

# Tuesday Afternoon, November 1, 2011

## Energy Frontiers Focus Topic

Room: 103 - Session EN+NS-TuA

### Nanostructured Materials for Thermophotovoltaics, Thermoelectrics & Plasmonics

Moderator: P. Nappal, Los Alamos National Laboratory

#### 2:00pm EN+NS-TuA1 Thermal Plasmonics as a Route to Photovoltaics?, *D.J. Norris*, ETH Zurich, Switzerland **INVITED**

Patterned metallic films allow the generation and manipulation of special electromagnetic waves known as surface plasmons that propagate along a metal interface. Because these waves allow the concentration of light in nanometer-scale volumes, they have implications for fundamental phenomena as well as applications such as imaging, sensing, and solar cells. Thus, the field of plasmonics has arisen to study and utilize surface plasmons. While light is typically used to create these waves, in some cases it would be more convenient to have a non-optical source for surface plasmons. One route is thermal excitation (*i.e.*, heat). Here, we will explore hot plasmonic structures for obtaining new optical behavior. For example, we will examine metallic films patterned with a series of circular concentric grooves (a bull's eye pattern). We show that, when heated, these films can emit light that is amazingly narrow, both in terms of its spectrum and its angular divergence. Thus, a simple metallic foil can generate a highly directional beam of monochromatic light by a thermal process. This effect has implications for creating efficient thermophotovoltaic devices, which convert heat into electricity. During these studies, we also developed a simple, high-throughput method for obtaining ultrasoft patterned metal films. Previously, roughness in such films has hindered the field of plasmonics. Therefore, our approach solves a critical problem and allows many high-quality plasmonic structures to be available for the first time.

#### 2:40pm EN+NS-TuA3 Nanocrystal Assemblies: A Modular Approach to Materials Design, *D.V. Talapin*, University of Chicago **INVITED**

Colloidal nanocrystals can combine the advantages of crystalline inorganic semiconductors with the size-tunable electronic structure and inexpensive solution-based device fabrication. Single- and multicomponent nanocrystal assemblies, also known as superlattices, provide a powerful general platform for designing two- and three-dimensional solids with tailored electronic, magnetic, and optical properties. Unlike atomic and molecular crystals where atoms, lattice geometry, and interatomic distances are fixed entities, the nanocrystal arrays represent ensembles of "designer atoms" with potential for tuning their electronic structure and transport properties. Generally speaking, nanocrystal assemblies can be considered as a novel type of condensed matter, whose behavior depends both on the properties of the individual building blocks and on the interparticle exchange interactions.

The ability to assemble precisely engineered nanoscale building blocks into complex structures is opening the door to materials where components and functionalities can be added, tuned or combined in a predictable manner. I will show how self-assembly of nanocrystals can lead to a palette of unprecedented phases including superlattices isostructural with the Archimedean tilings and dodecahedral quasicrystals.

Efficient charge transport is crucial for performance of nanocrystal-based electronic and optoelectronic devices. The insulating nature of surface ligands traditionally used for nanocrystal synthesis results in the poor electronic coupling between individual nanocrystals. To facilitate charge transport in nanocrystal solids, we introduced the concept of inorganic ligands for colloidal nanocrystals. These ligands, namely metal chalcogenide complexes, can be applied to a broad range of inorganic nanomaterials. I will demonstrate the power of this approach on several examples of prospective electronic, thermoelectric and photovoltaic materials.

#### 4:00pm EN+NS-TuA7 Photonic and Plasmonic Crystals for Thermophotonics and Energy Conversion, *R. Biswas*, Iowa State University & Ames Laboratory - US DOE **INVITED**

Photonic and plasmonic crystals that have various energy-related applications will be discussed. Metallic plasmonic crystals consisting of an array of nano-holes or nano-pillars on common substrates, with pitch at infrared length scales, have very sharp absorption properties at infrared wavelengths. Such arrays have diverse applications to sensors and thermophotonic applications. The absorption, thermal emission, and angular characteristics from these plasmonic arrays will be described with rigorous scattering matrix simulations and compared to measurements. I will also

survey the rich physics underlying plasmonic nano-arrays at optical length scales, and a few energy related applications.

#### 4:40pm EN+NS-TuA9 Molecular and Hybrid Solution Processible Thermoelectrics, *R.A. Segalman, S. Yee*, University of California, Berkeley, *N. Coates, J. Urban*, Lawrence Berkeley National Laboratory **INVITED**

Thermoelectric materials for energy generation have several advantages over conventional power cycles including lack of moving parts, silent operation, miniaturizability, and CO<sub>2</sub> free conversion of heat to electricity. Excellent thermoelectric efficiency requires a combination of high thermopower ( $S$ , V/K), high electrical conductivity ( $\sigma$ , S/cm), and low thermal conductivity ( $\kappa$ , W/mK). To date the best materials available have been inorganic compounds with relatively low earth abundance and highly complex, vacuum processing routes (and hence greater expense), such as Bi<sub>2</sub>Te<sub>3</sub>. Molecular materials and hybrid organic-inorganics bring the promise of inexpensive, solution processible, mechanically durable devices. While highly conductive polymers are now common place, they generally demonstrate low thermopower. Our work on molecular scale junctions suggests that nanostructuring of organics allows them to act as thermionic filters between inorganic junctions which can lead to enhanced thermoelectric properties. We have taken inspiration from this fundamental understanding to design material systems in which we combine a high electrical conductivity, low thermal conductivity polymer with a nanoparticle that contributes high thermopower. Additionally, the work functions of the two materials are well-aligned which introduces the possibility of thermionic filtering at the interface and an additional boost to the power factor. The combination of these effects results in a new hybrid, solution processible material with a thermoelectric figure of merit approaching those of Bi<sub>2</sub>Te<sub>3</sub>. In this talk, I will discuss both the use of thermoelectric measurements to gain insight to molecular junctions and how this insight translates to design principles for polymer and hybrid thermoelectrics.

#### 5:20pm EN+NS-TuA11 Semiconductor Nanowire Networks as Thermoelectric Platforms, *A.J. Lohm\**, University of California Santa Cruz, *E. Coleman, G.S. Tompa*, Structured Materials Industries, Inc., *N.P. Kobayashi*, University of California Santa Cruz

Current energy production mechanisms for electrical power and transportation are plagued by inefficiencies which results in most of the energy source being lost as heat. In most cases that heat is found in the form of low-grade heat with temperatures below approximately 200 degrees C. Unfortunately, typical methods such as the Rankine cycle for converting heat to electricity suffer from poor efficiency for low-grade heat. Direct thermoelectric conversion is currently struggling to match the efficiency of the Rankine cycle at high temperatures but offers advantages in terms of reduced maintenance and form-factor which enable energy scavenging in places such as the exhaust line of a vehicle where larger systems could not be implemented.

Dominated by recent progress in nanostructured materials, the unitless thermoelectric figure of merit  $ZT$  has been increased to well beyond 1 such that efficiencies are reaching a range which makes them cost effective. Typically thermoelectric materials include elements such as lead or tellurium which are toxic and rare therefore alternative materials are being sought. Recent progress in silicon nanowire thermoelectric has shown a reduction in thermal conductivity, and therefore an increase in  $ZT$  of two orders of magnitude, making them viable candidates in the thermoelectric marketplace. Decreased cost and toxicity of silicon as compared to conventional thermoelectric materials make it an attractive candidate but to date nearly all studies on thermoelectricity of nanowires have focused on nanowires in isolation. Our platform based on interconnected 3-dimensional nanowire networks grown directly on metallic substrates provides large area thermoelectric modules capable of scavenging low-grade heat for low cost. The materials properties comprising  $ZT$ : thermal conductivity, electrical conductivity and Seebeck coefficient will be discussed for undoped, p-type and n-type silicon nanowire networks with particular emphasis on electrical conductivity and Seebeck coefficient within the temperature range of low-grade heat.

#### 5:40pm EN+NS-TuA12 Diamond as an Electrode Material for the Direct Conversion of Thermal to Electrical Energy through Thermionic Emission, *W.F. Paxton, J.L. Davidson, W.P. Kang*, Vanderbilt University **Introduction**

\* NSTD Student Award Finalist

Thermionic energy conversion is a candidate technology for the efficient conversion of thermal energy directly to electrical energy. In a thermionic converter, thermally excited electrons are emitted from the surface of a heated cathode into a vacuum gap. These electrons are then collected by a cooler anode and driven through an external load back to the cathode. The thermionic emission current density of a heated cathode can be described by the Richardson Equation (Eq. 1).

$$J = AT^2 e^{-\Phi/kT} \quad (1)$$

where: J: Thermionic emission current density (A/cm<sup>2</sup>); A: Richardson constant (A/cm<sup>2</sup> T<sup>2</sup>); T: Temperature (K);  $\Phi$ : Material's work function (eV); and k: Boltzmann constant (eV/T)

It can be seen from Eq. 1 that a material with a lower work function,  $\Phi$ , can achieve higher current densities at lower temperatures than a material with a higher work function, which implies lower work function values translate into better energy converters. Prior attempts to construct efficient thermionic converters were limited by available materials with work function values ranging from 3.5eV to 5eV requiring extreme cathode temperatures in order to achieve useable output power values. In this study, the thermionic emission properties of nitrogen-incorporated diamond films are examined as a potential electrode material to enhance the efficiency of such a device.

#### Experimental

Polycrystalline diamond films were synthesized on molybdenum substrate via Microwave Plasma-Enhanced Chemical Vapor Deposition (MPCVD). The source gasses were H<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>, microwave power was 1.5KW, and the nominal pressure was 50Torr. Scanning electron micrographs of the samples demonstrated uniform film coverage and a thickness of ~100 $\mu$ m.

Thermionic emission characterization was performed in a vacuum environment with a base pressure of  $1 \times 10^{-7}$  Torr. The diamond films were resistively heated and the temperature was constantly observed by a dual color pyrometer. Electron emission current was collected with an electrically isolated anode biased at a constant voltage of 100V positioned 0.5cm above the heated cathode.

#### Results and Discussion

Observation of the electron emission current above the noise level began at 600°C and increased exponentially with temperature up to 800°C. Analysis of this data demonstrated agreement with the Richardson equation with a correlation coefficient of 0.99. From this data, the nitrogen-incorporated diamond samples were determined to have a work function value less than 2eV which is considerably lower than previously mentioned materials. These results exhibit diamond's potential as an interesting cathode material for a thermionic energy converter.

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