Functional Thin Films and Surfaces
Room Town & Country B - Session C3-2-FrM

Thin Films and Novel Surfaces for Energy II

Moderators: Dr. Clio Azina, RWTH Aachen University, Germany, **Prof. Carlos Tavares**, University of Minho, Portugal

8:40am **C3-2-FrM-3 Survey for Ferroelectric/Antiferroelectric Films for Energy Storage*, Mitsuru Itoh*,** *H. Takashima,* National Institute of Advanced Industrial Science and Technology/Tokyo institute of Technology, Japan **INVITED**

Ferroelectric (FE) materials such as $BaTiO_3$, $KNbO_3$, and $Pb(Zr,Ti)O_3$ have dipole moments aligned to one direction. FEs have been already industrially applied as capacitor, piezoelectric actuator, filters, optical devices, and so on. However, antiferroelectric (AFE), such as $PbZrO_3$, $AgNbO_3$, and $NaNbO_3$, has two sublattices of the dipole moments, and each sublattice have dipole moments with opposite directions. As a whole, AFE does not have a net polarization and is structurally centrosymmetric. Under a smaller external electric field (*E*), AFE shows a linear response of electric displacement (*D*) against *E* like a paraelectric. Applying larger *E* causes flipping of dipole moments in one sublattice parallel to *E*. This constrained aligned dipole moments in one direction are comparable to a FE state that has a net polarization. However, once *E* is decreased, dipole moments in one sublattice flip to the original direction and consequently the structure returns to an original centrosymmetric and non-polar state. Utilizing such a characteristic of AFEs under *E*, a field-induced FE, they can be applied for the energy storage especially for the power devices, utilizing two step *D-E* responses of a linear one near the origin followed by a hysteresis loop at larger *E*.

Design of FE is easier compared to AFE because of the rich accumulated scientific knowledge of FE both in the structure and property during last 100 years. However, chemical design of AFE is still difficult due to the reason that the number of AFEs is limited compared to that of FEs. This study is going to try giving a comprehensive explanation on the phase stability of complex oxide materials including perovskites in the bulk and thin film including metastable state. Candidate compounds of AFE will be discussed for various phases in A_2O_3 and ABO_3.

9:20am **C3-2-FrM-5 First Attempt to Describe the Effect of the Substrate Temperature on the Depth Concentration Profile of Reactively Sputtered $ZnGeN_2$ Thin Films***, A. Virfeu, F. Alnjiman, A. Borroto, S. Migot, J. Ghanbaja, D. Mangin, D. Pilloud,* ***Jean-Francois Pierson,*** Institut Jean Lamour - Université de Lorraine, France

The reactive sputtering process is widely used at the academic and industrial scales to deposit thin films of various nitrides, oxides, oxynitrides… For some materials, the crystallization of the film can occur even when the deposition temperature is fixed at room temperature (Cu_2O, ZnO, TiN, …). Nevertheless, other materials require to heat the substrates during the deposition to obtain a crystallized film (VO_2, $LaCoO_3$, Si_3N_4, …).

Zinc germanium nitride ($ZnGeN_2$) exhibit optoelectronics properties that makes this abundant material an interesting compound to replace the indium and gallium nitrides for LEDs applications. As previously mentioned by several groups, the deposition of crystalline $ZnGeN_2$ using sputtering processes can only be achieved by heating the substrate during the growth.

A new approach to describe the mechanism of growth induced by the temperature during reactive co-sputtered $ZnGeN_2$ deposition is reported. The complex crystallization of this system requires the deposition of films at high temperature involving difficulties in controlling the stoichiometry of the films due to the evaporation of zinc atoms relative to germanium at these temperatures. The range of temperature considered in this work is between 70°C to 280°C. The study of this material is done at different scales and a model is proposed to bring answers to the observations made. X-ray/electron diffraction, transmission electron microscopy combined with in-depth SIMS analyses reveal the origin of two different zones of composition and crystallization. At a temperature above 130°C, the first step of growth is described by an under-stoichiometry of Zn entailing an amorphous phase. The second zone appears after an increase of the zinc content makes it possible to obtain a stoichiometric crystallized material. Hypotheses are announced, supported by calculations of sputtered zinc atom energy and zinc vaporization temperature in the present conditions of growth. The model provides a good agreement with the observation of the difference of composition for films deposited at temperatures above 130°C in our sputtering process. In this paper, an original work on the phenomena taking place at different stages of the growth of $ZnGeN_2$ thin films is described and gives new elements of understanding to the previous studies in the literature.

9:40am **C3-2-FrM-6 CVD Process Development of Thin Film Triniobium-Tin on Copper SRF Cavities***,* ***Mohamed A. Cheikh,*** *S. McNeal, V. Arrieta,* Ultramet, USA

Innovative fabrication technologies for cost-effective high quality factor (high-Q), high-field superconducting radio frequency (SRF) components are needed for the economic viability of future accelerator facilities. The worldwide particle accelerator community continues to investigate alternatives and performance-enhancing modifications to bulk niobium accelerator components via the application of superconducting films. The Department of Energy (DOE) is interested in development of advanced process technologies to deposit superconducting materials such as triniobium-tin (Nb3Sn), which has the potential to exceed the performance capabilities of bulk niobium when formed on the interior surface of existing bulk niobium, or less costly copper, accelerator component structures, enabling substantial fabrication and operating cost reductions for continuous wave and high-gradient accelerators.

In recent research for DOE, Ultramet has developed chemical vapor deposition (CVD) techniques to create well-bonded layers of Nb3Sn on copper, niobium, and molybdenum substrates. Multiple copper single-cell 1.3-GHz SRF test cavities of the International Linear Collider (ILC) design were fabricated using the new CVD Nb3Sn process. The CVD Nb3Sn-on-copper fabrication methodology was scaled up and used to produce testable flanged Nb3Sn-lined copper cavities and copper/Nb3Sn cavities with an interlayer of CVD niobium formed using a thick film CVD process technology developed in concurrent research for DOE. RF performance capabilities and survivability at cryogenic temperatures were characterized by RF testing of the cavities at Cornell University.

Ultramet’s thick film niobium and thin film CVD Nb3Sn processes are uniquely well-suited for coating complex SRF accelerator component geometries because the virtually 100% dense coatings are formed on the substrate at the molecular level, and purity levels in excess of 99.99% are achievable. The CVD coating process exhibits the greatest throwing power, or ability to uniformly deposit materials onto/into intricately shaped or textured substrates.

Completion of this research was a necessary step toward the eventual commercial and scientific application of advanced accelerator component-forming technologies. A significant technical milestone was reached by the advances made in developing reliable fabrication techniques for reproducible CVD Nb3Sn- and niobium-lined copper accelerator components that offer high-gradient operation and substantial cost reduction for SRF applications worldwide.

10:00am **C3-2-FrM-7 Engineered Metal-Organic Framework-Based Heterogeneous Membranes with High Ionic Rectification for Ultrahigh Osmotic Power Generation from Organic Solutions***,* ***Amalia Rizki Fauziah,*** *L. Yeh,* National Taiwan University of Science and Technology, Taiwan

Taking inspiration from the electrocytes in the electric eel, consisting of numerous “subnanometer-scale” rectified ion channels allowing unidirectional and amplified ion transport, assorted artificial solid-state ion channel membranes have been developed over these past few years. Nevertheless, the conventional membrane designs were only limited to either one structure homogenous or two structures heterogeneous membranes. Herein, we report a feasible yet versatile strategy to fabricate the breakthrough membrane design that has never been reported before. An engineered metal-organic framework (MOF)-based ionic diode membrane (termed as ZIF-8/PSS@BANM), composed of a continuous zeolitic imidazolate framework-8 (ZIF-8) membrane incorporated with negatively space-charged polystyrene sulfonate (PSS) and branch-type alumina nanochannel membrane (BANM), was successfully developed (Fig. 1). Results obtained confirm that the heterogeneous membrane is with high geometry gradient from sub-micro-scale to sub-nano-scale and high space charge property. We show that the engineered MOF-based heterogeneous sub-nano-channel membrane can vividly rectify ion transport even in LiCl-methanol solution with a ratio as high as ~13 (Fig. 2a), capable of amplifying ionic current uni-directionally at the subnanometer-scale confinement, due to the broken symmetries in channel sizes, charges, and wettabilities (Fig. 2b). We thereby probe the use of this subnanometer-scale MOF-based ionic-diode membrane in harvesting osmotic energy from organic solutions. Captivatingly, a record power output of up to ~9.58 W/m^2 at a 50-fold LiCl gradient in methanol can be harnessed (Fig. 3a), majorly because of its unique geometry gradient channel structure (Fig. 3b), outperforming the bandgap of the commercial benchmark value (5 W/m^2) and the other conventional membranes structures. The continuous MOF-based heterogeneous membrane we developed here is with high novelty in membrane technology and the design strategy provides a promising approach for constructing new multifunctional biomimetic membranes towards advanced high-performance energy conversion devices.

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