

# Wednesday Afternoon, October 20, 2010

## Energy Frontiers Topical Conference

Room: Mesilla - Session EN+NS-WeA

### Nanostructures for Energy Conversion & Storage I

Moderator: S. Agarwal, Colorado School of Mines

2:00pm EN+NS-WeA1 **Electrochemical Performance of Nanostructured Sn Thin Films as Anodes of Thin film Li-ion Battery.** C.S. Nimisha, G. Venkatesh, T. Dhivya, G. Mohan Rao, N. Munichandraiah, Indian Institute of Science, India

Nanostructured Sn thin films have been prepared by rf sputtering and thermal evaporation on to silicon substrates for evaluating the electrochemical performance to use as anode layer of thin film Li-ion battery. The scanning electron microscopy (SEM) shows different film morphologies for evaporated and sputtered films which directly control the electrochemical performance. Crystallinity of the deposited films were ensured by X-ray diffraction (XRD). Bio-Logic SA potentiostat / Galvanostat (model:VPM3) is used for testing electrochemical performances. Sn thin films prepared by thermal evaporation from Sn granules of 99.99% purity resulted in films with nanograins of ~200nm size homogeneously distributed over the surface. Whereas films made by rf sputtering from Sn target (99.99% purity) with Ar as sputtering gas at a pressure of  $5 \times 10^{-3}$  mbar, resulted in highly porous film surface with 'nanobead' (~50nm size) formation inside the edges.

For electrochemical studies half cells were assembled using lithium as counter and reference electrodes in 1M LiAsF<sub>6</sub> dissolved in ethylene carbonate and dimethyl carbonate electrolyte. Charging was done with a constant current density of  $10 \mu\text{A} / \text{cm}^2$  up to 1.2 V, followed by discharging at  $10 \mu\text{A} / \text{cm}^2$  down to 0.2 V. The capacity obtained from both evaporated and sputtered films clearly shows the three plateau regions of lithiation and delithiation for both evaporated and sputtered films. From the evaporated film, a discharge capacity of  $83.6 \mu\text{Ah}/\text{cm}^2$  is obtained, whereas from sputtered film a much higher capacity of  $886 \mu\text{Ah}/\text{cm}^2$  is obtained.

We speculate that the increased surface area of the rf sputtered Sn film due to the porous nature and the presence of nano beads, resulted in higher capacities than the evaporated Sn films, which have relatively bigger sized grains. Also the presence of more nano sized features in the sputtered film surface reduces the pulverization of Sn films during cycling since the absolute volume change would be minimized. The reduction in diffusion length for Li-ion and increased effective surface area ensures higher discharge capacity from rf sputtered Sn films compared to evaporated films. The higher discharge capacity obtained from rf sputtered Sn thin films makes it ideal candidate for integrating as anode layer of thin film Li-ion battery.

2:20pm EN+NS-WeA2 **Lithographically Defined Porous Carbon Electrodes.** R. Polsky, B. Burckel, X. Xiao, C.M. Washburn, M. Roberts, B. Bunker, Sandia National Laboratories, A. Raub, S. Brueck, University of New Mexico, S. Brozik, D.R. Wheeler, Sandia National Laboratories

Pyrolyzed Photoresist Films (PPF) have electrochemical properties similar to glassy carbon electrodes with the unique feature that they can be lithographically defined to create microstructures and microfeatures. Previously we reported that the near atomically flat surface of PPF results in the deposition of gold nanoparticles (1-3 nm) with narrow size distributions. [1] Herein we describe the fabrication of porous carbon structures using interference lithography (IL) to generate 3-D structures in PPF that contain five patterned layers with microporous hexagonal lattices (~800 nm in diameter). [2] Because IL is a maskless approach porous carbon structures are able to be patterned over large volumetric areas (2.5 X 2.5 cm). We demonstrate the porous carbon structures can be used as a highly adaptable electrode material suitable for the deposition of metal nanoparticles (Au, Ag, and Pt) and conducting polymers with possible applications in such areas as fuel cells, ultracapacitors, and biosensors.

#### References

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- [2] D.B. Burckel, C.M. Washburn, A.K. Raub, S.J. Brueck, D.R. Wheeler, S.M. Brozik, R. Polsky, *Small*, **2009**, 5, 2792-2796.

2:40pm EN+NS-WeA3 **Designing Inorganic Nanostructures for Solar Cells and Energy Storage Devices.** Y. Cui, Stanford University INVITED

The capability of synthesizing materials with nanometer size and shape control has enabled exciting opportunities to engineer materials for controlling and understanding electronic, photonic, mechanical and ionic

processes, which are important for applications such as energy conversion and storage devices. In this talk I will show two examples on how we design nanoscale materials towards high performance photovoltaics and energy storage devices. In the first example, nanocone- and nanodome-shaped substrates are designed for efficient photon management and charge carrier separation, which result in significant improvement of solar cell power efficiency compared to the flat film devices. Second, nanowires are exploited to maximize efficiency of simultaneous electron and ionic insertion with facile strain relaxation, which enable novel ultrahigh capacity storage capacity materials towards next generation of high energy density batteries.

4:00pm EN+NS-WeA7 **Synthesis of Rare Earth Ion Co-Doped Core-Shell Nanostructures for Improved Energy Generation Efficiency.** J.A. Dorman, J. Hoang, J.H. Choi, J.P. Chang, University of California, Los Angeles

The development of rare-earth ion (RE) doped phosphors allows for the conversion of photons at various wavelengths to those at energies similar to that of the photovoltaic band gap. Work has been shown that through the incorporation Er<sup>3+</sup> and Yb<sup>3+</sup> into complex metal oxides, specifically yttrium based compounds, both energy upconversion and downconversion can be utilized to convert absorbed photons to a more desirable energy for Si based solar cells. However, both photoluminescence and energy transfer mechanisms are highly susceptible to the local crystal environment, including the overall crystal field and surrounding molecules. The addition of a shell layer increases luminescence by decreasing the effect of surface quenching sites while promoting energy transfer between layers.

This work focuses on the synthesis of core-shell nanostructures while controlling the luminescence spectrum through the spatial distribution within the particle architecture using a combination of wet chemical synthesis and atomic layer deposition (ALD). Y<sub>2</sub>O<sub>3</sub>: Er<sup>3+</sup>, Yb<sup>3+</sup> core nanoparticles (NPs) were synthesized using the molten-salt synthesis. Enhanced luminescence was observed after deposition of a high quality shell of Y<sub>2</sub>O<sub>3</sub>: Yb<sup>3+</sup>, roughly 5-10 nm thick, by radical enhanced ALD. However, the deposited shell layer has a slightly lower density, as shown in TEM imaging. The downconversion and upconversion luminescence spectra was collected for Y<sub>2</sub>O<sub>3</sub>:Er<sup>3+</sup>,Yb<sup>3+</sup> NPs, 1 mol % Er<sup>3+</sup> and the Yb<sup>3+</sup> mol % ranging from 0 to 8 %, with a 980 nm diode excitation. The various NPs cores emitted strongly in the green (532 nm) and red (650 nm) upconversion luminescence and IR (1540 nm) downconversion luminescence, the <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub>→<sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>F<sub>9/2</sub>→<sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>I<sub>13/2</sub>→<sup>4</sup>I<sub>15/2</sub> transitions, respectively. A systematic luminescent red shift, ~2 nm, was observed when comparing the core to core-shell structures for all samples. Visible luminescence occurs via an energy transfer process, requiring two absorbed photons (red) and three absorbed photons (green), between the Yb<sup>3+</sup> <sup>2</sup>F<sub>5/2</sub> and Er<sup>3+</sup> <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub> energy levels. The proposed energy transfer mechanism incorporates the interaction between RE ions at the core-shell interface based on the local binding environment modeled using enhanced x-ray absorption fine structure (EXAFS) spectroscopy. Additionally, the energy transfer coefficients are extracted using the excitation lifetimes and the red-to-green ratio is correlated to key spectroscopic parameters, such as the Judd-Ofelt parameters and branching ratio. These values can be compared to the bulk Y<sub>2</sub>O<sub>3</sub> luminescence and the actual measured lifetimes, 200 ms (green) and 600 ms (red), as the figure of merit.

4:20pm EN+NS-WeA8 **High Figure of Merit Nanostructured Bulk Thermoelectrics from Doped Pnictogen Chalcogenide Nanoplate Crystals.** R.J. Mehta, C. Karthik, B. Singh, Y. Zhang, E. Castillo, T. Borca-Tasciuc, G. Ramanath, Rensselaer Polytechnic Institute

Nanostructured pnictogen chalcogenides are attractive for realizing high thermoelectric figure of merit (ZT) materials for solid-state refrigeration and electrical power harvesting from heat. Here, we report a scalable surfactant-assisted microwave synthesis approach to realize bulk assemblies of sulfur-doped nanostructures with 25% to 250% higher room temperature ZT than the non-nanostructured bulk counterparts of both n- and p-type nanostructured bulk materials with room temperature ZT ~ 1. We synthesized ~5- to 20-nm-thick single-crystal hexagonal sulfur-doped nanoplates of the pnictogen chalcogenides in a microwave oven, followed by compaction and sintering to obtain bulk nanostructured pellets. The n-type material was obtained from single-component nanostructure assemblies of bismuth chalcogenides, while the p-type material was obtained by mixing bismuth telluride and antimony telluride nanostructures. Electron spectroscopy shows that <1% sulfur doping from thioglycolic acid, used as a nanoplate-sculpting and surface-passivating agent, increases the power factor  $\alpha^2\sigma$  to ~5% greater than that of the state of the art alloys. Electron microscopy analyses reveal that measured k values as low as 0.5 – 1.4 W/mK, which are ~50% lower than bulk alloys, are due to 50-100 nm

grains with intragrain structural modulations with characteristic wavelengths between 3-10 nm. Our findings open up completely new possibilities for realizing novel high ZT thermoelectric materials through the assembly of doped single-crystal nanostructures.

4:40pm **EN+NS-WeA9 Core-Shell Nanodielectrics through Hybrid Wet Chemistry/Laser Process for Embedded Energy Storage Capacitors**, *B. Rajesh*, University of Houston, *N. Badi*, University of Houston and Integrated Micro Sensors, Inc., *A. Bensaoula*, *R. Supparesk*, *T.R. Lee*, University of Houston

Extensive interest is being invested into the research of nanodielectrics because of their promising applications in energy storage solutions as both discrete and embedded capacitors. They are useful in integral passive technology for miniaturization, improvement of power distribution and as decoupling capacitors. Their applications include, but are not limited to, high speed computing boards (servers, routers, super computers) and module boards (cell phones, PDA, note book computers). We fabricated high capacitance density dielectrics for flexible electronics by embedding core-shell type gold-silica nanoparticles in a polymer matrix using a coupled sol-gel procedure with laser engineering technique.

We report on fabrication of nanodielectric capacitors based on core-shell nanoparticles embedded in polyvinyl pyrrolidone (PVP) dielectric matrix. We developed a process chain to optimize the use of PVP as dielectric and measured its dielectric constant (K) as 7 at 10 KHz and breakdown field as 130V/ $\mu\text{m}$ . Monodispersed core-shell nanoparticles (NPs) are prepared with two different structures: 1) 35nm gold core – 95nm silica shell and 2) coating 35nm gold NPs with polymer compatible self assembled monolayer (SAM). Pre-processing is performed to uniformly disperse the NPs in a polymer matrix and to selectively form the polymer shell around each of the nanoparticles. Post-processing is carried out to spin coat on substrates and to cure under UV light to make capacitor slabs.

The results from SEM and AFM analysis, thermal and frequency response, breakdown dielectric strength and dielectric loss of the films for different loadings of NPs will be reported in the talk. K value of 20 and breakdown field of 50V/ $\mu\text{m}$  were measured for a dielectric with 10% loading of Au/SiO<sub>2</sub> NPs. Resulting capacitance value of 11.5nF/In<sup>2</sup> is in par with commercially available capacitor devices. It is worth mentioning that currently manufacturers use ceramic based dielectric material which makes it hard to manufacture (reproducibility, stability and cost) and shows limited flexibility (a requirement in modern printed circuit board technologies) due to high ceramic loading. Our fabricated nanodielectrics have the advantage of ease of fabrication and high flexibility due to the low metal loading.

It is forecasted that the effective permittivity of the dielectric and thereby the K value increases with loading of NPs till a percolation threshold is reached and then rapidly decreases with further loading. Future research is aimed at using other inexpensive metal NPs like silver and testing different polymers for best desirable characteristics of the capacitors.

5:00pm **EN+NS-WeA10 Characterization of Vertical InN Nanorods and InN-GaN Core-Shell Structures Grown by Merged Metal Organic Hydride Vapor Phase Epitaxy**, *V.U. Chaudhari*, *D. Wood*, *R. Krishnan*, *T.B. Song*, *T.J. Anderson*, University of Florida

The pseudobinary solid solution Ga<sub>1-x</sub>In<sub>x</sub>N alloys exhibits a direct band gap in the range 3.4 to 0.7 eV and thus suitable for optoelectronic device applications. Recent simulations from our group have also suggested this alloy could produce high efficiency thin film photovoltaic devices on the order of 18% efficiency, similar to CIGS devices. The use of nanorod structures for light emitting and absorbing applications promises relatively high junction area, crystalline quality, and collection efficiencies. In addition, the nanorod assemblies are less rigid, and thus open to flexible substrates. The synthesis of nanorods with specific orientation, however, remains a challenge.

The synthesis of self-assembled, vertical InN nanorods and InN-GaN core shell nanostructures on Si without the need for a catalyst or template is reported. This self-catalyzed approach has made it possible to grow nanorods with uniform yet tunable diameter without any patterning of the substrate. The synthesis is performed in a Merged Metal Organic Hydride Vapor Phase Epitaxial growth system. This system allows growth of Ga<sub>1-x</sub>In<sub>x</sub>N by either metal organic CVD, using trimethylgallium, trimethylindium and NH<sub>3</sub>, or hydride VPE in which the metal organic precursor is reacted with HCl. This presentation summarizes properties of the nanorods grown in the temperature range 560 to 600 °C at atmospheric pressure in N<sub>2</sub>. As revealed by transmission electron spectroscopy, the grown nanorods are defect-free, single crystal showing the wurtzite structure. Scanning electron microscopy and X-ray diffraction results reveal growth in vertical direction with (002) preferred orientation. The InN-GaN core shell structures exhibited a polycrystalline GaN shell with (002) and (101) preferred orientations. This particular behavior of GaN is attributed to the high growth rates used. Annealing studies of these microstructures under

ammonia atmosphere showed the absence of alloy formation with virtually no inter-diffusion of In and Ga.

5:20pm **EN+NS-WeA11 Fabrication of InAs/GaAs Nanocomposites Using Ion Implantation**, *M.V. Warren*, *C. Uher*, *R.S. Goldman*, University of Michigan, Ann Arbor

The controlled formation of semiconductor nanocomposites offers a unique opportunity to tailor functional materials with a variety of novel properties. In particular, nanocomposites consisting of InAs nanostructures embedded in GaAs have been proposed for high efficiency photovoltaics and high figure-of-merit thermoelectrics. A promising approach to nanocomposite synthesis is matrix-seeded growth, which involves ion-beam-amorphization of a semiconductor film, followed by nanoscale re-crystallization via annealing [1]. In earlier studies of In<sup>+</sup> implantation into GaAs, the formation of InGaAs alloys upon annealing was reported [2-4]. Due to the large size difference between In and Ga, it is likely that phase separation occurs, especially for high indium fraction InGaAs alloys. Therefore, we are examining the possibility of selective formation of InAs-rich nanocrystals in a GaAs matrix using high dose In implantation into GaAs. However, Profile Code simulations suggest that the retained In dose in GaAs,  $4.5 \times 10^{20} \text{ cm}^{-3}$ , is limited by sputtering. To increase the concentration of implanted In, we have developed a sputter-mask method, for which a sacrificial layer with sputter yield lower than that of GaAs is used to prevent sputtering of GaAs:In. Using 100keV ions with fluences ranging from  $3.8 \times 10^{15}$  to  $3.8 \times 10^{17} \text{ cm}^{-2}$ , we have implanted In<sup>+</sup> ions into GaAs with 50 nm sputter-masks consisting of AlAs. Following implantation, the films were annealed at 500 to 600°C for 30 to 60 s. We will discuss the influence of In<sup>+</sup> dose and annealing conditions on the nucleation and growth of InAs, as well as the influence of nanostructuring on the temperature dependence of the resistivity and Seebeck coefficient of the implanted structures.

This work is supported in part by the GAANN Fellowship and the US Department of Energy, Office of Basic Energy Sciences as part of an Energy Frontier Research Center

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