

Thursday Afternoon, October 31, 2013

Advanced Surface Engineering

Room: 203 C - Session SE+NS+TF-ThA

Nanostructured Thin Films and Coatings

Moderator: C. Mitterer, Montanuniversität Leoben

2:00pm **SE+NS+TF-ThA1 John A. Thornton Memorial Award Lecture - Control of Micro- and Nanostructure in Hard Coatings: Recent Advances**, I.G. Petrov*, J.E. Greene, L. Hultman, University of Illinois at Urbana Champaign and Linköping University, Sweden **INVITED** Polycrystalline TiN and related transition-metal nitride (TMN) thin films are typically deposited by reactive magnetron sputter deposition and employed as diffusion barriers in microelectronics as well as hard, wear-, and corrosion-resistant coatings in mechanical and optical applications. We use a combination of HR-XRD, TEM, HR-XTEM, AFM, and STM analyses to characterize micro- and nanostructures. We will review the fundamental film growth processes - nucleation, coalescence, competitive growth, and recrystallization - and their role in thin film microstructure evolution as a function of substrate temperature. Special attention will be paid to in-situ substrate treatment by ion-irradiation and its effect on film microstructure and adhesion. Using spontaneous natural patterning processes, we show that self-organized nanostructures consisting of commensurate nanolamellae, nanocolumns, nanospheres, and nanopipes can be synthesized to further extend the range of achievable properties. All of these structures are a result of kinetic limitations and require low growth temperatures combined with low-energy (less than the lattice atom displacement potential), very high flux, ion irradiation during deposition. Quantitative information of adatom transport and surface site energies required for the models are obtained from in-situ high-temperature STM and LEEM analyses. In addition, we use classical molecular dynamics and the modified embedded atom method formalism to investigate the dynamics of atomic-scale transport and film growth on a low-index model compound surface, TiN(001). This approach allows us to gain insight in kinetics of the pathways of Ti, N, and TiN_x (x = 1 – 3) adspecies on terraces and single-atom-high TiN(001) in the picosecond regime which are not accessible by state of the art atomistic experimental techniques or by static DFT calculations. We will also review recent advances in the selective use of metal ions during HIPIMS co-sputtering to extend the attainable structures and properties in metastable TMN with examples of Ti_(1-x)Al_xN, Ti_(1-x)Si_xN, and Ti_(1-x)Ta_xN.

2:40pm **SE+NS+TF-ThA3 High Pressure and High Temperature Stabilization of Cubic AlN in Ti_{0.60}Al_{0.40}N**, N. Norrby, H. Lind, Linköping University, Sweden, G. Parakhonskiy, University of Bayreuth, Germany, M.P. Johansson-Jöesaar, F. Tasnádi, Linköping University, Sweden, L.S. Dubrovinsky, N. Dubrovinskaya, University of Bayreuth, Germany, I.A. Abrikosov, M. Odén, Linköping University, Sweden

As-deposited cubic Ti_{0.60}Al_{0.40}N, mainly used as a hard coating on metal cutting tools, decomposes in two steps at elevated temperatures and ambient pressure. The first step is a spinodal decomposition where coherent nanostructured cubic TiN- and AlN-rich domains are formed, after which a transformation of cubic AlN into hexagonal AlN is followed. In the present work, the decomposition of arc evaporated Ti_{0.60}Al_{0.40}N at elevated temperatures and quasi hydrostatic pressures has been studied both experimentally and by first-principles calculations. High pressure and high temperature treatment of the samples was realized using the multi anvil press and diamond anvil cell techniques. The products of the HPHT treatment of Ti_{0.60}Al_{0.40}N were investigated using x-ray diffractometry and transmission electron microscopy. Complimentary calculations show that both hydrostatic pressure and high temperature stabilize the cubic phase of AlN which is in excellent agreement with the experimental results. In addition, the experimental results suggest that the presence of Ti in the system serves to increase the stability region of the cubic AlN phase. The results are industrially important as they show that Ti_{0.60}Al_{0.40}N coatings on cutting inserts do not deteriorate faster under pressure due to the cubic AlN to hexagonal AlN transformation.

3:00pm **SE+NS+TF-ThA4 Surface Chemistry and Interaction with Polymers of TiAlNO Protective Coatings Deposited by HPPMS**, C. Kunze, S. Waschke, University of Paderborn, Germany, M. Baben, D. Music, J.M. Schneider, RWTH Aachen University, Germany, G. Grundmeier, University of Paderborn, Germany

Plasma deposited coatings of TiAlN and TiAlNO are a promising approach to decrease wear and friction of tools within polymer processing such as extrusion and injection molding. Up to now the mechanisms defining the interaction between the protective coating and the polymer melt are not well understood.

An experimental approach is presented that analyzes the surface chemistry of TiAlN and TiAlNO films as a function of film composition and deposition parameters by means of X-ray photoelectron spectroscopy (XPS). The investigated coatings were synthesized via high power pulsed magnetron sputtering (HPPMS) under varying plasma compositions.

It could be shown that the surface composition of TiAlNO films significantly differs from the integral film composition due to a passivation of the surface near region upon contact with ambient atmosphere or residual gas immediately after deposition[1]. These effects have to be taken into account considering adhesion phenomena and interaction with the polymer melt.

The formation of the passive layer on TiAlN was monitored *in-situ* by time resolved XPS spectroscopy with a time resolution of several seconds. It could be shown that the kinetics of the oxidation reaction is quite fast and occurs within a few minutes even at low oxygen partial pressures of less than 1·10⁻⁸ mbar. The experimentally observed preferential oxidation reaction of a single element (Ti vs. Al) is compared to DFT based simulations.

The interaction of the TiAlNO passive layer with polymers (polypropylene and polycarbonate) was studied towards a technical application within plastics processing. Besides the passive layer a native contamination film consisting of low-weight (hydro-)carbon species adsorbed from the environmental atmosphere has to be discussed when considering the adhesion to the polymer phase.

To investigate the role of the surface contaminations, an approach using a model adsorbate which carries a marker element (such as P or F) was chosen. TiAlNO coatings with model adsorbate surface layers were brought into contact with the polymer melt. The interface between the coating and the polymer was cleaved under high vacuum conditions to avoid re-contamination from the atmosphere. It could be shown that the adsorbate layer remains on the TiAlNO coating even during contact with the polymer melt. Thus the native contamination layer also has to be carefully considered for the interaction and adhesion to the polymer.

[1] C. Gnoth, C. Kunze, M. Hans, M. to Baben, J. Emmerlich, J. M. Schneider, G. Grundmeier, *Surface chemistry of TiAlN and TiAlNO coatings deposited by means of high power pulsed magnetron sputtering*. J. Phys. D., 46, 2013.

3:40pm **SE+NS+TF-ThA6 Oxidation Resistant Zr/Hf-Si-B-C(-N) Films with High Electrical Conductivity**, P. Zeman, S. Proksova, J. Kohout, P. Mares, R. Cerstvy, J. Vlcek, University of West Bohemia, Czech Republic Zr-B-C and Hf-B-C films prepared in our laboratories by nonreactive magnetron sputtering have showed very interesting properties, such as an enhanced hardness (~37 GPa), high electrical conductivity (~2x10⁶ Ωm) and resistance to oxidation up to 600°C in synthetic flowing air.

In the present paper, the effect of Si and N addition on high temperature behavior of Zr/Hf-Si-B-C(-N) films is systematically investigated with aim to extend oxidation resistance to higher temperatures while keeping the films electrically conductive. The Zr/Hf-Si-B-C(-N) films with hardness ranging from 20 to 30 GPa were deposited on Si(100) substrates by dc pulsed magnetron co-sputtering of a single B₄C-Zr/Hf-Si target (with a fixed 15% Zr/Hf fraction in the target erosion area) in argon or nitrogen-argon gas mixtures. The Si and N content in the as-deposited films was varied in a wide range by the Si fraction in the target erosion area and by the N₂ fraction in the nitrogen-argon gas mixtures, respectively. Oxidation resistance of the Zr/Hf-Si-B-C(-N) films was investigated in synthetic air using a symmetrical high-resolution Setaram TAG 2400 thermogravimetric system. Changes in the structure, elemental composition and surface morphology of the films subjected to oxidation tests were analyzed by X-ray diffraction, Rutherford backscattering spectroscopy and optical microscopy. Electrical resistivity of the as-deposited and annealed films was measured by a standard 4-point method and mechanical properties by microindentation.

* John A. Thornton Memorial Award Winner

The results obtained show that an addition of Si positively affects oxidation resistance of the films resulting in a reduction of their mass gains. The Zr-Si-B-C films deposited with the 20% Si fraction in the target erosion area are oxidation resistant up to 650°C and the mass gain detected at 800°C is less than 0.01 mg/cm². An addition of N into the Zr-Si-B-C films results in a further shift of the onset of oxidation to higher temperatures. The films deposited with the 20% Si fraction in the target erosion area and with the 15% N₂ fraction in the gas mixture are oxidation resistant at least up to 1000°C. As-deposited electrical conductivity and hardness of the Zr-Si-B-C-N films is maintained up to 900°C after dynamical heating in air for the 5% and 10% N₂ fractions in the gas mixture. Preliminary data on the Hf-Si-B-C and Hf-Si-B-C-N films deposited at the same process parameters show even better oxidation behavior and thermal stability of electrical conductivity and hardness. These results will be discussed as well.

4:00pm **SE+NS+TF-ThA7 Interfacial and Inter-Diffusion Studies of Epitaxial TiN/Cu Layers on MgO(001)**, *M. Mühlbacher, F. Mendez Martin*, Montanuniversität Leoben, Austria, *B. Sartory*, Materials Center Leoben Forschung GmbH, Austria, *J. Keckes*, Montanuniversität Leoben, Austria, *J. Lu, L. Hultman*, Linköping University, Sweden, *C. Mitterer*, Montanuniversität Leoben, Austria

Interface-controlled materials are widely applied in microelectronics as thin conductive or isolating layers and as diffusion barriers. Degradation of such barrier layers by segregation or diffusion typically results in failure of the device. Thus, as the basis for further enhancement of their reliability, a fundamental understanding of diffusion in these interface-controlled layer materials is necessary.

The Cu/TiN thin film system investigated in the present study is of particular technological relevance, with Cu layers being used as interconnectors and TiN as a diffusion barrier material. TiN layers were grown on (001) oriented MgO substrates by unbalanced DC magnetron sputter deposition at a substrate temperature of 700°C in an Ar/N₂ atmosphere. Subsequently, within the same deposition run, Cu top-layers were deposited at 50°C in pure Ar. To investigate the efficiency of the TiN barrier layer against in-diffusion of Cu, these bi-layer samples were then annealed in vacuum for 60 minutes at 600 and 900°C, respectively.

Pole figures and electron back-scatter diffraction orientation maps indicate that both layers in the as-deposited state are single-crystalline with a cube-on-cube epitaxial relationship with the substrate. This epitaxial relationship is confirmed by selected area electron diffraction patterns. The interfaces were studied on an atomic scale by a combination of high-resolution transmission electron microscopy (HRTEM) and laser-assisted three-dimensional atom probe tomography (3D-APT). HRTEM confirms the single-crystalline structure of each layer and atomically sharp interfaces between both Cu-TiN and TiN-MgO. 3D-APT and energy dispersive X-ray spectroscopy mappings were used to determine the elemental distribution over the interface in the as-deposited and annealed state, enabling to illuminate the inter-diffusion behavior.

4:20pm **SE+NS+TF-ThA8 The Effect of Si Alloying on the Thermal Stability of Al₂O₃ Films Deposited by Filtered Cathodic Arc**, *F. Nahif, D. Music, S. Mráz, H. Bolvardi, L. Conrads, J.M. Schneider*, RWTH Aachen University, Germany

The effect of Si additives on the phase transformation sequence and phase formation temperatures was investigated for filtered cathodic arc deposited Al₂O₃ thin films.

The here obtained XRD data suggest that by addition of Si the transformation of γ - to δ - and θ -Al₂O₃ is restrained by 100°C extending the thermal stability range of the δ - and θ -phase by $\geq 200^\circ\text{C}$ with respect to the unalloyed Al₂O₃ thin film. The formation of α -Al₂O₃ is restrained by 200°C upon addition of Si. Furthermore, the formation of orthorhombic mullite is observed at $\geq 1300^\circ\text{C}$ for the Si alloyed samples, while single phase α -Al₂O₃ is obtained for the unalloyed films at 1100°C.

According to the experimentally observed stabilization of the metastable γ - to δ - and θ -Al₂O₃ phases and the restrained α -Al₂O₃ phase formation upon Si addition the presence of amorphous SiO₂ at the grain boundaries, which may impede mass transport and hence crystalline growth, appears to be the cause of the here reported stabilization. Inconsistency of the Si bonding data obtained by XPS with the notion of a solid solution of Si in the alumina lattice suggests that this cannot serve as an explanation for the stability enhancement.

4:40pm **SE+NS+TF-ThA9 A Multitechnique Study of the Interfacial Reaction between TiO₂ Surfaces and Molybdenum**, *X. Noirfalise*, University of Mons, Belgium, *D. Cossement*, Materia Nova, *J.-F. Paul*, Université Lille, France, *F. Renaux*, Materia Nova, *R. Snyders*, University of Mons, Belgium

Recently, TiO₂ surfaces supporting metals, used in numerous fields of application, have generated a lot of works because of the relationship between the morphology of the deposit and the electronic interactions at the TiO₂/metal interface. As an example, oxygen deficient MoO_x compound supported on TiO₂ substrates demonstrate interesting catalytic properties. Accordingly, the growth of ordered MoO_x nanostructures (nano-particles or ultrathin films) on TiO₂ is of particular importance. Until now, the influence of the chemistry of the support on the deposit morphology is mainly studied. No systematic studies of the impact of the crystallographic constitution of the TiO₂ substrates on the morphology of ultrathin (< 5 nm) Mo films have been reported yet. The objective of this work is to address this question.

We grew, by non-reactive DC sputtering of a metallic Mo target, MoO_x films on home-made (reactive sputtering) and standard TiO₂ supports. The TiO₂ supports differ by their crystallographic constitution (amorphous, anatase and rutile). A particular attention is made on the influence of the TiO₂ properties on the diffusion mechanism and oxidation process at the interface TiO₂/MoO_x using XPS and ToF-SIMS measurement. Periodic DFT calculations have been performed to support the experimental data.

XPS measurements showed that the interfacial reaction between the TiO₂ surface and the deposited Mo is affected by the crystalline properties of the TiO₂ support. The strong oxidation of the first monolayer of the deposited Mo is evidenced. Differences were found in the electronic exchange and, as a consequence, in the growth mode for the three TiO₂ substrates. The emphasis is made with the Cabrera-Mott theory, namely the dependence of the interface reaction on the bulk electronic structure of the three phases.

The data are supported by ToF-SIMS depth profile measurements revealing the substrate-dependent diffusion of oxygen at the interface with appearance of a more or less important oxygen depleted zone at the surface of the TiO₂ support. Additional measurements performed with Ti¹⁸O₂ substrates as well as DFT calculations support the initial conclusion.

The growth mechanisms were estimated from the analysis of the peak and background shapes of the XPS signal by using the "QUASES" software. Due to the differences of the electronic exchange at the interface, a layer-by-layer growth mode is observed for Mo deposited on the (110)-rutile substrate, a Volmer-Weber growth mode is observed on the (101)-anatase substrate and a Stranki-Krastanov growth on the amorphous one.

5:00pm **SE+NS+TF-ThA10 Ordered Arrays of Solid and Nanoporous Nanostructures: Particles, Alloy Particles, Pillars, Composites - From Design to Applications**, *P. Schaaf, D. Wang, Y. Yan, A. Herz*, TU Ilmenau, Germany

INVITED

Nanostructured materials gained attention for many applications due to their size effects on both physical and chemical properties and the effects of increased surface area. Modern nanotechnologies can fabricate nanostructured materials in different forms and with different structures, compositions and phases. Furthermore, a combination of different methods in nanotechnologies provides even more possibilities to design nanostructured materials with more diversity and complexity. Here, some examples will be presented. Metallic nanostructures are very interesting in catalysis and plasmonics. Ordered arrays of pyramidal pits were structured into the Si substrate by using nanoimprint lithography. After deposition of a thin Au film on a pre-patterned substrate, a dewetting process leads to the formation of ordered arrays of nanoparticles. Dewetting is a simple method to form metallic nanoparticles by reducing the surface energy. Structured substrates can modulate the chemical potential during dewetting, so that the ordered arrays of nanoparticles can result from the dewetting on pre-patterned substrates. By dewetting of bi-layers with two different types of metals, alloy nanoparticles can be formed. By tuning the layer thickness ratio and the total layer thickness, the particle size and composition of the particles can be well controlled. For example, the ordered arrays of Au-Ag alloy nanoparticles are fabricated by a combination of nanoimprint lithography and dewetting of Au/Ag bi-layers. By that, ordered arrays of nanoporous gold nanoparticles can be realized by combining a further process step of dealloying. Dealloying is a selective removing process, and nanoporous gold particles are formed by removing the Ag out of the Au-Ag alloy particles via submerging the sample in a HNO₃ solution. The plasmonic property of the porous gold nanoparticles is clearly different from the solid gold nanoparticles with similar particle size.

Ordered arrays of single crystalline nanoporous Si nanopillars are fabricated by a combination of nanoimprint lithography and metal-assisted chemical etching. The pillar structure is first defined on the Si wafer via nanoimprint lithography, and then a thin Au film is deposited on the wafer. The metal-assisted chemical etching is performed in a solution consisting of HF and

H₂O₂, and the Au film acts as catalyst for the etching process. The etching process with highly doped p-type Si leads to the formation of porous pillars. By combining a further process step of biomimetic synthesis, porous Si/TiO₂ core/shell nanocomposite pillars are successfully produced. Besides, the TiO₂ is N-doped and also partially filled in the porous Si core.

5:40pm **SE+NS+TF-ThA12 Silicone Nanofilaments as a Novel Carrier Material for Catalysts**, *G.R. Meseck, S. Seeger*, University of Zurich, Switzerland

Immobilization of molecular and nanoparticulate catalysts on carrier materials is crucial to facilitate their handling and recycling as well as to minimize environmental and health risks. While ceramic and oxidic carrier materials provide stability under rough working conditions, engineering possibilities and applications are restricted to extruded or pressed shapes. We introduce silicone nanofilaments (SNFs) as a promising alternative because they can be grown as a thin film on a variety of substrates such as glass, metals and polymers of different composition and shape. A surface bound carpet of SNFs is formed which induces a high surface roughness and conveys the unique physico-chemical properties of a silicone polymer to the coated surface. The procedure uses easily available silane precursors and proceeds via either vapor deposition or solvent based routes. The shape and size of the single filaments within the carpet is tunable and they typically show a high aspect ratio with diameters from 50 to 100 nm and lengths on the micrometer scale. To exploit SNFs as a carrier material we applied deposition-precipitation (DP) to finely disperse titania nanoparticles (TiO₂-NPs) along the filaments. The thus obtained easily recyclable composite of SNFs and TiO₂-NPs showed photocatalytic performance in the degradation of methylene blue which was superior to TiO₂-NPs on a flat reference. While DP can in principle be used to deposit a variety of powerful catalysts, we also investigated physical vapor deposition as a complementary approach. Here, SNFs were uniformly coated with platinum metal via sputter coating. In the hydrogenation of 4-Nitrophenol we proved that this composite material represents a recyclable and easy to handle alternative to nanoparticle based systems.

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