

Monday Afternoon, November 10, 2014

Electronic Materials and Processing

Room: 314 - Session EM-MoA

Nanoparticles for Electronic Materials

Moderator: Jessica Hilton, Mantis Deposition, Joseph G. Tischler, Naval Research Laboratory

2:00pm **EM-MoA1 Synthesis of Nanoparticles Via Gas-Aggregated Sputtering**, *Cathal Cassidy*, Okinawa Institute of Science and Technology, Japan **INVITED**

Synthesis of nanoparticles via gas-aggregated sputtering allows direct integration with electronic devices and their manufacturing processes. In this talk, I will discuss the fundamentals of gas-aggregated sputtering, and the diverse capabilities it offers for synthesis of novel nanoparticle materials. Analytical models will be introduced, as well as molecular dynamics modeling insights into growth and substrate landing of nanoparticles. Example results, with a focus on transmission electron microscopy studies, will be presented. Finally, the strengths and weaknesses of sputtered nanoparticles for various device applications, such as sensor layers, data storage and backend interconnects, will be discussed.

2:40pm **EM-MoA3 Soft Landing of Size-Selected Nanoparticles: Novel Materials for Electrocatalysis**, *Grant Johnson, R.J. Colby, M.H. Engelhard, D. Du, Y. Lin, J. Laskin*, Pacific Northwest National Laboratory
Soft landing of mass-selected ions onto surfaces is a powerful approach for the highly controlled preparation of materials that are often unobtainable using conventional synthesis techniques. A non-thermal physical synthesis method, DC magnetron sputtering combined with inert gas-aggregation, has been employed to produce anionic metal nanoparticles in the gas-phase across a range of sizes, shapes and elemental compositions for controlled deposition onto conductive electrode surfaces. Simultaneous sputtering of multiple metal targets employing up to three independent DC magnetrons in the same gas aggregation region is demonstrated to produce complex binary alloy nanoparticles with well-defined elemental composition and morphology. Size-selection of the anionic nanoparticles employing a quadrupole mass-filter prior to soft landing is shown to provide effective control over the size of nanoparticles delivered to surfaces. A suite of cutting edge analytical techniques including atomic force microscopy, scanning and transmission electron microscopy, x-ray photoelectron spectroscopy and medium energy ion scattering is utilized to demonstrate how the size, shape, elemental composition and surface density of soft landed nanoparticles may be tuned to promote the efficient electrocatalytic reduction of oxygen.

3:00pm **EM-MoA4 Aerosol Spray Pyrolysis Synthesis and Characterization of CZTS Nanoparticles**, *Stephen Exarhos, L. Mangolini*, University of California - Riverside

A novel synthesis technique for the production of copper zinc tin sulfide (CZTS) nanocrystals has been developed using aerosol spray pyrolysis. CZTS is a quaternary semiconducting material that shows promise as a replacement to common semiconductors such as CdTe and CIGS for use in photovoltaic devices. CIGS is currently being commercialized in the photovoltaic industry, but rare and expensive indium and gallium components threaten its long term viability. CZTS looks to be one of the best alternatives to CIGS with all earth abundant and non-toxic materials and a band gap of 1.5 eV [1]. A number of synthesis techniques have been thoroughly studied and detailed previously. In our novel approach, we synthesize single-phase 15 nm nanocrystals starting with zinc, copper, and tin diethyldithiocarbamate precursors in a toluene solvent. The precursor solution is aerosolized using a Collision type nebulizer wherein the droplets are pushed through a tube furnace and nucleation occurs at atmospheric pressure. The powder is then collected in a series of methanol-filled bubblers. We reproducibly synthesize kesterite, $\text{Cu}_2\text{ZnSnS}_4$, nanocrystals. This technique continuously converts the chemical precursor into high-purity nano powder with a production rate of ~50mg/hour from ~100mL of precursor solution with ~500mg total of the three diethyldithiocarbamate precursors for an un-optimized lab-scale reactor. The motivation to use this synthesis process as an inexpensive, quick, and simple method of nanocrystal formation will be outlined. Further, a discussion of process parameters on the stoichiometry of the nanoparticles will be presented as well as results from extensive material characterization via Raman spectroscopy, EDS, XRD, and TEM. We are currently in the process of producing a printable ink technique with which to coat CZTS as the absorbing layer for use in photovoltaic devices.

[1] H. Wang. "Progress in Thin Film Solar Cells Based on $\text{Cu}_2\text{ZnSnS}_4$," International Journal of Photoenergy, 2011.

3:40pm **EM-MoA6 Peter Mark Memorial Award Lecture - Novel Semiconductor and Epitaxial Nanocomposite Materials for Electronic and Photonic Applications**, *Joshua Zide**, University of Delaware **INVITED**

Advances in electronic materials (specifically, semiconductors and nanocomposites) enable new device technologies and improve the properties of existing technologies. In this talk, I will present efforts within my group on the growth of new materials by molecular beam epitaxy and the resulting advances in solar cells, thermoelectrics, and optoelectronics.

Specifically, I will discuss two material systems: (1) nanocomposites consisting of metallic nanoparticles (such as ErAs and TbAs) within III-V semiconductors (such as InGaAs and GaAs), and (2) dilute bismuthide semiconductors in which bismuth is incorporated into III-V materials to reduce the bandgap significantly, with unique band alignments that cannot be easily achieved in other materials. In the former, the nanoparticles serve as buried Schottky junctions, pinning the Fermi level and significantly altering carrier dynamics. In the latter, we focus on In(Ga/Al)BiAs, where compositional variations permits independent tuning of valence and conduction bands.

Although these materials are built upon relatively-mature III-V systems, electronic, thermal, and optical properties can be quite different from those of conventional materials, with significant promise for applications in a variety of technologies. Understanding the properties of these materials enables the creation of designer semiconductors for particular applications of interest.

4:20pm **EM-MoA8 Assembly of Functional Nanocrystal Films at Fluid Interfaces**, *Kevin Whitham, T. Hanrath*, Cornell University

Opportunities to create materials with properties by design continue to emerge from our ability to control the structure and composition of nanomaterials through wet-chemistry synthesis methodologies. Access to these materials has provided critical insights into basic structure-property relationships. Concurrent advances in prototype nanomaterial-based devices underscored their immense technological potential in a broad range of energy applications including photovoltaics, catalysis, energy storage, and thermoelectrics. Along with rising expectations, there is growing recognition that sustained progress towards the acclaimed promise of nanomaterial-enabled energy technologies depends critically on solving outstanding processing challenges - in particular the directed assembly of nanoparticles (NPs) into functional superstructures. We embrace this challenge as an opportunity to establish the scientific and engineering foundation for the processing of ordered and multifunctional NP thin films via advanced liquid coating methods.

Our group recently demonstrated a significant advance to resolve this challenge by creating NP assemblies that combine high spatial coherence and strong interparticle electronic coupling. In brief, we discovered that spreading a NP suspension across the surface of a non-polar antisolvent subphase results in the formation of two-dimensional (2D) superlattice of epitaxially connected NPs. Our approach to 'connect the dots' was inspired by analogies to polymerize or crosslink NPs as monomers into highly connected superstructures. The ability to form 'confined-but-connected' 2D NP assemblies with predefined symmetries introduces exciting opportunities to create materials with properties by design. By analogy to atomic 2D systems (e.g. graphene), we see 2D NP assemblies as a fertile ground for scientific discovery with a clear path towards practical applications.

4:40pm **EM-MoA9 Characterization of $\text{Cu}_2\text{X}\text{S}$ Nanoparticles in Organic Matrices**, *Michael Majeski, I. Bolotin, L. Hanley*, University of Illinois at Chicago

Transition-metal chalcogenide nanomaterials show promise for applications in photovoltaics and plasmonic devices. Of these class of materials, Cu_2S encompasses the environmentally friendly and earth abundant qualities not afforded to many other heavy metal semiconductors. Copper sulfide nanoparticles are prepared by physical vapor deposition without the surface ligand capping effects known to inhibit and otherwise complicate charge transfer. Another obstacle to the use of copper sulfide for photovoltaics is the self-doping that occurs upon oxidation, which is compensated for here by all-gaseous preparation of $\text{Cu}_2\text{X}\text{S}$ nanoparticles into organic matrices. These films are characterized by X-ray photoelectron spectroscopy,

* Peter Mark Memorial Award Winner

transmission electron microscopy, high-angle annular dark-field scanning transmission electron microscopy, X-ray absorption experiments, and other methods. 2.3 ± 0.4 nm Cu_{2-x}S nanoparticles with copper in the +1 oxidation state were deposited into pentacene films and additional structural information will be presented.

5:00pm **EM-MoA10 Optical Properties of PbSe Nanorods with Controlled Diameter and Length**, *Diogenes Placencia, J.E. Boercker, E.E. Foos, J.G. Tischler*, Naval Research Laboratory

PbSe nanorods are attractive for use in next-generation optoelectronic devices due to their exceptional physical properties such as larger Stokes shifts and more efficient multiple exciton generation (MEG), relative to spherical nanocrystals.¹⁻³ However, further development of PbSe nanorods for viable technological components requires precise control of the nanorod diameter and length as well as an understanding of how the nanorod dimensions affect their optoelectronic properties. We have investigated the nature of the PbSe nanorod synthesis, yielding an understanding of how to independently control the nanorod diameter and length. Additionally we have developed an elementary comprehension of how the nanorod dimensions affect their optical properties.

Recently, single-crystal, homogeneous, PbSe nanorods were synthesized using a solution synthesis.⁴ In our work, we show that water present in this synthesis has a dramatic effect on the nanorod aspect ratio and yield. By varying the water concentration from 0 to 204 mM, the nanorod aspect ratio and yield can be controlled from 1.1 to 10 and 1 to 14%, respectively. Water *indirectly* affects the nanorod morphology and yield by reacting with the tris(diethylamino)phosphine used in the reaction to form bis(diethylamido)phosphorus acid. The latter is responsible for both the nanorod aspect ratio and yield variations. Furthermore, the excess oleic acid in the reaction can also create bis(diethylamido)phosphorus acid from tris(diethylamino)phosphine. When both excess oleic acid and water are removed, the reaction slows and highly uniform, non-branching, nanorods are formed.⁵

Exploration of various synthetic parameters (e.g., temperature, reaction time) within the nanorod reaction free of water and excess oleic acid resulted in our ability to independently control the nanorod diameter and length. Aspect ratios ranging from 1 to 14 have been synthesized, showing no branching, varying levels of quantum yields, and a wide absorption energy range (~1200 nm – 2000 nm).

References

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- [2] Cunningham P D, Boercker J E, Foos E E, Lumb M P, Smith A R, Tischler J G and Melinger J S 2011 *Nano Lett.* **11** 3476
- [3] Sandberg R L, Padilha L A, Qazilbash M M, Bae W K, Schaller R D, Pietryga J M, Stevens M J, Baek B, Nam S W and Klimov V I 2012 *ACS Nano* **6** 9532
- [4] Koh W-K, Bartnik A C, Wise F W and Murray C B 2010 *JACS* **132** 3909
- [5] Boercker J E, Foos E E, Placencia D and Tischler J G 2013 *JACS* **135** 15071

5:20pm **EM-MoA11 Plasmonic Behavior of Copper Iron Sulfide Nanoparticles**, *Katherine Plass, N.J. Freymeyer, C. Kim, C.J. Wisdo*, Franklin & Marshall College

Copper vacancies in copper chalcogenide result in sufficiently high levels of p-type doping to generate plasmon resonances. The natural tendency towards increased copper vacancies with time and air exposure is exacerbated in nanoparticles.¹ We present here investigations into the stabilization of plasmonic copper sulfide-based semiconductors. Incorporation of iron slows the transition to copper deficiency² Here we will discuss the affect of iron incorporation into copper sulfide nanoparticles on the plasmonic behavior. Various phases were produced, ranging from different polymorphs of Cu_2S to CuFeS_2 , including solid solutions. The solid-state structure, band gaps and edges, and plasmon band absorption of these copper iron sulfide nanoparticles were responsive to the extent of iron incorporation, as investigated by powder X-ray diffraction, cyclic voltammetry, and visible/near-IR light absorption spectroscopy. The surface chemistry influences the plasmonic behavior of these copper iron sulfide nanoparticles and will be examined.³

- (1) Lotfipour, M.; Machani, T.; Rossi, D. P.; Plass, K. E. *Chem. Mater.* **2011**, *23*, 3032–3038.
- (2) Machani, T.; Rossi, D. P.; Golden, B. J.; Jones, E. C.; Lotfipour, M.; Plass, K. E. *Chem. Mater.* **2011**, *23*, 5491–5495.
- (3) Freymeyer, N. J.; Cunningham, P. D.; Jones, E. C.; Golden, B. J.; Wiltout, A. M.; Plass, K. E. *Cryst. Growth Des.* **2013**, *13*, 4059–4065.

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