Thin Films
Room Naupaka Salons 4 - Session TF-TuM

Innovations in the Development of Multifunctional Thin Films

Moderator: Jolanta Klemberg-Sapieha, Polytechnique Montréal

8:00am **TF-TuM-1 Anion Interactions with Vapour Deposited Conducting Polymers**, ***Drew Evans***, University of South Australia, Australia

Conducting polymers offer several key advantages over their inorganic counterparts, such as mechanical flexibility, transparency, and material abundance, which can enable low-cost fabrication and novel applications such as printed and flexible electronics. The conducting polymer poly(3,4-ethylenedioxythiophene), PEDOT, is one material which displays (among others) high electrical conductivity [1], enhanced thermal conductivity [2], good electrocatalytic performance [3], as well as thermoelectric behaviour [4]. Enhancing the properties of PEDOT has been achieved through Vapour Phase Polymerisation (VPP), an oxidative polymerization process under vacuum conditions. We report that VPP PEDOT shows interesting interactions with anions, in some examples almost specific ion effects [5]. For example, the uptake of anions from an aqueous solution into electrochemically reduce PEDOT is highly dependent on the anion itself. More interestingly is nitrate is specifically absorbed by PEDOT when present in a mixed electrolyte solution [6]. This selective absorption is hypothesised to originate from anion-π interactions, in part validated by MD simulations [5]. Such interactions, relating to both chemistry and structure, lead to interesting opportunities in energy storage as well as (agricultural) sensing.

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8:20am **TF-TuM-2 Decorative Electro-magnetic Transparent Metal-semiconductor Thin-films for Consumer Electronics**, ***Bastian Stoehr***, *E Charrault, D Evans,* University of South Australia, Australia*; F Lacroix,* ENSCBP - Bordeaux INP, France*; J Parks,* University of Bath, United Kingdom*; P Murphy, C Hall,* University of South Australia, Australia

Electro-magnetic (EM) transparent decorative coatings with a metallic appearance are highly desirable for military, automotive and communication applications. More specifically, they are advantageous as decorative coatings for consumer electronics. Such coatings will enable device to device communication with minimal attenuation of the signal. This will allow devices to save energy and result in increased battery life.

Inherently, a metallic thin-film, e.g. aluminium, interferes with EM radiation rendering it unsuitable for these applications. Hence, to create multifunctionality, aluminium was alloyed with semiconductors in order to manipulate its EM transparency, whilst maintaining the decorative properties of the metal thin film. One challenge for these coatings is to maintain their desired properties during thermal events, either during manufacturing into a final device or as a result of environment conditions during use.

Metal-semiconductor thin films have the inherent advantage that the optical and electrical properties of the thin film can be manipulated in multiple ways.[1] The properties of the thin films can be controlled not only by changing the alloy composition (type and amount of semiconductor), but also by varying the deposition parameters. We report the influence of deposition parameters and thin film composition on the EM transparency, as well as the optical properties of these coatings.

We also report on their response to thermal stress. The optical and electrical properties of these thin films have been studied for relevant process temperatures of up to 240 °C. Their properties were analyzed and compared post processing. It was revealed that after processing the thin films at relevant temperatures, the properties changed. Interestingly, the magnitude and direction of change was dependent on the type of semi-conductor used. Possible mechanisms include oxidation, phase changes, grain formation, grain size changes and changes along grain boundaries. This information will be used to select composition and process properties so that aluminium-semiconductor alloys can be used in a number of applications.

1. Kawaguchi, T., Tahara, K. & Saga, T. Radio wave transmitting decorative member. (2008).

8:40am **TF-TuM-3 Applications of Polarized Neutron Scattering for Development of Novel Functional Heterostructures**, ***Valeria Lauter***, Oak Ridge National Laboratory, USA

New functionality often arises at the mesoscale where defects, interfaces, and non-equilibrium structures are formed [1]. Probing the internal structure morphology and spin structure in thin films and nanostructured materials via Polarized Neutron Reflectometry (PNR) is a type of experiments addressing not only a kind of "surface visualization" or integration over the whole sample size. PNR is a tool providing depth resolved information and establishes a direct and precise correlation between local interfacial characteristics and global physical properties and delivers the most exhaustive and detailed information on the 3-dimensional structure of thin films and hidden interfaces on enormous length scale [2]. In this talk I will present a spectrum of experiments performed at the Magnetism Reflectometer at the Spallation Neutron Source, that covers multiple scientific areas, e.g. new generation of heterostructures based on integrating topological insulators (TIs) with conventional materials to induce ferromagnetic interactions with symmetry breaking at the interface [3], tunnel barriers in hybrid organic/metallic spin-valve structures, asymmetric block-copolymer/nanoparticle composite structures. The specific details will be presented.

Research at Oak Ridge National Laboratory's Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, and the US Department of Energy, by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory.

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[2] V. Lauter, H.J.C. Lauter, A. Glavic, B. Toperverg, "Reflectivity, Off-Specular Scattering, and GISANS Neutrons," book chapter in Reference Module Material Science Elsevier, 2016

[3] F. Katmis, V. Lauter, F. Nogueira, B. Assaf, M. Jamer, P. Wei, B. Satpati, J. Freeland, I. Eremi, D. Heiman, P. Jarillo-Herrero, J. Moodera, "Achieving high-temperature ferromagnetic topological insulating phase by proximity coupling", *Nature 2016,* ***533****, 513*

9:00am **TF-TuM-4 Oxygen-Free Palladium/Titanium Coating, a Novel Non-Evaporable Getter Coating with an Activation Temperature of 133 °C**, *T Miyazawa,* SOKENDAI, Japan*; M Kurihara, S Ohno,* Yokohama National University, Japan*; N Terashima, Y Natsui, H Kato,* Hirosaki University, Japan*; Y Kato,* Irie Koken Co., Ltd., Japan*; A Hashimoto,* National Institute for Materials Science, Japan*; T Kikuchi,* ***Kazuhiko Mase***, KEK, Japan

We developed a novel non-evaporable getter (NEG) coating with an activation temperature as low as 133 °C, that is, a palladium/titanium coating with extremely low oxygen concentration (oxygen-free Pd/Ti coating) (Fig. 1) [1]. The substrate was coated with Ti, and then overcoated with Pd using sublimation under ultra-high vacuum conditions. The morphology and surface elemental composition of the Pd/Ti thin film were investigated with electron microscopes and X-ray photoelectron spectroscopy, respectively. The thicknesses of Ti and Pd films were approximately 1.3 μm and 50 nm, and the Ti film was completely overcoated by the Pd film. Ti and oxygen were found to be negligible on the oxygen-free Pd/Ti surface. The oxygen-free Pd/Ti coating was applied to formed bellows. The bellows was successively baked at 133 °C for 12 h, 176 °C for 3.5 h, and 200 °C for 3.5 h. After sealing off a turbomolecular pump from the vacuum system containing the bellows, the pressure reached values of 4.6×10^{-6} Pa, 1.7×10^{-7} Pa, and 6.1×10^{-8} Pa, respectively (Fig. 2). The pumping speeds of the bellows were estimated to be 0.028, 0.23, and 0.23 L s^{-1}, respectively. These results demonstrate that oxygen-

free-Pd/Ti deposition can be used as a new NEG coating for vacuum systems with a baking temperature of 133 °C or higher. Oxygen-free Pd/Ti coating was applied for a NEG pump that can be activated by baking at 150 °C for 12 h [2].

References

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[2] T. Kikuchi, T. Miyazawa, H. Nishiguchi, K. Mase, AIP Conf. Proc., submitted.

9:20am **TF-TuM-5 Droplet assisted Growth and Shaping (DAGS): A Broadly Applicable Method for Chemical *in situ* Shaping of Complex Polymeric Nano and Microstructures***, ***Stefan Seeger***, *G Artus, N Saddiqi,* University of Zurich, Switzerland

The synthesis of nano and microstructures is an emerging field in chemistry and materials science. They can be made from a large variety of materials, for example metals, semi-metals, or polymeric substances. Usually, these particles exhibit a simple shape.

Some years ago, we have presented the synthesis of silicone nano filaments in particular for surface coatings. Now, we have shown a mechanism, called **Droplet assisted Growth and Shaping (DAGS)** explaining how these one-dimensional growths can be explained. Based on this synthesis scheme we are able to synthesize silicone nanoparticles of different shapes depending on the reaction conditions at room temperature from gas phase and liquid phase. Some of these structures exhibit a shape complexity which goes clearly beyond wires and filaments. Very recently, we could show that the mechanism of this synthesis is applicable not only to silicone structures but also to other chemical compounds. For example we have synthesized Germanium oxide and Aluminumoxide nanostructures. For these structures we have used Germaniumchloride and Tributyl-Aluminum. The procedure for all of them is identical, does not require high temperature, pressure or other cost invcreasing conditions.The shape of the structures depend on the grade of humidity in the gas phase during the reaction.

In this presentation, we will give an overview about the synthesis and process reaction conditions allowing the directed growth of of nano and microstructures of complex shape.

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G Artus, S Olveira, D Patra, S Seeger, *Macromol. Rapid Comm*. **2017,** *38, 1600558*

9:40am **TF-TuM-6 Low Temperature Nitridation of Hafnia with Low Density of N-O Bonds***, J Torres-Ochoa, O Cortazar-Martinez, M Mayorga-Garay, A De Luna Bugallo, Y Chipatecua-Godoy, O Ceballos-Sanchez, D Silva-Cabrales, F Corona-Davila, J Raboño-Borbolla,* CINVESTAV-Unidad Queretaro, Mexico*;* ***Alberto Herrera-Gomez****,* CINVESTAV-Unidad Queretaro, Mexico, México

The nitridation of hafnia is attractive because it improves its dielectric properties and minimize its crystallization. The thermal budget employed might be large when nitridation is carried out through rapid thermal annealing [1]. Ultraviolet-assisted nitridation might be carried out at lower temperatures; however, N-O species dominates the N 1s spectrum [2], affecting the dielectric quality. These species are also present when the nitridation is carried out through decoupled-plasma processing [3] and can only be removed through high-temperature annealing.

We have developed a low-temperature nitridation process that minimize the formation of N-O species. It also minimizes the formation of a hafnium silicate interface layer in hafnia/Si structures [4]. It is based on remote-plasma employing a gas-mixture. The structure of the multilayer films was characterized through ARXPS, and the effect on the dielectric properties through I-V and C-V curves.

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10:20am **TF-TuM-8 Fundamental Properties of Transition-metal Nitrides: Materials Design Strategies for Extreme Properties***, **Joe Greene**,* Linköping University, Sweden, University of Illinois at Urbana-Champaign **INVITED**

Transition-metal (TM) nitrides exhibit an enormous range of properties and offer a smorgasbord of opportunities for materials scientists. Cubic TM nitrides have wide single-phase compound fields that can be exploited. We show results for vacancy hardening in 3d Group-IV TiN_x(001) and Group-V VN_x(001); the hardness H (and resistivity ρ) of epitaxial layers increases, while the elastic modulus E and the relaxed lattice constant decreases linearly, as x is decreased from 1.0 to 0.67 and 0.80, respectively. In contrast, H(x), E(x), and ρ(x) for 5d Group-V TaN_x(001) remain constant due primarily to the presence of isoelectronic antisites. Strong electron/phonon coupling in VN_x results in thermal conductivity at room temperature and above being dominated by electronic contributions.

All Group-IV TM nitrides, TiN, ZrN, and HfN, are very good metallic conductors with room-temperature resistivities of 12-14 μΩ-cm. 3d Group-III ScN(001) is a transparent semiconductor with an indirect Γ-X gap of 1.3 eV. Reflectivity measurements from $Sc_{1-x}Ti_xN$(001) layers show TiN is strongly reflecting up to the reflectance edge at $\hbar\omega_e$ = 2.3 eV, while ScN is transparent, and $\omega_e \propto x^{0.5}$ for the alloy. ZrN is intermediate with $\hbar\omega_e$ = 3.04 eV. Thus, hard decorative coatings can be obtained with a wide palette of colors.

Superconducting transitions T_c for the Group-IV TM nitrides range from 10.4 K for ZrN to 9.18 K for HfN to 5.35 K for TiN. For comparison, superconductivity is not observed for the Group-IV rare-earth (RE) nitride CeN. These results are consistent with electron/phonon coupling parameters of 1.11 (ZrN), 0.82 (HfN), 0.73 (TiN), and 0.44 (CeN). The acoustic phonon modes soften monotonically with increasing cation mass; optical mode energies remain approximately constant for the TM nitrides, but are significantly lower for the RE nitride due a lower interatomic force constant.

The extreme range of materials properties available in TM nitrides and related systems can be enhanced through the formation of self-organized superhard nanostructures consisting of commensurate nanolamellae, nanocolumns, nanospheres, and nanopipes.

An issue with hard ceramic films, however, is that they are typically brittle, leading to failure by crack formation and propagation. We show several approaches to obtaining TM nitride layers that are both hard *and* ductile (i.e., tough). IV-VI and V-VI alloys, e.g. $Ti_{1-x}W_xN$ and $V_{1-x}Mo_xN$, exhibit dramatic delocalization of electron density leading to a more ductile response to shear stress while exhibiting increased hardness under tensile and compressive loading. Vacancy-induced toughening is also observed in under-stoichiometric $(V,Mo)N_x$ alloys.

11:00am **TF-TuM-10 Surface Reactions of Metal and Metal Oxides on Hybrid Perovskite Materials for Optoelectronics Applications***, J Cazares-Montañez, M Martínez-Puente, R Garza-Hernández, E Martínez-Guerra,* CIMAV-Monterrey, Mexico*; M Quevedo-Lopez,* University of Texas at Dallas*;* ***Francisco Aguirre-Tostado****,* CIMAV-Monterrey, Mexico

Hybrid perovskites (HPV) have recently emerged as highly efficient optoelectronic materials and are currently being intensively investigated as alternative active layer materials for photodetectors, light-emitting diodes, laser devices, sensors and X-ray detectors, among others. Since HPV are direct band gap materials with high optical absorption coefficients (~ $10^5 cm^{-1}$) the majority of publications have been dedicated to hybrid organic-inorganic solar cells with certified efficiencies over 20%. However the realization of a long-lasting device implies the understanding of chemical and structural stability of HPV materials and their interface with electron and hole transport layers (ETL and HTL, respectively). This presentation will show detailed XPS analyses of the the chemical stability of the transition metal and transition metal oxides with ABX3 hybrid perovskites for A=MethylAmmonium (MA), B=Pb, and X=Cl, I, and Br. HTL/HPV interface is not trivial as the reactivity of halogen group elements

forms an unstable high resistance interlayer at the charge transport layer interface compromising the optimum operation of the device. The electrical characterization and work function measurements will be discussed and correlated to the chemistry and cristallyne structure of the materials of interest.

11:20am **TF-TuM-11 Thin-Film Alchemy: Engineering Oxide Films to Unleash their Hidden Properties*, Darrell G. Schlom,*** Cornell University **INVITED**

Guided by theory, unparalleled properties—those of hidden ground states—are being unleashed by engineering oxides at the atomic level. This engineering includes strain engineering, dimensional confinement, and defect engineering. Using these thin-film tricks, materials that are not ferroelectric or ferromagnetic in their unstrained state can be transmuted into ferroelectrics, ferromagnets, or materials that are both at the same time. Similarly, new tunable dielectrics with unparalleled performance have been created. Our studies reveal details about the microscopic growth mechanism of these phases, which are relevant to preparing multicomponent oxide heterostructures with atomic precision. A new era for engineering functional oxide thin films for electronics is upon us: oxides by design. This work was performed in collaboration with the coauthors listed in the references below.

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