Thin Films
Room Makai - Session TF-ThM

Advanced Protective Coatings/Stress Evolution, Nanostructure, and Physical Properties of Thin Films

Moderator: Grzegorz Greczynski, Linköping University, Sweden

8:00am **TF-ThM1 XPS Analysis of a Super-hard Material – Application of Ar Cluster Ions to Probe New Depths in Surface Analysis*, David Surman,*** Kratos Analytical Inc.*; J. Counsell, S.J. Coultas,* Kratos Analytical Ltd., UK*; C. Moffitt,* Kratos Analytical Inc.*; C.J. Blomfield, A.J. Roberts,* Kratos Analytical Ltd., UK

Super-hard inorganic multilayers have emerged in recent times as a distinct class of material, currently used in coatings of cutting tools for machining and in the aerospace industry. There has been significant effort to develop new coatings due to increased need for wear protection and friction reduction.

One such material we will discuss in this work is a TiN/CrN superlattice consisting of alternating TiN and CrN layers of nanometer-scale, deposited by the means of the reactive magnetron sputtering technique. This superlattice has been studied previously, examining performance properties under stress and temperature and the mechanisms of wear [1,2]. This material has been shown to have high oxidation resistance as well as superior mechanical properties. The hardness, high wear resistance and inertness of transition metal nitrides has been attributed to the unique bond structure. Typically 12-52 layers are deposited in a lattice with the extent of alloying, contamination, and roughening all critical to the performance of the lattice. Also, as the layers thin there are distinct changes in crystallinity and alloying affecting the tribological properties. As expected, deposition is difficult due to differences in the heat of formation of CrN and TiN – they each require different partial pressures of N_2 to form stoichiometric coatings.

To explore the stoichiometry and the extent of alloying in a TiN/CrN superlattice, we have employed the traditional surface analysis techniques of ion etch depth profiling with XPS. It has been historically accepted that monatomic Argon will typically suffice for this process however in this presentation a comparison will be made between conventional monatomic Ar^+ ions and the more recent cluster Ar_n^+ ions. The choice of impinging ion will be discussed with respect to stoichiometry and blending as will the practicalities of the depth profiling experiment and analysis. A novel method is proposed for the analysis of these materials, free of erroneous results.

S. Gallegos-Cantú *et al.,Wear*, **330–331**, 2015, pp 439–447.

H. C. Barshilia et al., *J. Mater. Research*, **19**, 2004, pp 3196–3205

8:20am **TF-ThM2 Hydrogen Permeability of Hydrogenated Amorphous Carbons*, Motonori Tamura,*** The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan

Diamond-like carbon **(**DLC**)** is an amorphous carbon with a significant fraction of CC *sp³* bonds. Tetrahedral amorphous carbon **(**ta-C**)** is the DLC with the maximum *sp³* content. These hydrogenated amorphous carbons have been classified into several types, such as a-C:H and ta-C:H.

Films of a-C:H with the highest H content (40–60 at. %**)** can have up to 70% *sp³*. However, most of the *sp³* bonds are hydrogen terminated and this material is soft and has low density. Films of a-C:H with intermediate H content (20–40 at. %**)** have better mechanical properties. Even if these films have lower overall *sp³* content, they have more C-C *sp³* bonds. These films have the advantage of possessing high hardness levels –in the range of conventional tribological PVD coatings (1500 – 3200 HV), coupled with a coefficient of friction that is less than half of the conventional coatings.

In this study, hydrogen permeability of a-C:H films with intermediate H content was measured. Films were deposited by PVD + plasma-assisted CVD (PACVD) on stainless-steel substrates Type 316L. Hydrogen-permeation tests were performed on the coated stainless steel samples. These tests were based on the differential-pressure methods described in ISO15105-1:2007, the international standard for determination of gas-transmission rates.

The permeation of hydrogen through solid materials involves a series of steps including adsorption, dissociation, diffusion, and recombination coupled with desorption. In our experimental conditions, it was indicated from the relation between the permeation flux and driving pressure of hydrogen (100～800 kPa) that hydrogen passed through the samples in the diffusion-limited permeation mode.

Hydrogenated amorphous carbon films (2.0-mm-thick) were effective to reduce the rate of hydrogen permeation through stainless steel (0.1-mm-thick) less than 1/100 at 573-773 K. Effect of hydrogen content in films to hydrogen permeation behavior was studied.

8:40am **TF-ThM3 Mass Transport and Plastic Deformation in Refractory Nitrides via Density Functional Theory and Ab Initio Molecular Dynamics*, Davide Sangiovanni,*** Linköping University, Sweden **INVITED**

Surface dynamics during film growth and mobility of defects such as vacancies, dislocations, and grain boundaries in bulk determine the properties and performances of refractory nitride thin films. *Ab initio* calculations, carried out at 0 K, provide useful information regarding adatom and admolecule migration on surfaces as well as defect formation and mobility in bulk. However, phase stability and mass transport are also strongly affected by lattice vibrations at finite temperatures. This results in molecular dynamics (MD) becoming the primary computational tool for evaluating the rate of thermally activated processes and revealing the occurrence of non-intuitive reactions. Estimating the rate of rare events via accurate, but computationally expensive, ab initio MD is a challenging task, thus requiring the use of acceleration techniques.

I present the results for mass transport and plastic deformation in transition metal nitride compounds and alloys determined via density-functional theory and ab initio MD. I show that lattice vibrations significantly affect adatom, admolecule, point-defect, and dislocation mobilities, with dramatic effects on surface reaction rates and bulk properties.

9:20am **TF-ThM5 Anticorrosion yet Conductive Hf Coatings on AZ91D Magnesium Alloy by Magnetron Sputtering*, Zhoucheng Wang,*** *D.F. Zhang,* Xiamen University, China

Magnesium and its alloy are prone to corrosion due to the high electrochemical activity, although they are promising materials in electronics and aerospace industries . Surface coating technique has become an effective method to enhance the corrosion resistance of the Mg alloys. In addition to offering high corrosion resistance, the protective coatings should be conductive to avoid static buildup and maintain other advantageous properties when Mg alloy been used in the electronics and aerospace applications. In this study, anticorrosion yet conductive Hf coatings were fabricated on the AZ91D Mg alloys by magnetron sputtering with different bias voltages. The microstructure and corrosion behavior were investigated as a function of bias voltage range from 0 to -125 V. Both potentiodynamic polarization and neutral salt spray tests reveal that the Hf coating deposited at -100 V exhibits the best protective performance. It possesses the lowest corrosion current density of 1.032 mAc/m^2 and the highest protection rate of 6, respectively. This perfect anticorrosion property is due to the dense structure and low porosity induced by applying the appropriate bias voltage. The chemical inert Hf oxide formed on the coating's surface also contributes to improve the corrosion resistance. Various types of corrosion sites after corrosion tests are examined by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). The results indicate that the coating failure is determined by the synergy between the defects in coating and the random phase distribution in substrate.

9:40am **TF-ThM6 Effect of Oxygen on the Self-formation of Carbonaceous Tribo-layer with Carbon Nitride Coatings under a Nitrogen Atmosphere*, Naohiro Yamada,*** *T. Takeno, K. Adachi,* Tohoku University, Japan

Carbon nitride (CN_X) is an expected coating material which shows high hardness and relatively low friction under a nitrogen atmosphere. These properties make it a good candidate for small precision machines in order to reduce energy consumption and material losses. We have already reported that a carbonaceous tribo-layer, whose structure is altered from that of the deposited coating, has been found on the worn surface of counterpart. Thus, a structural change of carbon is necessary condition for super-low friction. However, the outstanding properties cannot be achieved in the presence of oxygen or humidity, which has meant these coatings has not been used in practical applications under ambient air. In contrast, CN_X coatings can give super-low friction under ambient air when they are heated to 100 ˚C. Besides, we have reported that hydrogen atoms derived from water molecules in a nitrogen atmosphere chemisorb the worn surfaces, which provides super-low friction. These results indicate that CN_X coating has possibility to reduce friction and wear regardless of whether the nitrogen gas is mixed with oxygen and humidity. In this study, the effect of oxygen and humidity on friction and wear of CN_X coatings are clarified in detail. The possibility of super-low friction under an oxygen-contained humid nitrogen atmosphere is discussed from the viewpoint of formatting carbonaceous tribo-layer.

The CN_X coating is produced on the surfaces of SiC ball and disk using an ion beam assisted deposition system. We conduct a ball-on-disk friction and wear test in a glove box, which allows for control of the relative humidity (RH) and oxygen concentration within the range of 0.01-40 %RH and 0.01-25 vol.%, respectively.

When friction and wear tests of CN_X coatings are conducted, friction coefficients and wear volumes increase with increasing RH (3-40 %RH) and oxygen concentration (0.01-25 vol.%). However, friction coefficients and wear volumes remain low values regardless of RH and oxygen concentration when CN_X slides against hydrogenated-CN_X (CN_X:H) coating. Besides, we found that CN_X coatings gave specific wear rate below $3*10^{-8}$ mm^3/Nm when they achieved low friction coefficients below 0.05. These results indicate that there is a critical value of specific wear rate for formatting carbonaceous tribo-layer on the worn surfaces. TOF-SIMS depth analysis provides evidences that carbon derived from CN_X:H transfer to the surface of CN_X. This means that the carbonaceous tribo-layer is self-formed during friction. CN_X slid against CN_X:H achieved low friction coefficient below 0.05 regardless of RH and oxygen on the condition that the carbonaceous tribo-layer is self-formed.

10:20am **TF-ThM8 Complex Stress Evolutions during Sputter-deposition of Metal Films: Interface Reactivity, Alloying and Phase Transformation***, G. Abadias, **Jonathan Colin**, C. Furgeaud, A. Michel,* Institut Pprime, CNRS-Université de Poitiers, France **INVITED**

The understanding of morphological and microstructural development during thin film growth is of particular relevance to control islands shape, nucleation and growth of nanoparticles, phase transformation, texture or surface roughness. Due to oversaturated vapour fluxes employed in physical vapor deposition (PVD) techniques, dynamics usually prevails over thermodynamics in dictating growth and microstructural evolution in PVD films. Depending on the material type and process conditions, the film can develop different stress levels, evolving usually with film thickness. Recently, real-time wafer curvature measurements have contributed to increase our knowledge on the underlying mechanisms of stress development during growth, and to propose comprehensive physical models [1].

In this presentation, we will provide some examples of *in situ* and real-time diagnostics based on optical techniques (wafer curvature, surface differential reflectance spectroscopy) and electrical resistance measurements to probe with high sensitivity the early growth stages of a variety of metal films on Si during sputter-deposition. We will first review some typical compressive-tensile-compressive stress evolutions observed for high-mobility metals (e.g. Ag, Cu, Au) [2]. The influence of interface reactivity (using different buffer layers- SiO_x, *a*-Si or *a*-Ge) will be highlighted, and for the specific case of Cu, alloying with Ge (using co-sputtering) will be addressed.

In the second part of the talk, special focus will be placed on low-mobility metal systems (e.g., Mo, Ta, W) deposited on amorphous Silicon (a-Si), which exhibit a complex stress development with film thickness. In the case of Mo and Fe films, our *in situ* measurements reveal a structural transition at a film thickness of ~ 2-3 nm manifested by a concomitant tensile stress variation [3] and decrease in electrical resistance. Insights on the kinetics of the amorphous-to-crystalline phase transformation were gained from *in situ* synchrotron studies, coupling simultaneously X-ray diffraction, X-ray reflectivity and wafer curvature during sputter-deposition of a series of $Mo_{1-x}Si_x$ alloys.

[1] E. Chason, P.R. Guduru, J. Appl. Phys. 119 (2016) 191101.

[2] G. Abadias, L. Simonot, J.J. Colin, A. Michel, S. Camelio, D. Babonneau, Appl. Phys. Lett. 107 (2015).

[3] A. Fillon, G. Abadias, A. Michel, C. Jaouen, P. Villechaise, Phys. Rev. Lett. 104 (2010) 096101.

11:00am **TF-ThM10 First Steps Towards Accessing Aluminum's Far UV Reflectance for Space-based Telescopes***, **David Allred**, R.S. Turley, S.B. Perry, S.M. Thomas, S.G. Willett,* Brigham Young University, USA

We report on our progress on vacuum removal of protective layers on aluminum mirror surfaces using hydrogen plasmas and/or heating. One of NASA's flagship astrophysical missions of the 2020's or 30's will likely be a LUVOIR (large, UV-optical-IR) telescope. This space-based observatory will employ the largest mirrors ever flown. The reflective coating will almost certainly be aluminum since such telescopes would profit from truly broad-band mirrors. The top surface of such aluminum mirrors, however, need to be bare without the oxide layers that naturally form in air. (The local space environment for the observatory should be sufficiently oxygen-free that a pristine surface should remain bare for decades.) We will discuss our research into protecting as-deposited aluminum mirrors before atmosphere exposure with a robust, protective layer, or layers, that could be deposited to coat the aluminum immediately after its deposition, before it comes in contact with air, and cleanly and relatively easily removed once the mirror is in space. This removal must be gentle enough to not roughen the mirror surface nor redepositing material removed from the protec-tive layer on the mirror or other spacecraft components. Thus our choice of hydrogen plasmas. We will specifically discuss the deposition and removal of organic and inorganic (Cd-containing and Zn) films that were evaporated onto the aluminum immediately after its deposition. This could open up the 11-15eV band for space-based astrophys-ics without sacrificing IR, visible and UV reflectance.

11:20am **TF-ThM11 Microscale Measurement of Coating/Substrate Interfacial Shear Failures***, X. Zhang, Y. Mu, **WenJin Meng**,* Louisiana State University, USA

Quantitative evaluation of critical stresses governing interfacial failures in coating/substrate systems is crucial for surface engineering via the application of coatings to substrates. While a number of measurement techniques have been developed and studied over the past two decades, quantitative measurement of critical stresses leading to interfacial failures in coating/substrate systems has remained a challenge.

We report a new micro pillar compression testing protocol for quantitative measurement of interfacial shear failure stress in ceramic coating/metal adhesion layer/substrate systems. Three specimen series were investigated: CrN/Cu/Si, CrN/Ti/Si, and CrN/Cr/Si. All film/coating depositions occurred in a UHV plasma assisted magnetron sputtering system. Specimen characterization was accomplished through X-ray diffraction (XRD), focused ion beam and scanning electron microscope(FIB/SEM), and transmitted electron microscope (TEM). Scripted FIB cutting was used to fabricate cylindrical micro-pillars of the three specimen series, with interfaces inclined at 45deg with respect to the pillar axes. Compression loading of micro-pillars was carried out on an instrumented nano-indentation device. Depending on the interfacial adhesion layer used, the testing results show clear differences in the critical shear failure stress. The present results show the efficacy of this new microscale testing protocol, and motivate further study of the mechanical integrity of coating/substrate interfaces.

11:40am **TF-ThM12 Selectivity Control in the Electroreduction of CO_2 over Nanostructured Catalysts***, **Beatriz Roldan Cuenya**,* Ruhr University Bochum, Germany

The electrocatalytic reduction of CO_2 to industrial chemicals and fuels is a promising pathway to sustainable electrical energy storage and to an artificial carbon cycle, but is currently hindered by the low energy efficiency and low activity displayed by traditional electrode materials.

Using colloidal synthesis, nanoparticles (NPs) with well-defined size and interparticle distance were prepared and tested as catalysts for CO_2 electroreduction. Cu NP catalysts displayed a drastic increase in activity and selectivity for H_2 and CO with decreasing NP size below 5 nm. Hydrocarbon (methane and ethylene) selectivity was increasingly suppressed with decreasing NP size. For Au NPs, a drastic increase in current density was observed with decreasing NP size, along with a decrease in faradaic selectivity towards CO. The H_2/CO product ratio could be specifically tailored for different industrial processes by tuning the size of the Au NPs. In addition, we demonstrated that interparticle distance (IP) is also a critical parameter for controlling reactivity. For largely spaced NPs, selectivity to CO is enhanced, since this reaction intermediate is less likely to readsorb on neighboring NPs after formation. On the contrary, for closely spaced NPs we find that hydrocarbon selectivity is enhanced, since the re-adsorption of reaction intermediates on neighboring NPs can facilitate the multi-step pathway required for hydrocarbon production. This study addresses previously unexplored aspects of how product selectivity can be controlled using mesoscale transport processes during CO_2 electroreduction.

Another critical parameter for selectivity control in nanostructured electrocatalysts is the chemical state. We will discuss new oxide-derived metal catalysts that can reduce CO_2 with lowered overpotential and improved ethylene selectivity. We will also present critical insights into the catalyst reaction mechanism which were unraveled using structural and chemical information on the sample obtained under o*perando* conditions via X-ray absorption fine-structure spectroscopy. Finally, the role of the NP shape, in particular, the presence of (100) facets in Cu nanocubes and the evolution of the NP structure and dispersion under reaction conditions will be discussed based on *operando* electrochemical AFM data.

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