Thin Films
Room Naupaka Salon 4 - Session TF-MoM1

Innovations in the Development of Multifunctional Thin Films/Nanostructural and Surface Morphological Evolution: Experiment and Theory

Moderator: Jolanta Klemberg-Sapieha, Polytechnique Montréal, Canada

8:00am **TF-MoM1-1 Hybrid Technologies to achieve Multifunctional Properties**, ***Pierre Collignon,*** PD2-I, France; *A. Schuetze,* ACT

Author :Dr Pierre Collignon , PD2-I

Co-Author: Dr. Andreas Schuetze

Duplex Coatings involving a nitriding - and subsequent coating process are already used for forming tools to improve the carrying pressure load. We have worked to broaden this hybrid technology to applications requiring higher temperatures like Aluminum die casting or hot forming. These applications require high thermal fatigue resistance which can be obtained through a dedicated nitriding process and multifunctional coatings to achieve the appropriate properties required at the surface of the dies; i.e. heat and oxidation resistance, hot hardness, and low thermal conductivity.

This paper reports our developments and the investigations to achieve the aforementioned properties to achieve hot hardness and oxidation resistance of different coatings. First, we investigated properties like hot hardness and oxidation resistance on the basis of ALTiN, AlCrN, and CrN coatings. Secondly, to improve the properties we have studied the influence of elements like W, B, and Si as doping or alloying elements.

We found, that CrWAlN coating keep the highest hardness after annealing in air at 750 °C. In case of ALTiSiN the best results have been achieved using a multilayer of AlTiBN/TiSiN with 25% Si producing a high content of Si3N4. For hot applications requiring thick coatings (6 to 8 µm), the morphology and structure has been investigated using cross section SEM and residual stress measurements.

8:20am **TF-MoM1-2 Multifunctional Hybrid Optical Coatings for Flexible Substrates**, ***Ludvik Martinu,*** *J. Klemberg-Sapieha, O. Zabeida,* Polytechnique Montréal, Canada

Optical coating (OC) applications represent a multibillion dollar market worldwide; they range from antireflective coatings (ARC) found in most optical components and devices to complex optical interference filters (OIFs). Specifically, there has been considerable effort to develop optical films with multifunctional characteristics suitable for applications in ARCs and OIFs on plastic and flexible substrates. This includes a necessity to control and optimize the mechanical and thermal properties (hardness, Young's modulus, adhesion, thermal expansion coefficient), surface energy (hydrophobicity), and possibly provide complementary functionalities (color, electrical conductivity, etc.), while allowing one to well adjust the refractive index.

In this context, we focus our work on the hybrid organic-inorganic materials (such as SiOCH) that are shown to combine high mechanical resistance of ceramics with high elasticity of polymers. We demonstrate, that using the scalable ion beam assisted chemical vapor deposition (IBA-CVD) process the refractive index (n) of such films can vary from ultra-low (n less than 1.38@550nm) to low (1.47-1.53), while the extinction coefficient is kept below 10^{-4}. At the same time, the hardness-to-Young's modulus ratio, H/E, is substantially increased (to 0.16) compared to 0.08 for pure SiO_2, a result that is well correlated with the increased resistance to crack formation and propagation. This is also confirmed by the value of the crack onset strain (COS) of 4% for the hybrid films compared to 1% for inorganic SiO_2. Such hybrid layers, incorporated in multilayer structures on plastic substrates, provide significantly enhanced optical and mechanical stability in environments involving large temperature and humidity excursions.

We discuss the optical, chemical, morphological, and mechanical properties of the deposited films in relation to the discharge current and oxygen gas ratio during deposition, while showing that these main parameters provide an opportunity to manipulate the functional coating properties within a wide range.

8:40am **TF-MoM1-3 High-Sensitivity UV Photoemission Spectroscopy Using Low Energy Photon to Probe the Electronic Structures of Semiconductors, Insulators and Biomolecules**, ***Hisao Ishii,*** Chiba University, Japan **INVITED**

The information on electronic structure such as density-of-states (DOS), ionization energy, and energy level alignment at the interfaces of various materials is a key factor to understand and improve their functions. Photoemission spectroscopy (PES) has been, so far, widely applied to many materials. The detection limit is enough to investigate valence states, but not to probe weak density of states which is practically important to device performance as trap etc. By using well-monochromatized light source, minimum detection limit of PES has been recently much improved [1]. Our group have also developed high-sensitivity UV photoemission spectroscopy (HS-UPS) and photoelectron yield spectroscopy (PYS) using tunable low energy light source, achieving the detection of very low DOS less than 1015 cm-3eV-1 level[2]. Our technique has additional advantage: this method is tough for sample charging problem, opening chance to measure various isulating films. In this talk, I will report on its application to organic and inorganic semiconductors and insulators. First topic is the observation of density-of-states including both valence top region and band tail structures for polymers[3,4], perovskite[5], and transparent oxide semiconductor[6]. Second topic is the detection of negative carrier states in organic semiconductor films and devices using operando-PYS[7]. Finally, I will talk about our recent trial to measure the electronic structure of protein films[8,9].

[1] F. Bussolotti, J. Electron Spectrosc. Relat. Phenom. 204, 29 (2015).

[2] T. Sato and H. Ishii et al., Appl. Phys. Express 10, 011602-1 (2017)

[3] T. Sato and H. Ishii et al., Appl. Phys. Lett. 110, 111102-1 (2017)

[4] Y. Yamaguchi and H. Ishii et al., IEICE Trans. on Elect., E102.C 168 (2018).

[5] I. Levine and H. Ishii et al., J. Phys. Chem. C, 125, 9, 5217 (2021)

[6] R. Nakazawa and H. Ishii et al., Appl. Phys. Express,14, 071004 (2021).

[7] Y. Tanaka and H. Ishii et al., Appl. Phys. Express 11, 081601 (2018).

[8] D. Sano and H. Ishii et al., Molecular Crystals and Liquid Crystals, vol.687, No.1, 34-39 (2019).

[9] Z. Futera and H. Ishii et al., The Journal of Physical Chemistry Letters, 11, 9766-9774(2020).

9:20am **TF-MoM1-5 Stress Corrosion Cracking Simulation of FCC Type High Entropy Alloy via Reactive Molecular Dynamics Method**, ***Jo Watanabe,*** Institute for Materials Research, Tohoku University, Japan; *Q. Chen,* New Industry Creation Hatchery Center, Tohoku University, Japan; *Y. Asano,* Institute for Materials Research, Tohoku University, Japan; *Y. Ootani,* Institute for Materials Reseach, Tohoku University, Japan; *N. Ozawa,* New Industry Creation Hatchery Center, Tohoku University, Japan; *M. Kubo,* Institute for Materials Research, Tohoku University, Japan

Recently, FeNiCrCoMn-based high-entropy alloys (HEA) are expected to be used in extreme environments because of the superior properties that not found in conventional alloys. However, stress corrosion cracking (SCC) is a problem for HEA used in high-temperature and high-pressure water environments. SCC is the phenomena resulting from corrosion and tensile stress, and thus it is difficult to analyze detailed mechanism by experiments. Molecular dynamics (MD) method using reactive force field (ReaxFF) is suitable for analyzing phenomena involving chemical reactions. Recently, we showed that ReaxFF is useful to investigate the SCC of HEA (Fig.1). However, ReaxFF parameter set for FeNiCrCoMn HEA under the water environment has not been established because it shows complex mechanical and chemical phenomena. In this study, we develop ReaxFF parameters for FCC-type FeNiCrCoMn HEA using recently proposed Hybrid Real-Coded Genetic Algorithm (HIRCGA)[1]. Then tensile simulation of FeNiCrCoMn HEA was performed in vacuum and high-temperature water to elucidate its SCC.

First, we optimized the parameters for Mn-Mn interaction to reproduce the energy change of α-Mn and β-Mn crystals with respect to the change in lattice constant obtained by density functional theory (DFT). Fig.2 shows a

comparison of the energy change with respect to the change in lattice constant fraction of α-Mn and β-Mn obtained by DFT and MD calculations with optimized ReaxFF parameters. As shown in Fig.2 the optimized parameters reproduce the DFT results with good accuracy. Subsequently, we optimized the parameters for Mn-Fe, Mn-Ni, Mn-Cr, and Mn-Co interactions by using $Fe_{0.5}Mn_{0.5}$, $Ni_{0.5}Mn_{0.5}$, $Co_{0.25}Mn_{0.75}$, and $Cr_{0.4}Mn_{0.6}$ crystals with similar manner.

After the optimization of the ReaxFF parameters between Mn-Mn, Mn-Fe, Mn-Ni, Mn-Cr, and Mn-Co interactions by HIRCGA, we combined these parameters and re-optimize the combined parameters to reproduce the $Fe_{20}Ni_{20}Co_{20}Cr_{20}Mn_{20}$ crystal structure. The crystal structure analysis showed that the optimized parameter can reproduce the experimentally obtained crystal structure. The details of the tensile simulation of FeNiCrCoMn-based HEA with the optimized ReaxFF parameters will be reported at the conference.

[1] Song, H., Wang, J., Song, L., et al. Improvement and application of hybrid real-coded genetic algorithm. *Applied Intelligence,* 2022, https://doi.org/10.1007/s10489-021-03048-0.

Author Index

Bold page numbers indicate presenter