

Thursday Morning, November 3, 2011

Advanced Surface Engineering Division
Room: 104 - Session SE-ThM

Nanostructured Thin Films and Coatings

Moderator: C. Mitterer, University of Leoben, Austria

8:00am **SE-ThM1 Characterization of Solution-Processed HfO₂, HfSiO₄, and ZrSiO₄ Thin Films on Rigid and Flexible Substrates for Memristive Applications.** J.L. Tedesco, W. Zheng, O.A. Kirillov, S. Pookpanratana, A.A. Herzing, H.-J. Jang, P.P. Kavuri, N.V. Nguyen, C.A. Richter, National Institute of Standards and Technology

Memristors, nonvolatile bipolar resistive switching devices first intentionally fabricated in 2008 [1], have attracted attention for use in a wide range of applications. To date, most memristors have been fabricated from either TiO_x [1] or TaO_x [2]. However, it is necessary to explore other dielectric materials, because the memristive properties of these dielectrics have not yet been explored.

In this study, memristors were fabricated on both silicon and flexible polyethylene terephthalate (PET) substrates by using HfO₂, HfSiO₄, and ZrSiO₄ thin films and thermally evaporated aluminum contacts. The dielectric films were formed from sol-gel precursors synthesized based on the recipe of Meena et al. [3]. Following synthesis, the precursors were spun on to substrates, exposed to an oxygen plasma, and annealed in air at 150°C for 24 hours. Memristors with cross sectional areas ranging from 2×2 mm² to 0.5×0.5 mm² were fabricated.

The dielectric films were extensively characterized by using optical profilometry and microscopy, x-ray photoelectron spectroscopy (XPS), and deep ultraviolet spectroscopic ellipsometry (SE). The optical profilometry measurements demonstrate that the films show no evidence of significant inhomogeneities due to the solvent-based sol-gel synthesis methods. According to the XPS measurements, the films are ≈50% carbon. Such high levels of carbon are reasonable given the synthesis approach employed, and similarly high levels of carbon have been observed previously in TiO₂ films synthesized from sol-gels [4]. From the SE measurements, it is evident that the bandgaps of the HfO₂, HfSiO₄, and ZrSiO₄ films are similar to their predicted values, but the densities of the films are ≈0.5 due to the high amounts of excess carbon. Transmission electron microscopy measurements of the films will also be discussed.

Current-voltage (I-V), capacitance-voltage (C-V), capacitance-frequency (C-f), and conductance-frequency (G-f) measurements were performed at room temperature in a commercial probe station. The I-V measurements indicate that devices fabricated from these films exhibit bipolar resistive switching. Furthermore, optical microscopy images indicate that the switching events are often accompanied by significant changes to the morphology of the active region of the device, particularly when the switching occurs at high voltages. These changes suggest the formation of localized conduction pathways through the dielectric. The C-f and G-f measurements indicate that the capacitive properties of the devices also change following switching events. Additionally, after 24 days, retention tests show the devices are still in the ON state, thus, they may be considered nonvolatile.

References

- [1] D.B. Strukov et al., *Nature* **438**, 80 (2008).
- [2] J.J. Yang et al., *Appl. Phys. Lett.* **97**, 232102 (2010).
- [3] J.S. Meena et al., 2010 3rd International Nanoelectronics Conference (INEC), **1-2**, 992, 2010.
- [4] J.L. Tedesco et al., *ECS Trans.* **35**, 107 (2011).

8:20am **SE-ThM2 Tensile Testing of Substrate for Fracture Toughness of Thin Films.** S. Zhang, X. Zhang, Nanyang Technological University, Singapore **INVITED**

Measurement of fracture toughness for bulk materials is a routine but extremely difficult and still not standardized for thin films (or coatings). The difficulties in clamping a freestanding thin film and the requirement of a critical dedicate loading system are the main obstacles. In this talk, a method is proposed to carry out tensile loading of the substrate to avoid both problems. The film is deposited on a rectangular silicon wafer on which an edge crack is fabricated beforehand. The film is then "micromachined" into microbridges perpendicular to and ahead of the initial substrate crack. A displacement controlled tensile force is applied to propagate the substrate crack and fracture the "microbridges". The critical fracture strain of the microbridge is measured through measuring the strain of the substrate at the respective location of the microbridge. The fracture

toughness of the film is thus obtained in between the un-fractured and the last fractured bridge. A case study is also presented.

9:00am **SE-ThM4 Structure and Properties of TaN-(Ag,Cu) Nanocomposite Thin Films.** J.H. Hsieh, S.Y. Hung, Ming Chi University of Technology, Taiwan, Republic of China, S.Y. Chang, National Chung Hsing University, Taiwan, Republic of China, C. Li, National Central University, Taiwan, Republic of China

TaN-(Ag,Cu) nanocomposite thin films with various Ag/Ti ratios were deposited by reactive co-sputtering on Si(001) substrates. The samples were then annealed using RTP (Rapid Thermal Processing) at 400 °C to induce the nucleation and growth of Ag/Cu nano-particles in TaN matrix and on film surface. One set of TaN-(Ag₆₀Cu₄₀) were annealed at various temperatures. The structure and morphologies were examined using XRD, FESEM, and HRTEM. Nano-indenter was used to study the variation of mechanical properties. The results reveal that the mechanical properties were affected by the annealing temperature rather than the atomic ratios of Ag/Cu. However, the anti-bacterial behaviors against *E. coli* and *S. aureus* were significantly affected by the Ag/Cu ratios.

9:20am **SE-ThM5 Nanoporous Osmium-Ruthenium Thin Film Coatings for Dispenser Cathodes.** P. Swartzentruber, T.J. Balk, University of Kentucky

Nanoporous osmium-ruthenium may be applicable as an improved coating for dispenser cathodes used in travelling wave tubes and other various vacuum tube devices. Osmium-Ruthenium (OsRu) was co-deposited with either magnesium (Mg) or scandium (Sc) as a sacrificial element to form an intermetallic thin film. The sacrificial element was then selectively etched away, which dealloyed the film and left behind a nanoporous structure. Electron microscopy, x-ray diffraction, and x-ray photoelectron spectroscopy were used to characterize the morphology, structure, and composition of the films in both the as-deposited and dealloyed states. Various film compositions and dealloying conditions were studied to determine the optimal conditions for creating a nanoporous film structure.

9:40am **SE-ThM6 Influence of Chemistry and Structure on the Thermal Stability and Oxidation Resistance of Ti-Al-N.** P.H. Mayrhofer, L. Chen, J. Paulitsch, Montanuniversität Leoben, Austria, Y. Du, Central South University, China

The excellent hardness, good abrasive and sliding wear resistance and high thermal stability and oxidation resistance favor Ti_{1-x}Al_xN to be used as hard protective coating in a variety of industrial applications such as advanced machining and forming tools, automobile and aerospace industry or for semiconductor electronics. Although, thin films based on this material system are investigated in detail, only little is known on the sequential relations between deposition conditions, chemistry, structure and physical and mechanical properties.

Here we show that Ti_{1-x}Al_xN coatings can be synthesized by magnetron-sputtering in single-phase cubic (NaCl, c) structure for x = Al/(Ti+Al) ratios up to 0.62 and single-phase hexagonal (ZnS-wurtzite, w) structure for x ≥ 0.75. These critical values for the individual favored structures strongly depend on the deposition conditions used such as N₂-partial pressure and resulting growth rate. Generally, a low N₂-partial pressure and a high growth rate favor the cubic structure. Increasing Al content of the single-phase cubic coatings results in increased hardness (to ~35 GPa for c-Ti_{0.38}Al_{0.62}N), earlier onset of the decomposition towards the stable phases c-TiN and w-AlN (across the formation of Ti-rich and Al-rich cubic nm-sized domains) and increased oxidation resistance. The single-phase wurtzite-structure coatings exhibit a high thermal stability and better oxidation resistance as compared to the single-phase cubic structure coatings. Even after 40h at 800 °C in ambient atmosphere the w-Ti_{0.25}Al_{0.75}N coating exhibits only an ~1 μm thin dense oxide layer on top of the ~2 μm remaining nitride, whereas the other coatings are already fully oxidized.

The coatings with a dual-phase or mixed-phase structure in the as deposited state show a reduced thermal stability and oxidation resistance as compared to the single-phase cubic or wurtzite structure coatings.

Furthermore, we show that a post-deposition annealing treatment of c-Ti_{0.48}Al_{0.52}N to 900 °C results in a hardness increase from 29 to 32 GPa (due to the formation of cubic nm-sized domains) as well as an increased oxidation resistance. Hence, our results provide insight in designing-strategies for coatings with increased mechanical, thermal stability and oxidation resistance.

10:40am **SE-ThM9 Design of Catalytically Active Nanostructured Coatings for Severe Tribological Applications**, *A. Erdemir, O.L. Eryilmaz*, Argonne National Laboratory

Nanostructured and composite coatings are very unique in the field and offer many attractive properties for a wide range of demanding applications. They can also provide the kind of flexibility that is needed for achieving highly protective, super-slippery boundary films on lubricated tribological surfaces. In this study, we explored the possibility of nano-scale designing of a new class of catalytically active super-hard nitride coatings which when used under boundary lubricated sliding conditions can produce a carbon-rich boundary film. The Raman spectra of the carbon film are similar to that of the diamondlike carbon coatings typically produced by CVD and PVD methods. In a wide range of tribological test systems, such carbon-rich boundary films were shown to provide extreme resistance to scuffing and provide very low friction and wear even under the harshest tribological conditions. In this paper, we will mainly concentrate on the structural and chemical nature of these films and present a hypothetical model to explain their unusual tribological properties under severe contact conditions.

11:00am **SE-ThM10 Structure and Electrical Properties of Nb-Ge-C Nanocomposite Coatings**, *O. Tengstrand*, Linköping University, Sweden, *N. Nedfors*, Uppsala University, Sweden, *L. Fast*, SP Tech. Res. Inst. of Sweden, *A. Flink*, Impact Coatings AB, Sweden, *A.M. Andersson*, ABB AB, Corporate Research, Sweden, *U. Jansson*, Uppsala University, Sweden, *P. Eklund*, *L. Hultman*, Linköping University, Sweden

Nanocomposite ceramic coatings are being explored based on their good tribological and electrical properties, which can be tailored by changing e.g. the composition, microstructure, and surface morphology. For example, the nc-TiC/a-SiC nanocomposite system has shown promising properties for electrical contact applications [1, 2]. The tendency to form oxides and carbides greatly influences these properties. For instance, NbC has similar electrical properties as TiC, but has a lower tendency to form oxides. Especially for low force electrical contact applications, this makes NbC a suitable choice as replacement for TiC. Ge is in the same group as Si, but does, as a more noble element, not form carbides or oxides as easily. Here, we investigate the Nb-Ge-C material system with respect to nanostructure and electrical properties.

Nb-Ge-C thin films were deposited onto Si(001) and Ni-electroplated bronze substrates using dc magnetron sputtering in an Ar discharge at a low temperature (200 °C). By use of three elemental targets in current-regulating mode both the Nb/C ratio and the Ge content was varied to study the effect of composition. XRD, TEM, and SEM showed that the NbC films are columnar and exhibit a preferred 111 crystallographic orientation. With increasing Ge content up to 10 at.%, the NbC grain size was reduced to ~5 nm with a random orientation. While the nc-NbC/Ge nanocomposites have no discernable amorphous tissue phase, XPS showed predominantly Ge-Ge with only little Ge-C bonds. In contact resistance measurements the films performed well (1.7-3.7 mΩ) in comparison to Ag reference (1.2 mΩ) at a contact force of 10 N.

[1] Eklund,P., Surface Engineering, 23, (2007), 406

[2] Lauridsen,J.; et al. Surf. Coat. Technol., 205, (2010), 299

11:20am **SE-ThM11 Tuning the Properties of Chromium Oxynitride Coatings**, *L. Castaldi*, Oerlikon Balzers AG, Liechtenstein, *J. Patscheider*, EMPA, Switzerland, *V. Shklover*, ETH Zurich, Switzerland, *D. Kurapov*, *A. Reiter*, Oerlikon Balzers AG, Liechtenstein

CrO_xN_{1-x} coatings deposited by reactive cathodic arc evaporation were investigated for concentration levels oxygen between 0 and 1. The present study shows some of the possibilities for tuning the crystallographic and electronic properties of chromium oxynitride films by progressively increasing the oxygen concentration. Upon oxygen addition the CrO_xN_{1-x} films remain in the face-centered cubic B1 structure of CrN for oxygen fractions of up to x = 0.70. At higher oxygen contents the properties of the films approach those of Cr₂O₃ and crystallize in the corundum structure. The gradual decrease of the stress-free lattice parameter of the films with the B1 structure at higher oxygen concentrations is consistent with oxygen substituting progressively nitrogen atoms. The almost random orientation of oxygen-free CrN films transforms to a distinct (001) preferred orientation with the increase of oxygen concentration in the films. XPS investigations prove enhanced charge transfer from Cr to O 1s with increasing x with respect to N by changes in the core-level binding energies (BE) of the Cr 2p_{3/2} and N. A shift of the valence band edge toward higher BE indicates a decrease of electrical conductivity of the films with increasing oxygen content.

11:40am **SE-ThM12 Synthesis of Al-Cr-O and Al-Cr-O-N Thin Films in Corundum-Type Structure by Reactive r.f. Magnetron Sputtering**, *M. Stueber*, Karlsruhe Institute of Technology (KIT), Germany, *D. Diechle*, *Walter AG*, Germany, *H. Leiste*, *S. Ulrich*, Karlsruhe Institute of Technology (KIT), Germany

The PVD synthesis of wear and oxidation resistant aluminum oxide and derivative coatings is currently attracting large scientific and technical interest. Ternary Al-Cr-O thin films with mechanical properties comparable or superior to binary Al-O thin films can be deposited at moderate deposition temperatures. New coatings from the quaternary Al-Cr-O-N system could even offer increased strength, hardness and toughness. A combinatorial approach to the growth of Al-Cr-O-N thin films by means of reactive r.f. magnetron sputtering will be presented. For specific deposition conditions well adherent, nanocrystalline Al-Cr-O-N thin films with high Vickers hardness and elastic modulus values were grown at non-equilibrium conditions on cemented carbide and silicon substrates. Detailed results on the coatings composition, constitution, microstructure and properties will be presented and discussed in comparison to ternary Al-Cr-O thin films deposited under identical conditions.

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