Tuesday Afternoon, October 20, 2015

Advanced Surface Engineering
Room: 212A - Session SE+PS-TuA

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

2:20pm SE+PS-TuA1 Strategy for Tuning the Average Charge State of Metal Ions Incident at the Growing Film during HIPIMS Deposition, *Grzegorz Greczynski*, Linköping University, Sweden, *I. Petrov,* University of Illinois at Urbana Champaign, *J.E. Greene,* University of Illinois at Urbana-Champaign, *L. Hultman*, Linköping University, Sweden
Energy- and time-dependent mass spectroscopy is used to determine the relative number density of singly- and multiply-charged metal ions incident at the substrate during high-power pulsed magnetron sputtering (HIPIMS) as a function of the average noble-gas ionization potential. We selected Ti as the sputtering target since the microstructure, phase composition, properties, and stress-state of Ti-based ceramic thin films grown by HIPIMS are known to be strongly dependent on the charge state of Ti^{n+} ($n = 1, 2, \ldots$) ions incident at the film growth surface. [1,2] Mass spectroscopy results show that the flux of Ti_{n+} with $n > 2$ is insignificant; thus, the Ti_{2+}/Ti_{+} integrated flux ratio J_{Ti}^{2+}/J_{Ti}^{+} is measured at the substrate position as a function of the choice of noble gas -- Ne, Ar, Kr, Xe, as well as Ne/Ar, Kr/Ar, and Xe/Ar mixtures -- supporting the plasma. We demonstrate that by changing noble-gas mixtures, J_{Ti2+} varies by more than two orders of magnitude with only a small change in J_{Ti+}. This allows the ratio J_{Ti}^{2+}/J_{Ti}^{+} to be continuously tuned from less than 0.01 with Xe, which has a low first-ionization potential IP^{1}, to 0.62 with Ne which has a high IP^{1}. The value for Xe, $IP^{1}_{Xe} = 12.16$ Ev, is larger than the first ionization potential of Ti, $IP^{1}_{Ti} = 6.85$ Ev, but less than the second Ti ionization potential, $IP^{2}_{Ti} = 13.62$ Ev. For Ne, however, $IP^{1}_{Ne} = 21.63$ Ev is greater than *both* IP^{1}_{Ti} and IP^{2}_{Ti}. Therefore, the high-energy tail of the plasma-electron energy distribution can be systematically adjusted, allowing J_{Ti}^{2+}/J_{Ti}^{+} to be controllably varied over a very wide range, from 0.01 with Xe to 0.62 with Ne. [3]

[1] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Surf. Coat. Technol.* 206 (2012) 4202

[2] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Vacuum* 86 (2012) 1036

[3] G. Greczynski, I. Petrov, J.E. Greene, and L. Hultman, *Vacuum* 116 (2015) 36

2:40pm SE+PS-TuA2 Study of High Power Pulsed Magnetron Sputtering Under Differing Magnetic Field Configurations, *Priya Raman*, *I.A. Shchelkanov, J.T. McLain,* University of Illinois at Urbana Champaign, *S. Armstrong,* Kurt J. Lesker Company, *D.N. Ruzic,* University of Illinois at Urbana Champaign
There is an increasing demand for high quality, wear-resistant, low-friction and corrosion resistant coatings in the microelectronics, automotive, tooling and other industries. High power magnetron sputtering is a type of magnetron sputtering technique where short high power pulses are applied to the magnetron target at very low duty cycles leading to higher degree of ionization of the target material. These ionized sputtered material assist in film growth leading to more adhesive, dense, and smoother films compared to conventional DC Magnetron Sputtering (dcMS) techniques. Unfortunately HPPMS suffers from lower deposition rates due to "return effect" of the ionized sputter materials [1]. Further reach of the HPPMS technology largely depends on whether it can produce deposition rates comparable or higher than dcMS. Recent studies of HPPMS discharges have shown that the magnetic field in the region above the sputter target defines the plasma properties and potential distribution in that region. The "ε" magnet pack [2] had already demonstrated increased deposition rates by carefully changing the magnetic field pattern above the target surface. Cylindrically symmetric "TriPIMS" magnet was developed based on magnetic field design solutions from "ε" magnet pack to keep the high deposition rates but improve deposition uniformity. In order to fully understand the behaviour of high current pulsed discharge in this new magnetic field configuration, TriPIMS magnet pack, was tested with Huettinger HiPIMS, Z-pulser MPP, Starfire Impulse and DC power supplies. Plasma parameters (ne, Te, ionization fraction), deposition rate, deposited film density, uniformity, and stress were measured. Reason for higher deposition rate is discussed.

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

[2] Raman, Priya, et al. "High power pulsed magnetron sputtering: A method to increase deposition rate." *Journal of Vacuum Science & Technology A* 33.3 (2015): 031304.

3:00pm SE+PS-TuA3 Reactive High-power Impulse Magnetron Sputtering and Pulsed Magnetron Co-sputtering of Multifunctional Films, *Jaroslav Vlcek*, *J.R. Rezek, P.M. Mares,* University of West Bohemia, Czech Republic **INVITED**
In the presentation, we report on discharge and deposition characteristics (including the ion flux characteristics at the substrate), and on film structure and properties for two different pulsed reactive magnetron sputtering techniques.

High-power impulse magnetron sputtering (HiPIMS) with a pulsed reactive gas flow control was used for high-rate reactive depositions of densified, highly optically transparent, stoichiometric ZrO_2 and HfO_2 films, and of Ta-O-N films with tunable composition and properties. The depositions were performed using a strongly unbalanced magnetron with a planar directly water-cooled Zr, Hf or Ta target in $Ar-O_2$ or $Ar-O_2-N_2$ 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 $50 - 200$ μs voltage pulse lengths and the total pressure close to 2 Pa. An effective reactive gas flow control made it possible to produce high-quality ZrO_2, HfO_2 and Ta-O-N films with high deposition rates (up to 120 nm/min, 345 nm/min and 190 nm/min, respectively, for the target-to-substrate distance of 100 mm) and to adjust the composition of the Ta-O-N films from Ta_2O_5 to a mixture of Ta_3N_5 and TaN. We prepared almost stoichiometric TaON 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. Selected results obtained using a parametric model for the controlled reactive HiPIMS of the ZrO_2 films are presented.

Pulsed dc magnetron co-sputtering of a single segmented target (B_4C-M, where M = Ti, Zr and Hf, or B_4C-Hf-Si) in Ar gas or $Ar-N_2$ 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 $0.5 - 1.7$ Pa. Energy-resolved mass spectroscopy was used to correlate the energy of Ar^+ ions bombarding the growing films with high positive voltage overshoots after the negative voltage pulses and with the energy of Ar atoms backscattered from the sputtered targets. We present the results obtained for nanocolumnar ZrB_2-type Zr-B-C films and nanocomposite Zr-B-C-N films exhibiting a high hardness (37 GPa) and high electrical conductivity, and for nanostructured HfB_2-type 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.

4:20pm SE+PS-TuA7 Target Poisoning in Mixed Ar, N$_2$ and CH$_4$ Atmosphere, in Processes Using Different Target Materials for HIPIMS/DC and DC Cathode Modes., *Anna Oniszczuk*, *A.P. Ehiasarian,* Sheffield Hallam University, United Kingdom of Great Britain and Northern Ireland, *C.F. Carlström, M. Ahlgren,* Sandvik Coromant, Sweden
Reactive sputtering in mixed $Ar+N_2+CH_4$ atmosphere is a widely used industrial process however the poisoning of different target materials under different sputtering discharges in this complex environment is insufficiently described.

In mixed $Ar+CH_4+N_2$ atmosphere, at low flow processes were influenced by methane whereas at high flow they were dominated by nitrogen indicating the formation of carbide and then carbonitride compounds. This was observed for both TiAl and V targets in DC as well as in HIPIMS mode.

Vanadium targets operating in DC mode were poisoned at 55% of reactive gas flow. Poisoning resulted in a 2-fold increase in total pressure, a 50 % increase in discharge voltage/current ratio, a 5 fold drop in V(I) optical emission intensity and a 10 fold drop in V^+ and Ar^+ fluxes obtained from energy-resolved mass spectroscopy.

TiAl targets in DC mode poisoned at lower reactive gas flows and exhibited narrower hysteresis than V due to the higher reactivity of the target material. The voltage/current ratio of TiAl targets went through a minimum with a flow, while for V target it increased with flow.

For HIPIMS both targets poisoned earlier and the hysteresis was narrower than in DC mode. As confirmed by trends in the partial pressure, the voltage/current ratio and ion fluxes of metals and reactive gasses. These effects are due to higher reactivity of the plasma as evidanced by higher fluxes of N^+ and N_2^+ and radicals containing H, C and N. The voltage/current ratio reduced by 50% as the target is poisoned in contrast to

operation in DC mode where it increased. This could be attributed to efficient ionization and drop in plasma impedance.

Pathways for poisoning and resulting ion fluxes are discussed.

4:40pm SE+PS-TuA8 Structure and Properties of Cr$_2$O$_3$ Coatings Deposited using DCMS, PDCMS, and DOMS, *Jianliang Lin*, Southwest Research Institute, *W.D. Sproul*, Reactive Sputtering, Inc.

The properties of oxide coatings are strongly tied to the crystallinity of oxide phases. In general, a well-crystallized oxide phase is desired because it is usually related to improved mechanical and chemical properties. This paper presents a comparative study of the chromium oxide (Cr$_2$O$_3$) coatings deposited by deep oscillation magnetron sputtering (DOMS), mid-frequency pulsed dc magnetron sputtering (PDCMS) and continuous dc magnetron sputtering (DCMS). Without applying external substrate heating, the processing techniques strongly affected the crystallinity of the Cr$_2$O$_3$ coatings. The DCMS-Cr$_2$O$_3$ coating exhibited an amorphous like structure. The coating deposited by PDCMS contained a mixture of amorphous and crystalline phases. In contrast, the DOMS-Cr$_2$O$_3$ coating showed a strong crystallinity with a (110) preferential orientation. The improved crystallinity of the DOMS-Cr$_2$O$_3$ coating is due to the higher ion bombardment and higher substrate saturation temperature, which is related to the high energy electron bombardment associated with deep oscillation pulses. Improved mechanical properties and wear resistance were achieved in the DOMS-Cr$_2$O$_3$ coatings as compared to the coatings deposited using DCMS and PDCMS. This study also showed that the bias voltage strongly affected the structure of the DOMS-Cr$_2$O$_3$ coatings by changing the substrate current characteristics.

5:00pm SE+PS-TuA9 Strategy to Tailor the Composition of Silicon Oxynitride Thin Films Deposited by Reactive High Power Impulse Magnetron Sputtering using Nitrous Oxide as a Single-source Precursor, *Tuomas Hänninen, S. Schmidt, J. Jensen, L. Hultman, H. Högberg*, Linköping University, Sweden

Silicon oxynitride (SiON) is a material with tunable optical and electrical properties. It is used as thin films in antireflection coatings, surface passivation layers, and optical waveguides. Commonly two reactive gases, O$_2$ and N$_2$, have been employed for the reactive magnetron sputter deposition of SiON. The two-gas approach is, however, limited by the non-linear target effects as a function of reactive gas flow rates, which makes an accurate control of the deposition process challenging.

In this study we present SiON thin films deposited by reactive high power impulse magnetron sputtering from a pure Si target in Ar/N$_2$O plasmas. The influence of the average target power while maintaining a fixed pulse frequency (1000–4000 W at 1000 Hz and 1200–3000 W at 600 Hz) and the frequency at a fixed energy per pulse (300–1000 Hz at 4 J) on the resulting film properties were investigated.

The ~ 300 nm thick films show a dense and featureless morphology when viewed in cross-sectional scanning electron microscopy. X-ray diffraction reveals that the films are X-ray amorphous and exhibit compressive residual stresses in the range of 500–1500 Mpa. The chemical bonding structure and the elemental composition of the films were studied with X-ray photoelectron spectroscopy. The spectra acquired from the as-deposited samples show mixed Si—O, Si—N, and Si—Si bonding. The ratio between these type of bonds correlates with the atomic concentrations of Si, O, and N in the films. A decreased average power at a fixed pulse frequency induces an increase in O content (from 13 at.% to 51 at.% at 1000 Hz and from 17 at.% to 43 at.% at 600 Hz) while the N concentration remains virtually unaffected. An exception are films with the highest O content, showing a decrease in N content from ~ 26 at.% to 9 at.% at 1000 Hz and to 16 at.% at 600 Hz. A similar behavior is observed when the pulse frequency is lowered at a constant pulse energy, the film O content increases from 13 at.% to 43 at.%, followed by a decrease in N concentration from ~ 26 at.% to 17 at.%. Film densities as measured by X-ray reflectivity are found to range between 2.6–2.9 g/cm^3. The refractive indices and extinction coefficients at 633 nm, measured by variable-angle spectroscopic ellipsometry, show that the films with highest total O plus N content have the lowest refractive index (1.6–1.8) and extinction coefficient (~ 0) values. The refractive index values are comparable to those of SiO$_2$ (~ 1.45) and Si$_3$N$_4$ (~ 2.0), confirming that the optical properties of the studied films can be tailored to range between SiO$_2$ and Si$_3$N$_4$.

5:20pm SE+PS-TuA10 Phase Changes Observed on AlCr Composite Cathodes due to the Exposure to Cathodic Arc Plasmas in N$_2$ and O$_2$ Atmospheres, *Robert Franz, F. Mendez Martin, G. Hawranek*, Montanuniversität Leoben, Austria, *P. Polcik*, PLANSEE Composite Materials GmbH, Germany

Hard and wear-resistant coatings based on the system aluminium and chromium represent the state of the art in the protection of tools used in metal cutting operations. Using cathodic arc deposition techniques in nitrogen and/or oxygen atmospheres, nitrides, oxides or oxynitrides can be synthesised. The growth conditions encountered in processes employing cathodic arc plasmas are typically characterised by a high degree of ionisation and high deposition rates. For the supply of the non-gaseous elements during the deposition, it is common to use multi-element cathodes containing the desired Al/Cr ratio. These cathodes are usually composite cathodes and are widely used in industrial-scale deposition systems since they facilitate an easier process control and reproducibility. However, the plasma conditions in the cathodic arc plasma using such multi-element cathodes and their erosion behaviour in reactive atmospheres are only scarcely studied.

In the present investigation, AlCr composite cathodes with compositions of 75/25, 50/50 and 25/75 at.-% were exposed to cathodic arc plasmas in N$_2$ and O$_2$ atmospheres. Due to periodic melting and solidification of the cathodes' near-surface region in the cathode spots, an intermixing of the elements Al and Cr and the formation of intermetallic phases occurred which was analysed by recording elemental distribution maps in the cross-sections using scanning electron microscopy. By comparing regions of strong erosion with areas less affected by the cathodic arc plasma, poisoning effects due to reactions of the metals in the cathodes and the background gas could be identified and were analysed in detail. The conductivity of the formed nitrides and oxides on the surface of the AlCr composite cathodes was decisive for the characteristics of the cathodes' erosion behaviour. All results regarding the cathode erosion and the phase changes are compared to similar studies on TiAl [1] and Al$_{0.7}$Cr$_{0.3}$ [2, 3] cathodes and are put in context with recently reported arc plasma properties obtained with the same AlCr cathodes and gas atmospheres [4, 5].

References:

[1] D. Rafaja, C. Polzer, G. Schreiber, P. Polcik, M. Kathrein, Surf. Coat. Technol. 205 (2011) 5116–5123.

[2] J. Ramm, A. Neels, B. Widrig, M. Döbeli, L.D.A. Vieira, A. Dommann, H. Rudigier, Surf. Coat. Technol. 205 (2010) 1356–1361.

[3] M. Pohler, R. Franz, J. Ramm, P. Polcik, C. Mitterer, Surf. Coat. Technol. 206 (2011) 1454–1460.

[4] R. Franz, P. Polcik, A. Anders; *IEEE Trans. Plasma Sci.* 41 (2013) 1929–1937

[5] R. Franz, P. Polcik, A. Anders; *Surf. Coat. Technol.* 272 (2015) 309–321

5:40pm SE+PS-TuA11 Optimization of Linear Scanning Magnetron Array Performance, *Vladimir Kudriavtsev, A. Riposan, D.W. Brown, C. Smith, T. Bluck*, Intevac, Inc.

In this presentation we discuss Linear Scanning Magnetic Array (LSMA) technology for magnetron sputtering in conjunction with in-line substrate processing. In this approach, the magnet array (pole) scans over planar target spreading the erosion pattern in a controlled fashion. Thus, high quality, dense films with good uniformity can be produced at significant advantages over static magnetrons, such as significantly higher target utilization, longer uptime, and prevention/removal of target defects related to re-deposition.

We review the influence of magnet motion acceleration/deceleration, the influence of endpoint motion offset (stagger), and the influence of magnet - to - substrate velocity ratio, on target utilization and lead-to-trail edge film uniformity. Trade-offs between uniformity and target utilization were established and characterized.

The optimization method we use employs a combination of theoretical simulations and experimental measurements. Theoretical analysis utilizes ANSYS static magnetic field simulations, erosion profile calculations including motion integration effects, and ray tracing method for sputtering film thickness calculations (MATLAB). The structure and uniformity of LSMA-deposited thin films was characterized experimentally by XRF and SEM, and the target erosion measured by weight and erosion profiles of spent targets.

We have demonstrated that, with a judicious design approach, an optimal range of operating parameters can be defined and target utilizations above 70%can be reached, while maintaining deposition uniformity below 2% with excellent film properties. This makes the LSMA plasma source (using planar targets) more economically competitive than static and rotatable magnetrons.

6:00pm SE+PS-TuA12 Correlation of Microstructure of Deposited Thin Films with Discharge Characteristics by Modulated Pulsed Power Magnetron Sputtering (MPPMS), *M.K. Lei*, Dalian University of Technology, China

Pure Cu thin films and TiAlSiN nanocomposite thin films are deposited in a closed field unbalanced magnetron sputtering system using the modulated pulsed power magnetron sputtering (MPPMS), in order to understand the

correlation of the microstructure and texture of deposited thin films with the discharge characteristics by MPPMS. The discharge processes at different pressures on the metallic targets are numerically modeled with considering the loss of electrons by cross-B diffusion. With increasing the pressure from 0.1 to 0.7 Pa, both the ion bombardment energy and substrate temperature which are estimated by the modeled plasma parameters decrease, corresponding to the observed transition of the deposited Cu thin films from a void free structure with a wide distribution of grain size into an underdense structure with a fine fiber texture in the extended structure zone diagram. The TiAlSiN thin films are deposited at the ratio of the nitrogen flow rate to the total gas flow rate (f_{N2}) ranging from 0 to 40%. An optimized nanocomposite structure of nc-TiAlN/a-Si$_3$N$_4$ is formed with the 5–10 nm TiAlN nanocrystallites embedded in the 2–3 nm amorphous Si$_3$N$_4$ matrix. Further increasing f_{N2} up to 40%, the grain size of nanocrystallites increase to 10–20 nm with the gradually precipitation of AlN phase, albeit the composition keeps constant. With increasing the partial pressure, the increased ion bombardment energy and substrate temperature are believed to be responsible for the complete phase separation of the nc-TiAlN/a-Si$_3$N$_4$ nanocomposite thin films.

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