Advanced Surface Engineering
Room 304 - Session SE-ThA

Advanced Surface Engineering III

Moderator: Diana Berman, University of North Texas

2:15pm **SE-ThA-1 In-Situ Raman Spectroscopy of Adaptive Tribological Coatings**, ***Andrey Voevodin,*** University of North Texas **INVITED**

In-situ Raman spectroscopy is a powerful method to investigate adaptive tribological surfaces. The in-situ Raman spectroscopy is shown to capture tribologically induced changes of adaptive coatings inside the lubricated sliding contact in response to applied mechanical and thermal stresses. For solid lubricated adaptive contacts, duplex plasma-electrolytic oxidation (PEO) and chameleon coating produced on Al alloys were investigated. These were composed of a 80-160 mm thick hard load-supporting Al-Si-O coating and a 5–8 µm top layer of a chameleon coating made of graphite or BN, MoS_2 or WS_2, and Sb_2O_3. For liquid contacts, 52100 steel coupons were tested under lubricant starvation regimes using low viscosity hydrocarbons. The counterpart pins were made of 52100 steel and Si_3N_4. The tests were performed at temperatures ranging from room (liquid lubrication) to 600 °C (solid lubrication). In-situ Raman spectroscopy revealed that the lubricating phases, i.e. MoS_2, WS_2, and graphite, were protected from oxidation by the porous PEO structure. It also revealed a gradual evolution of chameleon composition with diminishing orthorhombic Sb_2O_3 phase presence at the surface in favor of hexagonal lubricating phases of chameleon components. The low shear strength of MoS_2, WS_2, and graphite and the integration of the chameleon coating with the PEO sublayer were responsible for the ultra-low friction behavior. In all examples, the in-situ Raman spectroscopy was shown to reliably detect contact chemical change correlated with the observed friction behavior.

2:45pm **SE-ThA-3 Automated Characterization of Combinatorial Thin Films and Their Stress**, ***David Adams***[1], *Finley Haines, Amun Jarzembski,* Sandia National Laboratories, USA

Combinatorial sputter deposition techniques provide an ability to fabricate a large variety of thin films in a relatively short time thereby accelerating materials discovery. Indeed, past studies have reported methods that produce 10s or 100s of unique films in a single vacuum deposition. Despite these advances, new, high-throughput characterization techniques are needed to match the pace of combinatorial synthesis. In particular, automated techniques that accurately reveal the structure and the relevant properties of combinatorial films are of great interest.

Toward this end, we describe automated, ex-situ characterization of biaxial film stress wherein >100 individual, combinatorial thin films are probed in concert. Combinatorial, magnetron sputter-deposited Pt-Au and Pt-Ni films are interrogated using a k-Space Co. Thermal Scan instrument wherein samples are affixed inside a vacuum test cell. This instrument precisely moves a laser spot array to each specimen (before and after deposition) to determine wafer curvature changes. The application of Stoney's equation to determine the stress of combinatorial films from measured curvatures is discussed. Films are much thinner than the substrates (which satisfies one Stoney assumption), but a laterally graded thickness across each specimen moves away from at least one separate assumption used in the derivation of this often-used equation. Accounting for measured thickness gradients, we demonstrate accurate stress measurements over a range of temperatures up to +600C. Combinatorial Pt-Au and Pt-Ni films produced in single depositions exhibit a variety of stress responses that are ultimately correlated to measured film density and composition. Altogether, we determine their thermal expansion coefficients, pinpoint their onset of relaxation, and reveal changes occurring at high temperature tied to secondary phase formation. The gathered information augments an extensive library of process-structure-property relationships that underly their high-temperature performance.

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3:00pm **SE-ThA-4 Designing Defect Structure and Interfacial Strain in an Epitaxial VN Bilayer Film by Tailoring N Concentration**, ***Marcus Hans,*** *Damian Holzapfel,* RWTH Aachen University, Germany*; Zhuo Chen,* Erich Schmid Institute of Materials Science, Austria*; Soheil Karimi Aghda, Michal Fečík,* RWTH Aachen University, Germany*; Daniel Primetzhofer,* Uppsala University, Sweden*; Zaoli Zhang,* Erich Schmid Institute of Materials Science, Austria*; Jochen Schneider,* RWTH Aachen University, Germany

A bilayer of $V_{0.49}N_{0.51}/V_{0.56}N_{0.44}$ has been grown epitaxially on MgO(001) by reactive high power pulsed magnetron sputtering in an industrial-scale deposition system at a temperature of 400 °C and it is demonstrated that the defect structure and interfacial strain are governed by the N concentration. Based on the lattice mismatch between MgO and $V_{0.49}N_{0.51}$ with V vacancies, an interfacial strain of -2.3(1)% is expected. From ab initio calculations, X-ray diffraction and transmission electron microscopy data it is inferred, that the $V_{0.49}N_{0.51}$ layer exhibits V vacancies, N Frenkel pairs and a high dislocation density of ~0.20 nm^{-2}, causing an interfacial strain of -1.4(5)% at the $MgO/V_{0.49}N_{0.51}$ interface. The phase formation of understoichiometric $V_{0.56}N_{0.44}$ is governed by N vacancy formation, while the dislocation density is reduced to ~0.04 nm^{-2} at the $V_{0.49}N_{0.51}/V_{0.56}N_{0.44}$ interface and to < 0.01 nm^{-2} within $V_{0.56}N_{0.44}$ at a distance of ~35 nm from the interface. Based on ab initio calculations, a strain of -1.7(6)% is predicted at the $V_{0.49}N_{0.51}/V_{0.56}N_{0.44}$ interface in very good agreement with the experimentally obtained value of -1.6(8)%. It is evident that control of the N concentration allows for the design of layered architectures with well-defined strained interfaces and tailored defect structures. Finally, the employment of only one transition metal is chemically simple and therefore, from a recycling point of view, also more sustainable than combining different transition metals as commonly done in layered architectures, including superlattices.

3:15pm **SE-ThA-5 Towards Reliable X-Ray Photoelectron Spectroscopy: Understanding Fundamental Differences between Analyses Performed on Samples with and Without Electrical Contact to Spectrometer**, ***Grzegorz (Greg) Greczynski***[2], Linköping University, Department of Physics, Sweden

X-ray photoelectron spectroscopy (XPS) analyzes of insulators or inhomogeneous samples containing insulating phases are often done with specimens electrically isolated from ground and the surface potential controlled by the flood gun. While such approach offers the possibility of delivering non-distorted spectra, the consequences for the energy level alignment between sample and the spectrometer are often not considered. The present contribution highlights these aspects by discussing several, carefully selected, case studies that visualize fundamental differences between XPS analyses performed on samples with and without electrical contact to ground. Consequences for core level shifts, energy splitting between peaks from different samples, and spectra referencing are discussed in detail. It is shown that the choice of the measurement configuration (samples with *vs*. without contact to the spectrometer) determines to what extent binding energies of core level peaks from conducting and insulating samples (or conducting and insulating phases of the same sample) depend on the specimens' work function. Recognizing these aspects is crucial for the correct spectra referencing and interpretation of core level shifts for series of samples with varying work function.

3:30pm **SE-ThA-6 High Throughput Thin Film Materials Synthesis via Laser Spike Annealing**, ***Drake Austin,*** Air Force Research Laboratory (AFRL) **INVITED**

As the discovery of new materials and functionalities are occurring at an unprecedented rate, new strategies to accelerate the connection between material state or property to a desired application are necessary. Despite the availability of modern tools, the slow, tedious, and Edisonian research practices of the past are still the standard for areas such as thin films and coatings. The development of a new thin film requires either starting from a known, reported recipe, or the use intuition to determine a suitable starting condition. After thin film deposition is complete, there may be post-growth optimization and characterization, with many iterations of this process necessary until the initial growth conditions match some desired end state.

Laser spike annealing (LSA) is a promising technique for rapidly investigating the modification of thin film materials due to thermal annealing. By scanning a focused, continuous-wave laser across a thin film surface, localized heating can be achieved with heating/quenching times as short as microseconds and temperatures exceeding 1000°C. The laser intensity, scan

[1] **JVST Highlighted Talk**

[2] **JVST Highlighted Talk**

rate, and annealing environment can be varied, allowing thousands of distinct annealing conditions to be studied on a single sample, including dwell times several orders of magnitude shorter than what can be achieved with rapid thermal annealing. This approach can therefore be used for accelerated materials discovery and optimization by modifying existing thin films in a localized, high throughput manner.

In this work, LSA is applied to the oxidation of various thin film materials, including transition metals such as Hf and transition metal dichalcogenides such as MoS2. Tunable oxidation is achieved by varying the laser conditions in a controlled oxygen environment, enabling access to a wide range of effective temperatures and heating times. The resulting structural and compositional modifications are characterized using X-ray diffraction, Raman spectroscopy, ellipsometry, UV-vis absorption spectroscopy, and X-ray photoelectron spectroscopy. Applications in the study of optical and electronic materials are presented, including refractive index optimization and the development of materials for neuromorphic device applications.

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