

Advanced Surface Engineering Division Room 202C - Session SE-MoA

New Challenges and Opportunities in Surface Engineering

Moderators: Robert Franz, Montanuniversität Leoben, Austria, Jianliang Lin, Southwest Research Institute

1:20pm SE-MoA1 From Passive to Active Optical Coatings - Challenges and Opportunities for Pulsed Plasma Deposition Processes, *Ludvik Martinu*, Ecole Polytechnique de Montreal, Canada **INVITED**

Optical coating (OC) applications represent a multibillion dollar market worldwide; they range from antireflective (AR) coatings found in most optical components and low emissivity windows in buildings and automobiles to narrowband optical interference filters used in telecommunications. As the range of applications of OCs continuously broadens and extremely attractive market opportunities arise, it is becoming increasingly important to develop new nanostructured thin film materials with specific multifunctional properties. Further progress in this fast evolving field is strongly stimulated by a simultaneous action of two forces: a) the “pulling force” represented by the economic, technological and societal needs, including sustainable development, and b) the “pushing force” related to the curiosity-driven nanotechnology combining new design concepts of materials and devices, fabrication processes and innovative characterization tools, where the only limitation frequently appears to be our imagination.

This presentation will describe a holistic approach to OCs based on a broad and in depth knowledge of the interplay between the design, material, process and performance assessment with respect to specific applications and coating system durability in demanding environments. It will review the progress and future opportunities for the use of discrete, graded, and nanostructurally-controlled architectures benefiting from the nanomaterials’ meta-structures, advanced deposition techniques including high power impulse magnetron sputtering (HiPIMS) and tailored plasma- and ion-surface interactions, as well as complex systems implementing active (smart, tunable) materials.

Tomorrow’s trends will be illustrated by examples from different fields of applications ranging from passive hybrid elastic OC for ophthalmic lenses, hard protective OC for displays, and optical interference filters for gravitational waves detection to active OC and advanced glazings for energy saving using smart windows, active color-shifting security and authentication devices, and smart radiators with self-tuned emissivity for the thermal management in satellites.

2:00pm SE-MoA3 Anomalous Orientation-dependent Slip during Uniaxial Compression of TaC Crystals, *M. Chen*, ETH Zurich, Switzerland; *D.G. Sangiovanni*, Ruhr-University Bochum, Germany and Linköping University, Sweden; *A. Aleman*, *H. Zaid*, University of California at Los Angeles; *J.M. Wheeler*, ETH Zurich, Switzerland; *G. Po*, *Suneel Kodambaka*, University of California at Los Angeles

Binary carbides of group IV-VI transition-metals are hard, stiff, and high-melting solids with excellent high-temperature mechanical and chemical stabilities and good resistance to wear, ablation, and corrosion. Recent studies suggest that cubic B1-structured group IV and V transition-metal carbides, ZrC and TaC, are not intrinsically brittle and that they can exhibit plasticity under compression. Here, we present our results obtained using a combination of *in situ* scanning-electron-microscopy-based uniaxial micro-compression tests and *ab initio* molecular dynamics simulations conducted on TaC crystals, along with density functional theory calculations and finite-element based modeling of discrete dislocation and crack dynamics. We find that the room-temperature mechanical behavior of TaC is highly anisotropic and the operating slip systems are not necessarily those expected based on their Schmid factor. We find that the room-temperature mechanical behavior of TaC is highly anisotropic with yield strengths as high as ~17 GPa for $\{110\}$ and as low as ~5 GPa for $\{111\}$ crystals. Interestingly, the operating slip systems are not necessarily those expected based on their Schmid factor. We attribute the observed behavior to the normal component of the applied forces (in the direction perpendicular to the slip), whose magnitude varies with the slip plane and the crystal orientation. This anomalous slip results in the activation of $\{110\}$ slip systems during uniaxial compression of $\{110\}$, $\{111\}$, and $\{111\}$ crystals and $\{111\}$ slip systems in $\{110\}$ crystals and leads to the observed anisotropy in yield

strengths. We suggest that similar behavior should be expected in this class of materials.

2:20pm SE-MoA4 Selectable Phase Formation in Al-based Transition Metal Nitride Films by Controlling Al⁺ Subplantation depth during HIPIMS Deposition, *Grzegorz Greczynski*, Linköping University, Sweden; *S. Mraz*, *M. Hans*, RWTH Aachen University; *J. Lu*, *L. Hultman*, Linköping University, Sweden; *J.M. Schneider*, RWTH Aachen University, Germany

Alloying with Al is a common strategy to improve thermal and chemical stability of transition metal nitride (TMN) coatings deposited by magnetron sputtering. The solubility of Al in rock-salt-structure TMNs is, however, limited which presents a great challenge to increase Al concentration substantially, while avoiding precipitation of thermodynamically-favored wurtzite-AlN phase (*w*-AlN), which is detrimental to mechanical properties.

We present a novel thin film deposition method, which allows for unprecedented control over the phase formation in metastable TMN layers. The technique relies on hybrid high power impulse/dc-magnetron co-sputtering (HIPIMS/DCMS) of elemental targets in Ar/N₂ gas mixture with precise synchronization of the substrate bias pulse to the Al⁺-populated portion of the HIPIMS discharge which is superimposed onto a continuous TM neutral flux supplied from a DCMS-operated target. This results in a separation of film-forming species in time and energy domains and enables us to overcome the limitations of the conventional processing where phase formation is to large extent determined by the high adatom mobility and gas-ion-induced mixing, both taking place at the very surface, which drive the system towards thermodynamic equilibrium.

To demonstrate versatility of this technique we grow three series of high-Al-content films, namely Ti_{0.28}Al_{0.72}N, V_{0.26}Al_{0.74}N, and Zr_{0.48}Al_{0.52}N, all as a function of the amplitude of the synchronized bias pulse, which corresponds to varying the incident energy of Al⁺ ions E_{Al^+} . For all materials systems, the crystalline phase content is a very sensitive function of E_{Al^+} and can be tuned from completely hexagonal in the limit of low E_{Al^+} values (≤ 60 eV) to pure cubic obtained with $E_{Al^+} \geq 250$ eV. A complete transition from hexagonal *w*-AlN to supersaturated cubic NaCl structure is a consequence of the fact that the subplantation depth of Al⁺ metal-ions increases with increasing E_{Al^+} , as supported by Monte Carlo TRIDYN simulations. This innovative synthesis methodology enables unprecedented control over the phase formation and, hence, film properties and opens novel scientific avenues.

2:40pm SE-MoA5 Metallic-Glass Nanotube Arrays: A Novel Device for Various Applications, *Jinn P. Chu*, *J.K. Chen*, *C.C. Yu*, National Taiwan University of Science and Technology, Taiwan, Republic of China **INVITED**

A new group of thin film metallic glasses have been known to exhibit properties different from conventional crystalline metal films, though their bulk forms are already well-known for properties such as high strength because of their amorphous structure. We successfully fabricated the first-ever metallic glass nanotubes (MGNTs) on Si by a simple lithography and sputter deposition process for very large-scale integration. Like biological nanostructured surfaces, MGNTs show some surprising water repelling and attracting properties. Nanotubes are 500-750 nm tall and 500-750 nm in diameter, shown in Figure 1 [1]. The MGNT surface becomes hydrophobic, repelling water. By heating and cooling the array, water can be repelled and attached to the surface [1]. There are two examples presented in this talk based on modifications of this scheme. First, after modification of biotin, the array acts as a waveguiding layer for an optical sensor. The MGNT sensor waveguide could readily detect the streptavidin by monitoring the shift. The detection limit of the arrays for streptavidin is estimated to be 25 nM, with a detection time of 10 min. Thus, the arrays may be used as a versatile platform for high-sensitive label-free optical biosensing [2]. Second, the array is prepared on a heating device on Si and, with an applied electric voltage to the heating device underneath, the array surface was heated to generate an extending force from these nanochambers so that the array are functioned as biomimetic artificial suckers for thermally adhesion response in biological systems [3].

References

- [1] J. K. Chen, W. T. Chen, C. C. Cheng, C. C. Yu and J. P. Chu, Metallic glass nanotube arrays: preparation and surface characterizations, *Materials Today*, 21 (2018), 178-185.
- [2] W. T. Chen, S. S. Li, J. P. Chu, K. C. Feng, J. K. Chen, Fabrication of ordered metallic glass nanotube arrays for label-free biosensing with diffractive reflectance, *Biosensors and Bioelectronics*, 102 (2018), 129-135.

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[3] W. T. Chen, K. Manivannan, C. C. Yu, J. P. Chu and J. K. Chen, Fabrication of an artificial nanosucker device with a large area nanotube array of metallic glass, *Nanoscale*, 10 (2018) 1366-1375.

3:40pm **SE-MoA8 Biocompatibility and Antibacterial Behaviors of TaON(porous)/TaN-TaN-Ag-Ta Multi-layered Thin Films**, *Joe. H. Hsieh*, Ming Chi University of Technology, Taiwan, Republic of China; *C. Li*, National Yang Ming University, Taiwan, Republic of China; *C.C. Hsu*, Ming Chi University of Technology, Taiwan, Republic of China

In this study, a triple-layered thin film structure was designed and fabricated in order to realize porous and tunable TaOxNy thin films with enhanced biocompatibility and antibacterial behavior. In the design of film structure, the top layer was made of porous and tunable TaOxNy. The porous structure was obtained from TaOxNy-Cu (>50 at.%) thin films deposited by reactive sputtering. After the film was annealed by using RTA (1st annealing), the Cu phase was etched away to form TaOxNy network structure. The bottom layer was TaN-Ag (11 at.%) which is used as a Ag source layer. It also provided toughness and hardness. A thin TaN film was inserted between porous TaOxNy layer and solid TaN-Ag layer, and used as Ag diffusion control layer. The function of this layer was to withstand the 1st annealing, then, during the 2nd annealing, to let certain amount of Ag diffusive to the porous TaOxNy layer, and formed Ag nanoparticles. The films fabricated based on this design were studied systematically on their mechanical properties, Ag particle formation, as well as pore size and morphology. Finally, antibacterial property and biocompatibility of these films were studied in terms of O/N ratio, dealloying process, and Ag diffusion control. The relationships among O/N ratio, Ag nanoparticle formation, porosity, and bio-reactions will be discussed and reported systematically.

4:00pm **SE-MoA9 Electrochemically Deposited Coating with Antibacterial Properties against the Spread of Health Care-associated Infections**, *Nicole Ciacotich*, Technical University of Denmark, Denmark; *J.B. Rasmussen*, Elplatek A/S, Denmark; *K.N. Kragh*, University of Copenhagen, Denmark; *P. Møller*, *L. Gram*, Technical University of Denmark, Denmark

Health care-associated infections (HCAIs) are one of the major causes of patient morbidity during hospitalization. Most, if not all, HCAIs are the consequence of proliferation and transmission of pathogenic microorganisms in hospitals, especially in intensive care units. In addition, a range of items and devices, including hospital furniture (bedrails, frames, door handles) are fomites that often have a high load of pathogenic agents.

In a previous study, we developed an electroplated copper-silver alloy as antibacterial coating on stainless steel to minimize adhesion and transfer of pathogenic bacteria on environmental surfaces. We have characterized the electroplated copper-silver alloy in its microstructure, chemical and electrochemical nature and demonstrated a pronounced antibacterial activity.

The purpose of the present study was to evaluate the antibacterial efficacy in a standardized surface adhesion tests against *Staphylococcus aureus* 8325. We determined the influence of chlorine and phosphorus compounds, well-known complexing agents of copper common in hand sweat and surface detergents, by comparing the antibacterial effect of stainless steel, silver, copper and copper-silver alloy. In presence of phosphates and chlorides, the copper-silver coating showed the highest antimicrobial efficacy followed by copper, compared to stainless steel and silver. In absence of chlorides, there was no statistically significant difference among the different metal surfaces.

We also demonstrated that the antibacterial effect of the copper-silver alloy was considerably reduced if the direct contact between surface and bacteria, but not the passage of ions, was prevented. This suggests that the antibacterial action is mainly due to the so-called contact killing mechanism, which is distinctive of metallic copper, rather than the release of copper ions.

Furthermore, we performed confocal microscopy of bacteria on copper-silver coated surfaces using a modified live/dead staining in order to follow over time the bacterial killing front at the surfaces. This demonstrated, as the assays based on counting, a rapid killing spreading upwards in the bacterial biofilm within 30 minutes.

In conclusion, we believe that the electroplated copper-silver coating can be an effective instrument limiting spread of pathogenic microorganisms causing HCAIs in hospitals and intensive care units.

4:20pm **SE-MoA10 Tunable Self-Healing Thermal Barrier Coatings**, *S.S. Joshi*, *J.J. Gu*, *Y.-S. Ho*, *B.W. Wei*, *T.Y. Hung*, *Y.Y. Liu*, *N.B. Dahotre*, *S.M. Aouadi*, University of North Texas

Oxide ceramics exhibit a wide spectrum of unique properties, but can suffer from unpredictable and often catastrophic crack propagation and fracture, which limits their use in some applications. One possible solution to overcoming this limitation is to leverage the ability of oxides to repair their inherent flaws and cracks, i.e. to self-heal. The aim of the work is to gain new insights into self-healing mechanisms of a subset of ceramic surfaces, namely thermal barrier coatings, in response to thermal stimuli. TBCs are extensively used to protect metallic blades in gas-turbine engines against harsh operating conditions that include elevated temperatures and corrosive environments. Model systems that were investigated include YSZ-Al₂O₃-SiC and YSZ-Al₂O₃-TiC laser processed coatings. The healing process occurs when the carbide phase oxidizes and the resulting oxide flows to the crack site and bonds to the YSZ matrix. The formation of the oxide phase was observed using X-Ray diffraction its formation in the crack site was confirmed using cross-section scanning electron microscopy. The optimum process to create a self-healing composite was determined. Finally, the mechanisms responsible for how the self-healing process impacts deformation and failure resistance as well as corrosion resistance at elevated temperatures was investigated.

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