

# Tuesday Morning, November 11, 2014

## Thin Film

Room: 305 - Session TF+SE-TuM

### Energetic Thin Films/Optical Characterization

**Moderator:** David Adams, Sandia National Laboratories, Christophe Vallee, LTM - CEA/LETI, France

8:00am **TF+SE-TuM1 Investigations on  $\text{LiMn}_x\text{Ni}_y\text{O}$  Thin Films Deposited by RF Sputtering using Powder Target for Thin Film Battery Applications.** *Kosuri Yellareswara Rao*, Indian Institute of Science, India

Cathode materials in the form of thin films for all solid state Li ion batteries (thin film batteries) application have attracted wide attention among the scientific community because of the inherent benefit of studying pure phase of the active materials without any binders and conductive additives such as carbon black, NMP etc [1,2]. In the present work thin films of  $\text{LiMn}_x\text{Ni}_y\text{O}$  have been prepared in a cost effective approach using powder sputtering on nickel coated stainless steel (SS 304) substrates. Powder sputtering is more convenient with the advantages like less material consumption, slightly higher deposition rates and cost effective approach compared to pellet sputtering. The advantage of utilizing powder sputtering for the deposition and electrochemical performance of  $\text{Li}_x\text{MnO}_y$  thin films has been reported [3]. Post deposition annealing at 500 °C for one hour was carried out in air ambient. XRD, XPS and electrochemical characterizations have been carried out to investigate the phase, surface atomic concentration and electrochemical performance. XPS analysis indicates the presence of manganese, nickel, oxygen, and lithium at the surface as shown in Figure. 1. Electrochemical investigations delivered a specific discharge capacity of 54  $\mu\text{Ah} \cdot \mu\text{m}^{-1} \cdot \text{cm}^{-2}$  in the potential window 2.0–4.4 V vs  $\text{Li/Li}^+$  in the first discharge cycle. Charge discharge profile up to 40 cycles have shown in the Figure.2. Discharge capacity values are in good agreement with the literature achieved using pellet sputtering.

References:

1. J.M. Tarascon, M. Armand. *Nature* 414, 359 (2001)
2. J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda, C.D. Evans. *Solid State Ionics* 135, 33– 45 (2000)
3. K.Yellareswara Rao, D. Shanmugha sundaram, C.S. Nimisha, Tirupathi Rao Penki, N. Munichandraiah, G. Mohan Rao. *J. Electrochem. Soc* 161, A28-A32 (2014)

8:20am **TF+SE-TuM2 The Dynamics of Reactive Foil Ignition after Pulsed Laser Irradiation.** *Ryan Murphy, R.V. Reeves*, Sandia National Laboratories, *J.P. McDonald*, Dow Corning Corporation, *D.P. Adams*, Sandia National Laboratories

It has been shown that forced mixing of reactive layers (foils) leads to an exothermic release of energy after initiation of mixing by forced impact or pulsed laser irradiation. In order to understand the ignition of foils initiated by laser irradiation, we study the interaction of laser pulses with Al/Pt multilayer reactive foils prepared by sputter deposition. It will be shown that the single-pulse ignition threshold and dynamics are dependent on the length of the laser pulse as the pulse length is varied from 100 fs to 100 ns. The dependence of the ignition threshold on pulse length is a combination of laser-material interactions such as the size of the heat affected zone, changes in reflectivity with pulse length, and the onset of ablation for ultrafast irradiation. The laser spot size is varied for each pulse length to explore the effects of heat confinement on the ignition threshold. The dynamics of foil ignition is further investigated by imaging ignition and the subsequent reaction with a high-speed camera. Varying the bilayer thickness and laser pulse length is shown to change properties such as mixing, ignition in the solid-state, and the onset time of reaction.

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8:40am **TF+SE-TuM3 Probing Rapid Formation and Oxidation Reactions with Multilayer Films and Foils.** *Timothy Weihs*, Johns Hopkins University

**INVITED**

Vapor-deposited multilayer films and foils provide model structures for studying exothermic formation and oxidation reactions. These reactions can proceed at slow to moderate rates ( $10^1$  to  $10^3$  K/s) using controlled heating or at very rapid rates ( $10^6$  to  $10^8$  K/s) by initiating self-propagating mixing within the films or foils. In this presentation we will probe the sequence of

intermetallic phase formation and the kinetics of rapid oxidation as a function of heating rate, chemistry, and concentration gradients using novel characterization tools such as nanocalorimetry, bomb calorimetry, dynamic transmission electron microscopy and synchrotron X-ray diffraction. The experimental results will be compared with analytical predictions and molecular dynamic simulations and controlling factors will be identified.

9:20am **TF+SE-TuM5 Detonation in Vapor-deposited Explosive Films at the Micro-scale.** *Robert Knepper, M.P. Marquez, A.S. Tappan*, Sandia National Laboratories

Recent advances in physical vapor deposition of explosive materials have led to films that are capable of detonating at thicknesses smaller than 100 microns. The critical thickness needed to sustain detonation can be reduced even further (down to a few tens of microns) by confining the explosive with thin layers of a dense, inert material. The ability to sustain detonation at such small length scales opens the potential for such films to be integrated into micro-scale systems using standard micro/nanofabrication methods for use in actuation, gas generation, or similar functions. In this work, we present vapor-deposited hexanitroazobenzene (HNAB) and copper films as a model system to study the effects of confinement on the detonation properties of secondary explosives. Both the HNAB and copper confinement layers are vapor-deposited to promote intimate contact between the explosive and confinement and to provide precise control over both layer thicknesses and microstructure. Confinement thickness is varied to determine the minimum necessary to behave as though the confinement was effectively infinite, and the effects on detonation properties are quantified. In addition to the practical impact of these experiments, identification of the minimum effectively infinite confinement condition can provide insight into the kinetics of the detonation reaction.

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9:40am **TF+SE-TuM6 Investigating the Effect of Heating Rate on the Al/Ni Formation Reaction using In Situ Nanocalorimetry.** *Michael Grapes*, Johns Hopkins University, *M.K. Santala, T. LaGrange, G.H. Campbell*, Lawrence Livermore National Laboratory, *D.A. LaVan*, National Institute of Standards and Technology (NIST), *T.P. Weihs*, Johns Hopkins University

The Al/Ni formation reaction is highly exothermic and of both scientific and technological significance. In particular, Al/Ni thin-film multilayers have been used as a model system to understand how steep concentration gradients and large heating rates affect the identity and sequence of phases that form at the interface between two materials. We have developed an *in situ* nanocalorimetry system that enables us to simultaneously measure the heat generated by the Al/Ni reaction and observe the phases formed. The added ability to controllably vary the heating rate from 1000 K/s to 100,000 K/s makes possible a systematic assessment of the phase transformation sequence with heating rate that we hope will shed light onto the relative effects of kinetic and thermodynamic phase suppression in determining the first phase to form. In this talk I will describe the experimental system, present the baseline results that are obtained at low heating rates, and provide an update detailing recent results and potential conclusions of the systematic study.

11:00am **TF+SE-TuM10 The Role of Magnesium in Heat Generation from Al-Mg/Zr Laminate Foils.** *Kyle Overdeep*, Johns Hopkins University, *D.J. Allen, N.G. Glumac*, University of Illinois at Urbana-Champaign, *K.J.T. Livi, T.P. Weihs*, Johns Hopkins University

This study examines the ability of reactive multilayer foils to generate heat as a function of magnesium composition. This is accomplished by comparing the heat generated from the reactions of three chemistries: Al:Zr, Al-8Mg:Zr, and Al-38Mg:Zr, which correspond to foils with alternating aluminum and zirconium layers where the Al is either pure, an 8 at.% Mg alloy, or a 38 at.% Mg alloy, respectively. We have found that Al-8Mg:Zr releases 53% more heat than the Al:Zr foils when reacted in air (from 2.5 kJ/g for Al:Zr to 3.8 kJ/g for Al-8Mg:Zr), and 28% more heat than Al-38Mg:Zr (3.0 kJ/g), based on measurements performed in a specially designed bomb calorimeter. This may be a result of the expulsion of particles and vapor which is unique to the Mg-containing foils, because the increase in surface area enhances combustion. In order to understand this mechanism more thoroughly, the ejected particles, ejected vapor, and remaining foils were all characterized to understand the amount and composition of all species being ejected, and how that influences the combustion of each foil.

11:20am **TF+SE-TuM11 Dynamics of the Inverse MAPLE Process for Deposition of Nanoparticles and Nanoporous Thin Films, Matthew Steiner, P.J. Steiner, J.M. Fitz-Gerald, University of Virginia**

Matrix assisted pulsed laser evaporation (MAPLE) was developed in the late 1990s at the U.S. Naval Research Laboratory as a non-destructive method of thin film deposition for polymers that could potentially be damaged by the ultraviolet radiation utilized for pulsed laser deposition. Conventionally MAPLE starts with a dilute organic compound dissolved in a volatile solvent that serves as a solid matrix when frozen at liquid nitrogen temperatures. By choosing a solvent with a significant UV absorption coefficient, the frozen matrix can be heated by preferential photothermal excitation during irradiation, leading to evaporation and desorption of the less volatile solute molecules onto a substrate in thin film form. Since its conception, use of MAPLE has expanded from the deposition of molecular polymers and proteins to more macroscopic species such as carbon nanotubes, living cells, and recently a number of inorganic nanoparticles.

Inspired by the laser decomposition of metal-acetate based sol-gels to form nanoparticle networks, it is also possible to simultaneously synthesize and deposit well-dispersed nanoparticles or nanoporous films through an inversion of the conventional MAPLE process, utilizing weakly absorbing solvents and photo-sensitive chemical precursor solutes. The chain of events following the laser pulse first entering the target and culminating with observation of nanoparticles on the substrate has been principally interpolated backwards from the nanoparticles produced; suggesting photothermal decomposition of the acetate precursors and formation of nanoparticles within the target prior to and eventually driving ejection. The research presented represents major developments in the understanding of the underlying sequence of multi-scale events controlling the inverse MAPLE deposition process. Modeling addresses optical absorption via Mie theory and the role of matrix conduction in solving nanoparticle heat balance within the target, which in turn is shown to play critical role in the deposition process. New supporting evidence is offered through direct observation of irradiated targets via cryo-stage scanning electron microscopy, as well and conventional scanning and transmission electron microscopy of deposited films and nanoparticles.

11:40am **TF+SE-TuM12 Structural, Optical and Electrical Properties of Fe-doped BiOCl, Yoon Myung, S. Banerjee, F. Wu, P. Banerjee, Washington University, St. Louis**

BiOCl is an attractive p-type semiconductor with a wide band-gap of 3.4 eV. It has a unique layered structure of alternating  $[\text{Bi}_2\text{O}_2]^{2+}$  layers, interleaved by double slabs of Cl<sup>-</sup> ions. The ionic layering guides the growth of BiOCl along the c-axis to form a 2D nanosheet morphology, favoring rapid and efficient electron/hole separation. Thus, BiOCl nanosheets can be naturally exploited as a photoactive material in applications such as solar harvesting, photocatalysis and sensing. However, given the large band-gap of BiOCl strategies to sensitize the BiOCl to the visible spectrum must be made. Substitutional doping of transition metal ions is an attractive approach given that many of the transition metal oxides are earth-abundant and have their band-gaps in the visible spectrum.

In this study, we demonstrate the effect of Fe doping on the structural, optical and electrical properties BiOCl nanosheets. Fe-doped BiOCl were synthesized by a facile hydrolysis process. Next, the samples are subjected to various annealing temperatures. We show that anneal temperatures >200 °C can initiate successful Fe incorporation in BiOCl crystal lattice. X-ray diffraction (XRD) shows a higher angle shift after thermal annealing, corresponding to decrease in the lattice constant as a result of Fe<sup>3+</sup> substitution of the Bi<sup>3+</sup> ions. Raman spectroscopy shows the  $E_g$  stretching mode of the Bi-Cl bond has lower frequency shift, which is consistent with the XRD analysis of Fe<sup>3+</sup> substitution. Electrical property measurements including IV characteristics show a linear behavior with a resistance of ( $2.5 \times 10^{11}$ ,  $9.8 \times 10^{10}$  and  $9.32 \times 10^{10}$  Ω) for samples annealed at 200, 300 and 400°C respectively.

Finally, we demonstrate a highly sensitive O<sub>2</sub> sensor using Fe-doped BiOCl nanosheets, operating at room temperature. The interaction of vacancies and O<sub>2</sub> is explored in the context of the Fe-doping in BiOCl.

12:00pm **TF+SE-TuM13 Cathodoluminescent and Photoluminescent Properties of Sr<sub>2</sub>SiO<sub>4</sub>:Dy<sup>3+</sup> Thin Films Prepared by the Sol-gel Spin Coating Technique, M.A. Tshabalala, H.C. Swart, O.M. Ntwaeaborwa, University of the Free State, South Africa, Bakang Mothudi, University of South Africa, South Africa**

Phosphor thin films have been attracting attention because they play important roles in high resolution devices such as cathode ray tubes, thin film electro-luminescent panels and field emission displays<sup>1</sup>. Displays based on thin film phosphors are characterized by high contrast and resolution, good thermal conductivity as well as high degree of uniformity and better adhesion to substrates<sup>2</sup>. Efforts have been made in the past years to develop various types of luminescent thin films via the sol-gel method by using

either dip-coating or spin-coating<sup>3</sup>. However spin-coating has emerged as the preferred technique because it is more versatile than the dip-coating technique. Thin film phosphors based on oxide hosts have received considerable attention for use in flat-panel displays due to their outstanding luminescent properties, high chemical stability in high vacuum and lack of emission of corrosive gases under electron bombardment<sup>4</sup>. In this study we investigated the structure, particle morphology, surface topography, chemical composition and luminescent (photoluminescent (PL) and cathodoluminescent (CL)) properties of dysprosium (Dy<sup>3+</sup>) doped oxide based strontium silicate (Sr<sub>2</sub>SiO<sub>4</sub>) thin-film phosphor prepared by the sol-gel spin coating technique. Several parameters including number of sol drops, deposition times and post-deposition annealing temperatures were varied. Both the PL and CL intensities were dependent on the deposition conditions and post deposition annealing temperature. Data from scanning electron microscope and atomic force microscope show that the major influence of the deposition conditions on the CL/PL intensity was through changes in the morphology and topography of the films, which affects light scattering and out-coupling. The chemical states and composition, and the depth profiles of the films were examined using the x-ray photoelectron spectroscopy and Auger electron spectroscopy. The influence of the various deposition conditions on the luminescent intensities and the quality of the films will be discussed.

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