiN/SiN and TiCN/SiCN systems. We will also discuss the ion-controlled growth mechanisms in the context of new deposition approaches such as plasma pulsing.

3:40pm **SE+PS-MoA6 Microstructure Evolution in High Power Magnetron Sputter Deposited Titanium Nitride**, ***M. Lattemann***, *D. Jädernäs, U. Helmersson*, Linköping University, Sweden

Transition metal (TM) nitrides are well known for their remarkable physical properties including high hardness and mechanical strength, chemical inertness, high temperature stability, low resistivity, and good optical properties. As a result they have become of high technological and scientific importance and are used in a wide range of applications. NaCl δ-TiN has received by far the most attention and is therefore often used as a model system. In this work, TiN thin films were deposited onto MgO(100) and MgO(111) substrates in an Ar/N_2 atmosphere using high power impulse magnetron sputtering (HIPIMS). HIPIMS has earlier been proven to produce a highly ionized metal flux exhibiting a broad ion energy distribution with energies up to 100 eV advancing surface processes. It was shown that these ion energies are sufficient to produce fully dense films even at ambient temperature. However, the high amount of metal species with an energy around 1 eV promote the formation of underdense grain boundaries as the energy only allows the ions to interact with the nearest neighbor sites by single hop events. At ambient temperature and grounded substrate, the TiN thin films show a columnar structure with almost random orientation of the crystals as a result of combination of arriving species with high and low mobility as well as highly energetic ions creating defects and nucleation sites. The window for epitaxial growth of TiN for a variety of different process parameters was investigated. E.g. a more monoenergetic ion energy distribution can be achieved by tailoring the substrate bias and process conditions. In addition to the metal ion energy and substrate temperature, also the effect of assisting gas ion irradiation was investigated both during the pulse and in between the pulses, where no deposition occurred. In this way, the onset and breakdown of structure relation towards polycrystalline morphology can be monitored. The resulting structure of the TiN thin films was investigated by x-ray diffraction and high resolution transmission electron microscopy.

4:00pm **SE+PS-MoA7 High Power Impulse Magnetron Sputtering (HIPIMS): Scaling Up to the Industrial Level**, ***G. Greczynski***, *J. Bohlmark*, Chemfilt Ionsputtering AB, Sweden

High Power Pulsed Magnetron Sputtering (HIPIMS or HPPMS) is a novel magnetron sputtering technique that draws increasing interest due to the ability to form the droplet-free films out of highly ionized vapor of the target material. Invented by Kouznetsov in 1999 (US patent US6296742) HIPIMS has gone the long way and is nowadays entering the stage of commercial applications. The focus of the work presented here is the basic parameter study performed on the industrial system equipped with HIPIMS power supply capable of delivering up to 10 kW average power in MW pulses. The target material used is Ti/Al and Ti. Purely metallic films, as well as, reactively sputtered TiAlN and TiN films were grown. The deposition rate and film quality were studied as a function of the energy per pulse (up to 20J), pulsing frequency (up to 500Hz), working gas pressure and the substrate bias. The degree of ionization, that was simultaneously monitored with optical emission, reached 90% under optimum conditions. Results are compared to the films produced with the state-of-the-art industrial DC coater. It is apparent from this study that the technique can be successfully used in the industrial applications.

4:20pm **SE+PS-MoA8 Mechanisms of Adhesion Enhancement by High Power Impulse Magnetron Sputtering**, ***A.P. Ehiasarian***, Sheffield Hallam University, UK **INVITED**

Adhesion to steel and carbide substrates is one of the primary factors determining coating performance under environmental attack such as wear in cutting and automotive engine operations, errosion-corrosion, and high temperature oxidation. Technologies that improve adhesion aim to sputter-clean the substrate by high energy ion bombardment with energy >500 eV. These energies are sufficient for ions to be implanted into the bulk of the substrate to a depth of several monolayers (1-3 nm). Therefore the chemical composition of the bombarding flux can have a strong influence on the structure of the coating-substrate interface. Technologies that use gas ion bombardment typically incorporate Ar as interstitial or at vacancy sites generated in the steel or carbide lattice by the high energy of irradiation. The inert nature of Ar means that it does not form bonds with the surrounding atoms and thus greatly disturbs atomic ordering and increases stress. In the case of high power impulse magnetron sputtering (HIPIMS) plasmas operating at peak current of 2 Acm^{-2}, the ion bombardment flux contains high fractions of metal ions. For HIPIMS of Cr and Ti, the ratio Ar^{1+} : Me^{1+} = 1 : 1 was observed with energy-resolved mass spectroscopy, whilst the metal ion-to-neutral ratio was Me^{1+} : Me^{0} = 1 : 1 as determined from atomic absorption spectroscopy. Scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) analysis of 304 stainless steel bombarded at 600 V by HIPIMS of Cr showed a layer of implanted Cr ions with depth of 5-8 nm, resulting from ballistic implantation as confirmed with TriDyn simulations. High-resolution TEM revealed that this region is highly crystalline with low defect density, probably due to the substitutional incorporation of Cr ions in the steel lattice. Incorporation and retention of Cr is improved by irradiation- and temperature- enhanced diffusion. As a result of the crystalline interface, the coating nucleated in local epitaxial growth mode which was maintained over several microns in lateral direction. A number of susbtrate-coating combinations demonstrated such epitaxy, for example for steel substrates: CrAlN, CrN, VN, TiAlN, and for γ-TiAl substrates - CrAlN, and CrN. This resulted in significant improvements to the adhesion and performance in wear and cutting of Ti and Al tests.

5:00pm **SE+PS-MoA10 Deposition Rate of High Power Pulsed Magnetron Sputtered Cu**, ***J. Emmerlich***, *S. Mráz, R. Snyders, K. Jiang, J.M. Schneider*, RWTH Aachen University, Germany

In high power pulsed magnetron sputtering (HPPMS), several kW target power are dissipated during μs pulses resulting in a high degree of ionization of the sputtering gas as well as the sputtered target material.[1] A major drawback of this deposition process is reported to be the low deposition rate compared to d.c. magnetron sputtering (dcMS). Self-sputtering, due to a metal-ion dominated plasma later in the pulse, and plasma conductivity may play a large role in the deposition rate loss. However, the high target potential (up to ~2kV) applied during HPPMS influences the sputtering yield induced by both, the sputtering gas and the target ions (self-sputtering). The effect of the energy dependent sputtering yield on the deposition rate is discussed for Cu. Using transport-of-ions-in-matter (TRIM) software, we simulated the sputtering yield for a Cu target bombarded with energetic Ar^{+} and Cu^{+} ions for dcMS and HPPMS target potentials. The results show that the deposition rate of HPPMS compared to dcMS based on an energy dependent sputtering yield is in the range of 77% to 43%.

[1]K. Macák, V. Kouznetsov, J. Schneider, and U. Helmersson, J. Vac. Sci. Technol. A 18, 1533 (2000).

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