Advanced Surface Engineering
Room: 302 - Session SE+NS+TR-TuM

Nanostructured Thin Films and Coatings
Moderator: Robert Franz, Montanuniversität Leoben, Andrey Voevodin, Air Force Research Laboratory

8:00am **SE+NS+TR-TuM1 Electrostatic Coating with Ligandless Copper Nanoparticles**, ***Lance Hubbard***, *A.J. Muscat*, University of Arizona

Physical vapor deposition is currently used to deposit copper seed layers in through Si vias, but this approach is already close to its limit and may not be an option for future scaling of high performance integrated circuits. An alternative is electroless deposition (ELD) since it produces conformal, selective coatings at low temperature. ELD occurs by chemical reduction of metal ions without an externally applied potential. In the conventional approach, a metal catalyst such as Pt, Pd, or Ni is used that can be both expensive and increase the resistance of interconnect lines. Previous work was done in an aqueous phase using a complexing agent or polymer to protect the particles. Good film continuity was demonstrated, but the sheet resistance was low.[1,2] In this study, we report on a nonaqueous ELD process that uses a charge compensator, but not a ligand or complexing agent. The weak electrostatic attachment of the charge compensator to the ions and particles in solution and the high pH conditions improve the driving force for metal deposition. Si(100) coupons were hydroxylated using sulfuric acid-hydrogen peroxide mixture. The surface was terminated with an amine adhesion layer by immersion in a 4 mM solution of either (3-aminopropyl)-trimethoxysilane (APTMS) or (3-mercaptopropyl)-trimethoxysilane (MPTMS) in methanol followed by a 150^{o}C anneal. Metal films were deposited by suspending samples in a bath made by dissolving Cu(II) chloride in ethylene glycol, which also served as the reducing agent, and adding 1-butyl-3-methylimidazolium tetrafluoroborate as a charge compensator. The surface plasmon resonance (SPR) peak of the Cu nanoparticles in the bath and film was at 585 nm. Light scattering measurements and transmission electron microscopy (TEM) images yielded a size distribution of 3.1±1.6 nm. The complex consisting of the Cu particle core and ion shell is attracted to the positively charged amine groups at high pH, and a thin metal film is deposited that is both continuous and cohesive. Annealing the coupons at 200^{o}C in nitrogen promoted the formation of an electrically conductive film. Electron microscopy images of the coated substrates show a 20-50 nm thick film of 3 nm dia. particles; spectroscopic ellipsometry shows both bulk and nanophase properties. Four-point probe measurements of the films yielded electrical conductivities in the range 10^5-10^6 S/m (bulk Cu conductivity 4-6x10^7 S/m).

References

1) 1) Armini and Caro, J. Electrochem. Soc. 2010, 157(1), D74-D80, doi: 10.1149/1.3258026.

2) 2) Inoue et al. J. Electrochem. Soc. 2012, 159(7), D437-D441, doi: 10.1149/2.070207jes.

8:20am **SE+NS+TR-TuM2 Electrically Stable Pt-ZrB_2 Nanocomposite Thin Films for High Temperature Applications**, ***Julia Sell***, *D.M. Stewart, G.P. Bernhardt, D.J. Frankel, R.J. Lad*, University of Maine

Considerable cost savings could be achieved by incorporating high temperature sensors into high temperature machinery to optimize processes and monitor materials degradation. However, in order to achieve reliable sensor operation, the thin film electrodes, sensing elements, and packaging materials must remain stable over long times at high temperature. Metallic thin films, such as Pt, agglomerate and lose conductive pathways quickly when exposed to temperatures exceeding 700°C. In this work, we show that Pt-ZrB_2 nanocomposite films retain a continuous morphology and remain electrically conductive up to at least 1100^{o}C in air. Nanolaminate Pt-ZrB_2 films comprised of ten alternating layers of Pt and ZrB_2 were deposited to a total thickness of 200nm at ambient temperature onto sapphire substrates using e-beam evaporation. Annealing the nanolaminate films above 800^{o}C in air causes intermixing, resulting in a nanocomposite Pt-ZrB_2 film architecture. Film electrical conductivities were measured using a 4-point probe as a function of time and temperature in air up to 1200°C. These results show that Pt-ZrB_2 nanocomposite films have conductivities in the 10^6-10^7 S/m range and remain stable above 1000°C, but that the overall conductivity and stability depends on the Pt-ZrB_2 layer thickness ratio. Analysis via x-ray photoelectron spectroscopy and x-ray diffraction indicates that both monoclinic and tetragonal ZrO_2 nanocrystallites are formed in the films during the annealing treatment, and they serve to hinder agglomeration of the Pt phase. Scanning electron microscopy shows highly conductive Pt-rich pathways in the films that coexist with the ZrO_2 phase. Some films were coated with an amorphous Al_2O_3 protective capping layer using atomic layer deposition (ALD), and this capping layer helped to limit oxygen diffusion into the films, thereby increasing the long term stability of film conductivity.

8:40am **SE+NS+TR-TuM3 A Novel Reactive Plasma-Assisted Coating Technique (RePAC) for Thin BN/Crystalline-Si Structures and their Mechanical and Electrical Properties**, ***Koji Eriguchi***, Kyoto University, Japan, *M. Noma*, SHINKO SEIKI CO., LTD., Japan, *S. Hasegawa*, Osaka University, Japan, *M. Yamashita*, Hyogo Prefectural Institute of Tech., Japan, *K. Ono*, Kyoto University, Japan

Cubic boron nitride (c-BN) has attracted much attention as a hard coating film on cutting tools, owning to its high oxidation resistance and hardness—the second hardest material to diamond. Although various methods of forming c-BN films on various substrates have been proposed, the interface between c-BN and the substrate material was unstable against delamination and oxidation [1] after long-time machining and air exposure. In this study, we propose a novel reactive plasma-assisted coating technique (RePAC) for forming sub-µm-thick BN film directly on crystalline Si substrates, where magnetically-confined high-density Ar/N_2 plasma was generated with a stable anodic current to promote the reaction between N radicals and B atoms evaporated onto a Si substrate placed on a sample stage [2]. Controlling substrate bias voltage V_{sub} in the RePAC, we fabricated various thin-BN/Si structures and identified a correlation among the properties such as mechanical hardness, friction coefficient, leakage current, and dielectric constants. TEM analyses revealed that nano-structures of the BN films were varied from bulk amorphous (a)-BN, layered hexagonal (h)-BN, to c-BN phase in turbostratic (t)-BN domain, in accordance with V_{sub} ($|V_{sub}|$=10–120 V). We speculate that bombardment of incident ions (Ar^+ and/or N_2^+) plays a key role in forming these characteristic features, in addition to stoichiometric N and B contents. Moreover, we clarified the high hardness (> 4000HK, by the Knoop indenter) and the dielectric constant higher than previously-reported values (10–20, by the electrical capacitance measurement) for the present thin c-BN/Si structure with anti-delamination feature after long-time air exposure. The obtained results suggest that the present BN film formed by the RePAC has wide applications not only as a hard coating film but also as a high dielectric-constant layer in electronic devices.

[1] For example, P. B. Mirkarimi *et al.*, Mater. Sci. Engin., **R21**, 47 (1997).

[2] M. Noma *et al.*, Jpn. J. Appl. Phys. **53**, 03DB02 (2014).

9:20am **SE+NS+TR-TuM5 Multifunctional Protective Coatings for Aerospace Applications**, ***Etienne Bousser***, *L. Martinu, J. Klemberg-Sapieha*, Ecole Polytechnique de Montreal, Canada **INVITED**

Ever increasing technical, economic and environmental requirements give rise to situations where modern equipment and components are often pushed beyond the limits of their design capabilities. This frequently leads to tribological deficiencies, such as lubrication breakdown, excessive wear and tribo-corrosion, resulting in increased operational costs, decreased efficiency and premature failure. Therefore, appropriate material's selection for a given application must be guided by an accurate understanding of the intervening tribological processes while ensuring the maintained functionality of the surface for optimal application performance.

Solid Particle Erosion (SPE) occurs in situations where hard particles, present in the environment, are entrained in a fluid stream, and impact component surfaces such as in aircraft engines. It is well known that ductile materials erode predominantly by plastic cutting or ploughing of the surface, while brittle materials do so by dissipating the particle kinetic energy through crack nucleation and propagation. In the first part of this presentation, we examine the mechanisms by which surfaces dissipate the kinetic energy of impacting particles, and discuss the erosive response of hard protective coating systems. We investigate the means by which surface engineering can enhance erosion resistance, and correlate surface mechanical properties to the erosion behaviour. In addition, we will show that the architectural design of advanced coating systems is also well supported by finite element modelling of single particle impacts of the coated surfaces.

The second part of the talk will focus on the repairability of advanced coating systems. Indeed, because of the high fabrication costs of engine components, it is desirable to develop an effective and efficient industrially-viable technique to remove defective coatings with the aim of recycling the costly engine components. In particular, we will present our recent studies on the removal of TiN-based erosion resistant coatings using a non-line-ofsight reactive ion etching technique and a complementary laser ablation process.

11:00am **SE+NS+TR-TuM10 Hard Coatings with Designed Thermal Conductivity**, *P.H.M. Boettger,* Empa, ETH Zurich, Switzerland*, V. Shklover,* ETH Zurich, Switzerland*, M. Sobiech,* Oerlikon Balzers Coating AG, Liechtenstein*, **Joerg Patscheider***, Empa, Switzerland

Hardness, thermal stability and oxidation resistance are often the main properties to optimize for most tool coatings developments for industrial applications. The thermal conductivity, however, has been regarded to a much lesser extent as property to improve tool life. So far, only little attention has been given to this fact and the explicit role of thermal conductivity in machining Ti and Ni-based alloys. These materials typically have low thermal conductivity, as well as modern tool coatings such as CrAlN and TiAlSiN. This unfavorable combination may lead to the formation of thermal hot spots during machining, which adds to the premature degradation of such coatings. For these reasons the thermal conductivity is an important process parameter.

This talk will discuss the relations between hardness, coatings architecture and thermal conductivity and how advanced coatings can be tuned to achieve significant anisotropy of the thermal conductivity. In arc-evaporated TiO_xN_{1-x} and CrO_xN_{1-x} thermal conductivity can be adjusted in a wide range between 2 and 35 W/m·K, while keeping hardness and oxidation resistance intact. The data for single phase oxynitrides as well as of multilayered coatings agree well with a newly developed model based on constant phonon scattering cross section of the introduced oxygen. It will be shown how temperature-mitigating multilayer coatings can be prepared using these materials by introducing highly anisotropic thermal conductivity.

11:20am **SE+NS+TR-TuM11 Microstructure and Hardness Gradients in Sputtered CrN Films**, *A. Riedl,* Materials Center Leoben, Austria*, R. Daniel,* Montanuniversität Leoben, Austria*, T. Schoeberl, M. Stefenelli,* Austrian Academy of Sciences*, B. Sartory,* Materials Center Leoben, Austria*, J. Keckes, **Christian Mitterer***, Montanuniversität Leoben, Austria

Hardness and elastic modulus of a sputtered nanocrystalline CrN thin film, grown under varying ion bombardment conditions, were studied by nanoindentation using a depth-profiling technique and related to cross-sectional X-ray nanodiffraction data on the local microstructure. Changes in texture are shown to have almost no effect on the elastic modulus due to the isotropic response of the polycrystals. However, the locally varying growth conditions, which affect crystal size and number, determine the hardness values across the film thickness. Regions with highly distorted small crystals result in higher hardness in comparison to those with well-developed coarsened grains. This work confirms the notion of the existence of growth-related hardness gradients in single-phase nanocrystalline thin films.

11:40am **SE+NS+TR-TuM12 Development of Low Friction Nanocomposite Coatings for Diesel Engine Piston Rings**, ***Jianliang Lin****, R. Wei, K. Coulter, C. Bitsis, P.M. Lee*, Southwest Research Institute

Hard and thick (15-20 µm) TiSiCN nanocomposite coatings have been developed to improve the wear resistance and reduce the overall average friction for diesel engine piston rings. The coatings were deposited by sputtering Ti metal targets in a reactive atmosphere using a plasma enhanced magnetron sputtering (PEMS) process. The reactive mixture contains argon, nitrogen, acetylene gases, and hexamethyldisilazane vapor which were introduced into the chamber using a liquid evaporation/delivery system. The substrates were AISI 304 stainless steel coupons and piston rings. The TiSiCN coatings with different elemental compositions and microstructures were prepared by varying the hexamethyldisilazane and acetylene gas/vapor concentrations and the target power. The microstructure of the coatings was characterized using scanning electron microscopy, energy dispersive spectroscopy, and X-ray diffraction. The adhesion strength and mechanical and tribological properties of the coatings were measured using HRC tests, nanoindentation and ball-on-disk wear tests. By optimizing the composition and microstructure of the coatings, thick TiSiCN nanocomposite coatings with excellent adhesion and a dry sliding friction less than 0.2 have been obtained. The optimized coating systems were applied on the piston rings, which were evaluated on a Plint TE77 reciprocating bench rig and in the real diesel engine test. The principle for the increased wear resistance and the potential applications will be discussed in the paper.

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