

Thursday Afternoon, October 18, 2007

Thin Film

Room: 602/603 - Session TF1-ThA

Photovoltaics, Fuel Cells, and Alternative Energy Materials and Applications

Moderator: M. Drees, Luna Innovations Incorporated

2:00pm **TF1-ThA1 High Throughput Fabrication and Screening of Thin Film Electrocatalysts for Fuel Cell Applications**, *J.M. Gregoire, M. Kostylev, J. Jin, R.B. van Dover, F.J. DiSalvo, H.D. Abruna*, Cornell University

We describe methodologies for the generation and screening of combinatorial libraries of electrocatalyst materials for fuel cell applications. Composition spread thin films are codeposited via DC magnetron sputtering. The films are then screened for catalytic activity using a fluorescence indicator. The high-throughput nature of both the fabrication and screening processes, coupled with the versatility of the deposition system, allow for the rapid testing of a broad range of potential fuel cell electrocatalyst materials. Details of the techniques, fluorescence test results and characterization data for some catalytically active films will be presented.

2:20pm **TF1-ThA2 Atomic Layer Deposition of Alternative Energy Materials**, *X. Jiang, J.S. King, S.F. Bent*, Stanford University

Atomic layer deposition (ALD) is a method for depositing thin films of semiconducting, insulating and metallic materials using an alternating series of self-limiting reactions between gas phase precursors and the substrate. Over the past several years, ALD has grown steeply in popularity as a choice for the semiconductor industry. However, ALD's real potential for impact may lie in even more novel applications, including those in alternative energy. This presentation will describe our recent studies using ALD for the deposition of thin films for both fuel cell and solar cell applications. For solid oxide fuel cells (SOFCs), we have explored ALD for the fabrication of an ultra-thin Pt film for use as the electrocatalyst, and a Pt mesh structure for a current collector, as a means of improving catalyst performance at lower temperatures. Pt ALD was carried out using (methylcyclopentadienyl)trimethylplatinum (MeCpPtMe₃) and O₂ as precursors and N₂ as a carrier and purging gas. Ex situ analysis of the as-deposited Pt films shows that the platinum film is of excellent uniformity, with no measurable impurities and low electrical resistivity. In addition to the blanket deposition of platinum, we have used the technique of area selective ALD, by combining the methods of ALD and microcontact printing, for fabrication of spatially patterned Pt, to be used as a current collector grid for SOFCs. Working SOFC fuel cells were fabricated with ALD-deposited Pt, and their performance was characterized by a potentiostat-impedance system. The results show that comparable initial performance can be achieved with ALD deposited Pt anodes compared to the RF sputtered Pt anodes with only one-eighth the platinum loading required in the ALD film. For the photovoltaic application, we will describe a vertical nanostructured geometry in which the carrier diffusion length is decoupled from solar radiation absorption, enabling high efficiency cells to be fabricated inexpensively out of low quality materials. We will describe how ALD and other deposition methods can be used to deposit thin films of photovoltaic materials to make nanocomposite solar cells.

2:40pm **TF1-ThA3 Investigation of Bulk and Grain Boundary Diffusion of Oxygen in Yttrium Stabilized Zirconia Via Nuclear Reaction Analysis***, *M. Finsterbusch*, Montana State University and Technische Universitaet Ilmenau, Germany, *H. Chen, W. Priyantha*, Montana State University, *V. Shuthanandan*, Pacific Northwest National Laboratory, *R.J. Smith*, Montana State University, *J.A. Schaefer*, Technische Universitaet Ilmenau, Germany

Yttria stabilized zirconia (YSZ) is one of the most common solid ionic conductors considered for the electrolyte in solid oxide fuel cells operating at temperatures near 800°C. The addition of yttria into zirconia not only stabilizes the cubic fluorite phase of zirconia over a wide temperature range, but also introduces oxygen vacancies due to the smaller valency of Y³⁺ vs. Zr⁴⁺. High oxygen ionic conductivity associated with vacancy hopping is seen in YSZ for yttria doping levels around 10%. Numerous studies have been carried out to understand oxygen transport and surface exchange kinetics in single crystal YSZ.¹⁻³ However, for polycrystalline YSZ the description of diffusion processes is more complex due to the presence of interfaces and grain boundaries that act as preferential sites for variation in

composition and chemical state of the atomic species with respect to the bulk. In this study ¹⁸O tracer depth profiles were obtained using ¹⁸O(p,α)¹⁵N nuclear reaction analysis for both YSZ single crystals and sintered polycrystalline pellets. Samples were cleaned and pre annealed in a tube furnace for 8 hours at 800°C in air. Afterwards they were exposed for various times at a pressure of 10 Torr of 99% pure ¹⁸O at various temperatures up to 900°C. By contrasting the differences of ¹⁸O transport for the two structures, the influence of grain boundaries on oxygen transport and exchange kinetics were extracted.

*HiTEC is funded by DOE as a subcontract from Battelle Memorial Institute and Pacific Northwest National Laboratory under Award No. DE-AC06-76RL01830.

¹ R. Roewer, G. Knoener, K. Reimann, H.E. Schaefer, U. Soedervall; phys. stat. sol. (b) 239, No. 2, R1-R3 (2003)/DOI 10.1002/psb.200309011

² N.I. Joos, P.A.W. van der Heide, J.R. Liu, R. Christoffersen, W.K. Chu, C.A. Mims; Mat. res. Soc. Symp. Proc. Vol. 548, Page 605-610

³ P.S. Manning, J.D. Sirman, R.A. De Souza, J.A. Kilner; Solid State Ionic 100 (1997) 1-10.

3:00pm **TF1-ThA4 Thermal Stability and Oxidation Resistance of Protective Coating on Stainless Steel Interconnect for Solid Oxide Fuel Cells**, *H. Chen, J.A. Lucas, W. Priyantha, R.J. Smith, P.E. Gannon, M. Deibert*, Montana State University, *V.I. Gorokhovskiy*, Arcocomac Surface Engineering, *V. Shuthanandan, P. Nachimuthu*, Pacific Northwest National Laboratory

Chromia forming ferritic stainless steels are being considered for application as interconnects for planar solid oxide fuel cells (SOFC) because of their low cost and flexibility. Many SOFC designs will operate at temperatures exceeding 700°C. At these temperatures, ferritic steels lack environmental stability in the SOFC environment, and as a result may degrade the performance of the SOFC. In this study, an effective, dense and well adherent TiCrAlYO coating was deposited on 430SS using filtered arc deposition technique. XRD indicates that nanocrystalline spinel is the dominant crystal structure in the coating. Rutherford backscattering with He and non-Rutherford scattering with proton were used to characterize the composition and the thermal stability of the coatings. The chromium volatility of the coated steel plates at 800°C was measured using ion beam analysis. Significant reductions in oxidation rates as well as reduced Cr volatility were observed for the coated alloys.

3:40pm **TF1-ThA6 Optimizing the Structure and Composition of Heterostructured Ceria / Zirconia Multilayers through Oxygen Plasma Assisted Molecular Beam Epitaxy**, *S.V.N.T. Kuchibhatla, P. Nachimuthu, C.M. Wang, V. Shuthanandan, M.H. Engelhard, L.V. Saraf, S. Thevuthasan*, Pacific Northwest National Laboratory, *S. Seal*, University of Central Florida

Mesoscopic fast ion conduction in nanometer-scale planar heterostructures is gaining attention from researchers in the field of solid-state ionic conducting devices. One such device and the most popular among alternative energy sources is solid oxide fuel cell (SOFC). In SOFCs oxygen ions should be effectively conducted from cathode to anode through an electrolyte. Hence, it is quite essential to develop electrolyte materials that offer low and intermediate temperature ionic conductivity. Currently, yttria stabilized zirconia (YSZ) is the most widely used electrolyte, but the need for temperatures in the range of 800°C-1000°C imposes various restrictions in expanding the SOFC technology. Samaria doped ceria has been extensively studied as an alternative to YSZ at intermediate temperatures. Structural configuration of these thin films plays a major role in oxygen ionic conduction and we have initiated several studies to understand the influence of structure and chemistry of these thin films on oxygen ionic conductivity. We have synthesized high quality single- and poly- crystal films of Sm doped ceria (SDC) and Sc stabilized zirconia (ScSZ) using oxygen plasma assisted molecular beam epitaxy and characterized those using several surface and bulk sensitive techniques. The effect of growth temperature on the domain structure and the ionic conductivity are features of interest in the research associated with single- and poly- crystal SDC films. It appears that the strain, chemistry and structure at the interface play a role on ionic conduction in the SDC and ScSZ multi-layer films. The enhancement in oxygen ionic conductivity through some of these films at low temperatures are encouraging.

4:00pm **TF1-ThA7 Controlling the Doping Concentration and Thermoelectric Applications of Na_xV₂O₅ Thin Films**, *S. Iwanaga, M. Marciniak, R.B. Darling, F.S. Ohuchi*, University of Washington

A high thermoelectric coefficient has been reported for Na_xV₂O₅ thin films. Na_xV₂O₅ structure consists of V₂O₅ layers, where Na atoms are retained between the layers, leading to various phases depending on the Na concentration. From the view point of processing this class of material for thermoelectric device applications, the precise control of the Na concentration and stabilization of the desired phase are the key issues.

Recently, we presented a possibility of a solution route to make $\text{Na}_x\text{V}_2\text{O}_5$ thin films. Here, we report that through this new processing route, we can control the crystal phase of $\text{Na}_x\text{V}_2\text{O}_5$ thin films, specifically between β - and γ - phases, through annealing conditions and the choice of the substrates. β -phase is preferred for thermoelectric applications due to high Seebeck coefficient and a relatively good electrical conductivity. We found that on quartz substrate, high temperature annealing (600 C) leads to predominantly β - phase. By using soda-lime glass, which contains high Na_2O , as a substrate, the Na concentration in $\text{Na}_x\text{V}_2\text{O}_5$ films increases with increasing annealing time: coexistence of β - and γ - phases (10 minutes annealing) develops into γ - phases dominated film upon annealing for >30 minutes. Our results suggest that the Na concentration can be kinetically controlled in this material system. The possibility of $\text{Na}_x\text{V}_2\text{O}_5$ - based thermoelectric device is proposed.

4:20pm **TF1-ThA8 From Uncontrolled and Controlled Size and Shape Intercalated Nanostructures to Bulk Materials for Thermoelectric Device Applications: Old and New Materials - New Techniques**, *N. Sorloaica-Hickman*, University of Central Florida

The properties of all materials are highly dependent on structure, composition, size and shape. As we seek to explore and utilize novel phenomenon at the nano, 2-dimensional and 3-dimensional scale, a basic understanding of structure/composition/size/shape property relations alone are not enough unless this understanding is made in the context of a specific device and in relation to the practical, economic considerations. This investigation requires a highly integrated approach to all aspects of development of these integrated devices, including theoretical prediction, synthesis, processing and characterization in concert with device design, optimization and implementation. Theoretical and experimental results predicted that the nano-scale materials have better thermoelectric properties than bulk materials.¹ Previous theoretical work on the effect of the grain boundaries in polycrystalline materials indicated that the scattering of the phonons in smaller grains could be very beneficial for the efficiency of the thermoelectric materials.² This presentation will highlight some new directions in size and shape controlled nanostructure (grains) and bulk thermoelectric materials research based on our theoretical and experimental investigations. Specific configurations where size and shape of the nanostructures that will constitute the bulk materials are controlled during fabrication will be discussed. Preliminary calculations of the electronic and thermal properties as a function of the composition, size and shape of the intercalated nanostructure will be also presented. We will also describe the synthesis techniques of the nanostructures and the method to incorporate these structures into bulk materials during fabrication. However, the challenge remains to achieve higher performance results in integrated systems in order to more rapidly incorporate them into standard thermoelectric devices.

¹M. S. Dresselhaus, J. P. Heremans, in *Thermoelectrics Handbook: Macro to Nano* (Ed: D. M. Rowe), Taylor and Francis, CRC, Boca Raton, FL 2006, Ch. 39, p. 39-1-39-24.

²J. W. Sharp et al., *Boundary Scattering and the Thermoelectric Figure of Merit*, *Phys. Stat. Sol. (a)* 187, No. 2, 507-516 (2001).

4:40pm **TF1-ThA9 Fabrication of Multilayered Thin Film Cooling Devices**, *Z. Xiao*, Alabama A&M University

Multilayered thin film cooling devices were designed and fabricated for the application of highly efficient solid-state micro cooling. Multilayered $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ (p-type) and $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_x\text{Se}_{3-x}$ (n-type) superlattice thin films were used as the material systems for fabrication of the cooling devices. The multilayered films were grown by e-beam evaporation and had a periodic structure consisting of alternating $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ layers or $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_x\text{Se}_{3-x}$ layers, with 5-10 nm thickness each. The cooling device consists of pairs of n-type and p-type legs, which are connected electrically in series and thermally in parallel. Under the applied voltage, both electrons in n-type legs and holes in p-type legs move from the cooling end, carrying heat, therefore, heat is pumped away from the cooling end to the hot end, where the heat is finally ejected away. Large number of pairs of n-type and p-type legs with size ranging from 7 μm by 14 μm to 30 μm by 40 μm is integrated in a single device using microfabrication techniques. Photomasks were designed for the fabrication of the cooling devices, and clean room-based microfabrication techniques were used to fabricate the devices. The developed cooling device is a good candidate for the application of high-efficiency solid-state micro cooling. The electrical and thermal parameters of the material systems such as the electrical conductivity, thermal conductivity, and Seebeck coefficient will be characterized and the cooling efficiency will be measured. The results will be reported in the conference.

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5:00pm **TF1-ThA10 Optical Characterization of InN layers grown by High-Pressure CVD**, *M. Alevli, G. Durkaya*, Georgia State University, *R. Kirste*, Technische Universität Berlin, Germany, *A. Weesekara, A.G.U. Perera*, Georgia State University, *A. Hoffmann*, Technische Universität Berlin, Germany, *N. Dietz*, Georgia State University

A growing number of potential applications such as high-efficient heterojunction solar cells, thermoelectric devices and terahertz detector will become possible as Indium Nitride (InN) and In-rich group III-nitride (N) materials become more mature and can be integrated with other-rich group III-N alloys. Understanding and controlling the physical properties of the InN is of essential importance next to its integration as a component of $(\text{Ga}_{1-x}\text{In}_x)\text{N}$ alloy system, which is crucial for fabrication of wavelength tailored high-efficient LEDs and displays. The present limitations in this area are in the growth of high quality InN and In-rich group III-N at processing conditions that are compatible with GaInN alloys. The difficulties arise from the low dissociation temperature of In-rich group III-N, requiring extraordinarily high nitrogen overpressure to stabilize the material up to optimum growth temperatures. Our research explores the growth of InN and In-rich group III-N by high-pressure chemical vapor deposition (HPCVD), an approach that allows controlling and stabilizing the vast different partial pressures of the constituents. The results show that the chosen HPCVD pathway leads to high-quality single crystalline InN, demonstrating that HPCVD is a viable tool for the growth of In-rich III-N alloys. The structural analysis of InN deposited on GaN-Sapphire substrate by XRD show single phase InN(0002) peaks with full width half maximum below 400 arcsec. The optical transmission analysis shows that an apparent band gap is around 1.4 eV with absorption centers at 0.8 eV and 0.4 eV. The strength of the low energetic absorption centers are closely related to the precursor ratios and the utilized growth temperatures. Infrared reflectance spectroscopy is used to estimate the high frequency dielectric constant, the free carrier concentrations and carrier mobilities in these layers. The free carrier concentration is found to be in the upper 10^{19} cm^{-3} with the corresponding mobilities around $600 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. A further reduction of residual extrinsic impurities in the precursor and carrier gas is presently explored to further reduce the free carrier concentration in the layers. The modeling of the IR-reflectance spectra indicate the presence of two distinct InN layers: one with electron concentrations below $5 \times 10^{17} \text{ cm}^{-3}$, which is followed by second layer in the upper 10^{19} cm^{-3} closer to the surface.

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