

# CSTEC Conversations

SPRING 2011

The Newsletter of the  
Center for Solar and Thermal  
Energy Conversion,  
an Energy Frontier Research  
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Office of Basic Energy Sciences

## Intermediate Band Solar Energy Conversion in ZnTe:O and ZnTe/ZnSe

Affordable photovoltaic solar cells are highly desirable for achieving a sustainable and renewable energy source. In order for solar energy to become cost-competitive with fossil fuels, technological breakthroughs are needed to both improve solar cell efficiency and reduce module cost. Advances in efficiency will rely upon efficient collection of the full spectrum of solar radiation while minimizing energy loss mechanisms. Conventional solar cells based on a single material are limited to approximately 30% efficiency (Shockley-Queisser limit). Reduction of losses may be realized through the introduction of multiple absorption bands within a solar cell. The multi-junction concentrator solar cell introduces distinct absorption bands via different materials in each junction of the solar cell and has demonstrated record conversion efficiencies of up to 42%. The intermediate band solar cell (IBSC) is based on a similar principle, but in this case alloys, nanostructures, or intentional impurities will form multiple absorption bands in a single material, providing both high efficiency and reduced cost. Sub-bandgap absorption in the IBSC converts low energy solar photons to electrical current while maintaining a large open circuit voltage related to the large bandgap energy of the host material. Key requirements for the IBSC are that the intermediate states have strong optical transitions and that the lifetime of electrons are extremely long to ensure energy



**Weiming Wang growing II-VI compound semiconductor materials by molecular beam epitaxy.**

is converted to electricity rather than to heat. A team of CSTEC researchers have observed that the optical transitions in oxygen-doped ZnTe and ZnTe/ZnSe quantum structures are favorable for IBSC solar energy conversion.

The ZnTe:O approach utilizes oxygen substitutional impurities that provide strong optical transitions at 1.8eV (ZnTe bandgap energy of 2.3eV). Time-resolved photoluminescence studies of ZnTe:O have revealed large carrier lifetimes in the oxygen states that exceed 1 $\mu$ s (Figure 1a). However, carrier lifetimes <100ps have been observed for carriers in the conduction band, attributed to fast decay of electrons from the conduction band to the oxygen states. We are studying the origin of (and methods to increase) this fast decay time. The intermediate band energy conversion concept has been demonstrated in this material (Figure 1b and 1c)

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# Letter from the Center Director

This has been a very exciting year for the University of Michigan's Center for Solar and Thermal Energy Conversion (CSTEC), which was established in the fall of 2009. CSTEC is one of 46 Energy Frontier Research Centers (EFRC) established by the U.S. Department of Energy (DOE) to address America's energy consumption challenges.

Renewable sources, such as solar, wind, and hydroelectric, account for less than 1% of the world's current energy consumption and offer the most promise for meeting the world's future demand for energy, which

is expected to triple by the end of the century. The goal of CSTEC is to investigate the science necessary to mitigate and to tailor energy loss processes in low dimensional, and complex, nanostructured materials for high-efficiency photovoltaic (PV) and thermoelectric (TE) energy conversion. Researchers in the Center are involved in a range of activities and have made important scientific discoveries that impact our basic understanding of energy conversion.

During the last decade, discoveries derived from the investment of resources into research on nanoscience and nanotechnology have paved the way for a better understanding of how to synthesize and manipulate the structure and properties of materials at the nanoscale. Consequently, we are now in a position to address grand scientific challenges articulated by DOE in *Directing Matter and Energy: Five Challenges for Science and the Imagination*, which are necessary to secure America's energy future. These challenges, involving the control of processes at the level of charge carri-

ers and understanding how macroscopic properties of materials emerge from the interactions of its constituents, are an important aspect of the goals of the EFRCs. Twelve principal investigators, together with sixteen senior researchers, as well as graduate students and postdoctoral researchers, are engaged in a collaborative and interdisciplinary program involving the use of state-of-the art microscopies and ultrafast spectroscopies, together with computer simulations/theory to understand molecular and electronic structure and dynamics in materials.

The efforts of the center are organized into three main areas: (1) the *Inorganic PV* thrust investigates site-controlled nanostructures, type-II band-offset materials, and highly mismatched alloys; (2) the *Thermoelectric* thrust studies the properties of single-molecular junctions, quantum-dot structures, thin films, and bulk nanocomposites; and (3) the *Organic and Hybrid PV Materials* thrust investigates (a) absorption phenomena in organic and hybrid systems and (b) molecular design, carrier transport, and device performance. During this past year, center activities included an internal workshop in April and an external workshop in August, in which members of our external advi-

sory board and researchers from industry participated. The activities in our center also included a large number of discussion group meetings, presentations, and seminars involving faculty, students, and postdocs covering the areas in which center research is focused. A number of technical advances were made in areas that span the synthesis of new materials, the development of new techniques to measure thermal energy transport, the manipulation of transport phenomena at the nanoscale, and device performance.

Specific examples of our scientific advances, among other things, are described herein. I hope that you will find our newsletter informative and that you will continue to share our excitement and enthusiasm for scientific discoveries.

*Peter Green*

Peter Green



# Cage Macromolecules Show Enhanced Energy Harvesting Capabilities

Important progress has been made in the development of new materials that exhibit enhanced absorption over the visible, near IR (infrared) and IR regions of the solar spectrum. Absorption is the initial process in the conversion of sunlight into electricity by solar cells. Enhancements of absorption improve the efficiency of solar cells, a major goal toward developing superior devices that harness as much of the sun's energy as possible. The new materials used in CSTECH are based on a class of macromolecules known as silsesquioxanes (SQs). The SQ molecule is cage-like, with the corners of the cage readily functionalized with different molecular groups in order to tailor the properties of the molecule (Figure 1).

A team of researchers at CSTECH has been developing a fundamental understanding of the mechanisms by which a broad class of SQs would become effective materials for solar cell applications. Advanced spectroscopic techniques and theoretical modeling, including electronic structure calculations, are utilized to understand how the absorption properties of SQs change when the corners of the cage are functionalized with chromophores (dye molecules). Figure 2 illustrates an example of one of the models that describe how the shape and location of the electron orbitals (shown in pink and blue) change to

accommodate interactions with the SQ cage upon absorption of a photon of light. This reorganization of orbitals suggests that molecular functionalization improves charge separation efficiency. Moreover, the agreement between theory and experiment supports the concept that these models can be used to predict the structure

of molecules that possess specific absorption properties. In another experiment, the effect of molecular symmetry on silsesquioxanes' ability to absorb light was examined. Three molecules were synthesized, each representative of an SQ molecule with different numbers of chromophores attached to the cage (Figure 3). Optical spectroscopy shows that absorption increased considerably when the cage was symmetrical. The absorption cross-section of the molecule with eight chromophores is almost 20 times that of the molecule with one chromophore. This result suggests that these systems are rigid, enhancing the transport of charge through the molecule.

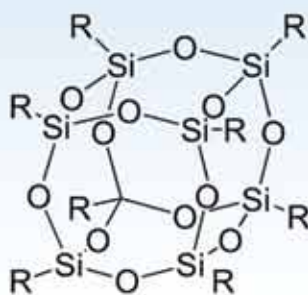


Figure 1. General structure of silsesquioxanes.

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Figure 2. A plot of a silsesquioxane molecule demonstrating how the shape and location of the molecular orbitals (in pink and blue) change to include involvement with the SQ cage upon absorption of a photon of light. This reorganization of charge density implies the prospect of using molecular functionalization to improve charge separation efficiency in silsesquioxanes.

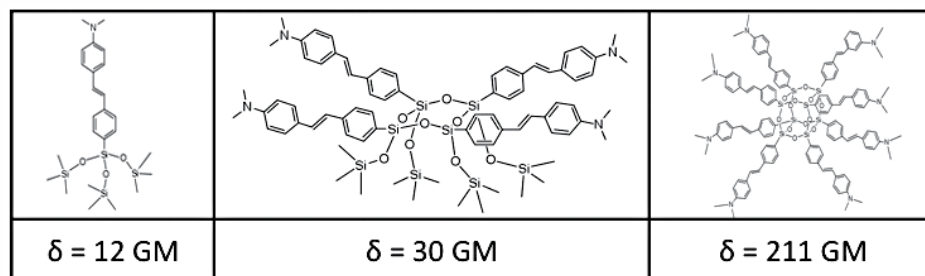


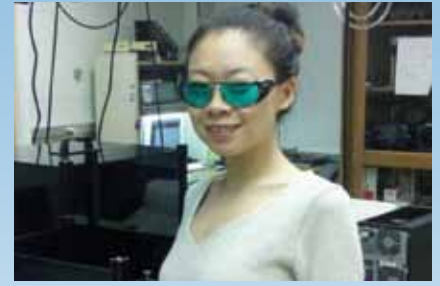
Figure 3. Molecules used to test symmetry effects in functionalized silsesquioxanes—chromophores at one corner, four corners, and eight corners. Optical spectroscopy shows that absorption spikes considerably when the cage becomes symmetrical. The absorption cross-section ( $\delta$ ) of the molecule with eight chromophores is almost 20 times that of the molecule with one chromophore (when normalized to absorption per chromophore, the absorption cross-section still almost doubles).

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The degree of flexibility in SQs is the focus of current studies with ultra-fast fluorescence upconversion and transient absorption spectroscopy.

With the use of computational models, combined with experimental studies, researchers in the center have learned how to design and synthesize this energy-harvesting material to create materials for devices.

Polymer synthesis and characterization was completed by Jae Hwan Jung in the laboratory of Professor Rick Laine (materials science and engineering); spectroscopy was conducted by Jin Zhang in the laboratory of Professor Ted Goodson (chemistry); computational modeling was carried out by postdoctoral fellow Shaohui Zheng and graduate student Heidi Phillips under the direction of Professors Barry Dunitz (chemistry) and Eitan Geva (chemistry).



Top: Jin Zhang; bottom: Shaohui Zheng

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based on multi-photon excitation experiments, where increased electrical power generation is observed for pumping at sub-bandgap wavelengths corresponding to the optical transitions of the intermediate band states. Intermediate-band solar energy conversion is also being studied for type-II ZnTe/ZnSe quantum structures. The type-II band lineup of the structure results in optical transitions where electrons and holes are spatially separated, resulting in significant increases in carrier lifetime ( $>10\text{ns}$ ) in comparison to type-I quantum structures ( $\sim 1\text{ns}$ ). We have recently demonstrated optical transitions in type-II ZnTe/ZnSe, where photoluminescence spectra (Figure 1d) reveal a broad emission near  $2.2\text{eV}$  due to the type-II transition, in comparison to emission from ZnSe ( $2.8\text{eV}$ ), isoelectronic Te impurities in ZnSe ( $>2.48\text{eV}$ ), ZnTe ( $2.3\text{eV}$ ), and defect level emission in

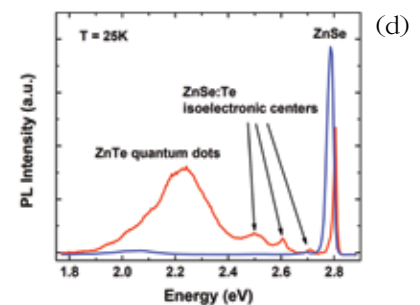
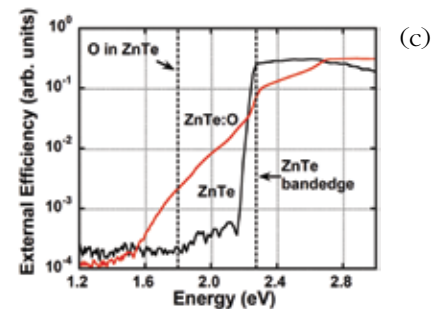
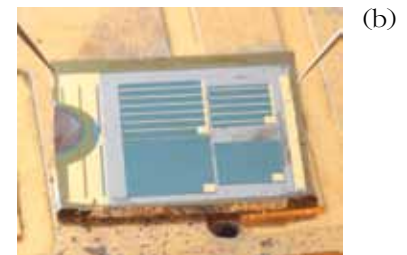
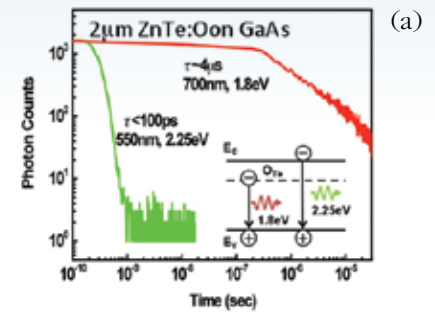
**Figure 1: (a) Time-resolved photoluminescence data showing long decay lifetime for electrons in oxygen states in ZnTe, (b) microscope image of ZnTe:O intermediate band solar cell, (c) response of ZnTe:O solar cell exhibiting response below the ZnTe band-edge, and (d) photoluminescence spectrum of ZnTe/ZnSe quantum dots showing emission corresponding to type-II band lineup.**

ZnSe ( $<2.0\text{eV}$ ). Further study of the structural, optical, and intermediate band solar energy conversion of these materials is under way.

Researchers on this project were Weiming Wang and Bor-Chau Juang under the direction of Professor Jamie Phillips (electrical engineering and computer science) and in collaboration with Professor Xiaoqing Pan (materials science and engineering).

Further details of the carrier lifetime study are presented in the following paper:

*W. Wang, A. Lin, J. D. Phillips, and W. Metzger, "Generation and Recombination Rates at ZnTe:O Intermediate Band States," Appl. Phys. Lett. 95, 261107 (2009).*



# A New Understanding of Organic Semiconductor Junctions

The foundation of almost all conventional inorganic semiconductor devices is the  $p$ - $n$  junction, defined by the interface between an electron rich ( $n$ -type) and an electron poor ( $p$ -type) semiconductor. First developed in 1949, the Shockley ideal diode equation comprehensively describes the current-voltage characteristics of inorganic semiconductor  $p$ - $n$  junctions, providing both physical insight and a quantitative analytical tool that has aided our understanding of the most fundamental properties of semiconductor devices, and, in particular, solar cells, over the past six decades. Organic, or “plastic” electronics, are a relatively new technology that holds the prospect of providing ultra-cheap, lightweight, and flexible electronic applications. Indeed, organic solar cells (OSCs) provide a particularly useful and compelling application of organic electronics. These devices operate on the basis of a heterojunction formed between “donor” and “acceptor” organic semiconductors, often viewed as analogs to  $p$ - and  $n$ -type inorganic semiconductors, respectively. As a result, the Shockley Equation has often been applied to analyze OSCs since their inception, but the inherently different physics of organic semiconductors has limited its ability to make useful predictions and direct improvements for both materials and device architectures. In particular, organic semiconductors are characterized by hopping transport on the nanoscale and tightly bound, localized exciton states that require significant energy to dissociate into free charge carriers

as opposed to delocalized free charge carriers in inorganic semiconductors.

Recently, scientists at the University of Michigan Center for Solar and Thermal Energy Conversion collaborated with scientists from the Center for Nanoscale Materials at Argonne National Laboratories to develop and test an ideal diode equation for organic semiconductor junctions. The work focuses on the dynamics of bound charge carrier pairs at the heterojunction and results in an equation that is analogous to the Shockley Equation (Figure 1). It predicts the temperature and light intensity dependence of solar cell parameters such as the dark current, open circuit voltage ( $V_{oc}$ ) and short-circuit current ( $J_{sc}$ ), particularly in situations where Shockley-based models break down. Furthermore, the analysis predicts the maximum  $V_{oc}$  attainable for a given heterojunction material pair, in agreement with the empirically based conclusions of experimental studies.

The model is successfully applied to two archetype, planar heterojunction organic photovoltaic cells composed of copper phthalocyanine (CuPc) and boron subphthalocyanine chloride (SubPc) donors, and a fullerene ( $C_{60}$ ) acceptor. These results should have a significant impact on both the understanding and further development of this exciting new class of solar cells.

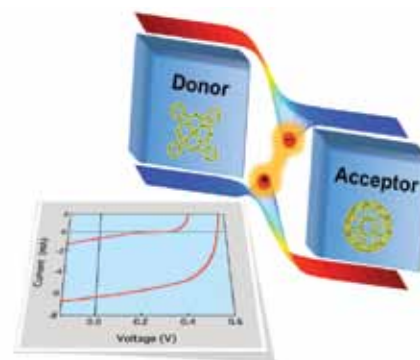
The researchers on this project at Argonne National Laboratory were Noel Giebink (George Wells Beadle Postdoctoral Fellow) and Gary Wiederrecht. The University of Michigan scientists were Stephen Forrest and Brian Lassiter. The Northwestern University

scientist was Michael Wasielewski, who also holds a senior scientist appointment at Argonne National Laboratory.

Additional information on this research can be found in the following publications:

*The Ideal Diode Equation for Organic Heterojunctions. I. Derivation and Application*, N. C. Giebink, G. P. Wiederrecht, M. R. Wasielewski, and S. R. Forrest, Phys. Rev. B **82**, 155305 (2010).

*The Ideal Diode Equation for Organic Heterojunctions. II. The Role of Polaron Pair Recombination*, N. C. Giebink, B. E. Lassiter, G. P. Wiederrecht, M. R. Wasielewski, and S. R. Forrest, Phys. Rev. B **82**, 155306 (2010).



**Figure 1. Schematic illustrating the current-voltage characteristics and energetics of Coulombically bound charge carrier pairs at the heterojunction in organic semiconductor junctions.**

# Ordering of the Filler Species on Void Sites of Skutterudite Thermoelectrics

Thermoelectric (TE) energy conversion, on account of its fully solid-state nature characterized by exceptional reliability, noiseless operation, and scalability, is considered a promising means of harvesting waste industrial heat and converting it into electricity. A converse process, making a solid-state cooler by passing an electric current through a thermoelectric module, is equally important and offers rapid spot cooling of electronic devices. The efficiency of energy conversion is measured by a material's parameter called the thermoelectric figure of merit  $Z = \sigma S^2/\kappa$  that combines three important transport parameters: electrical conductivity  $\sigma$ , Seebeck coefficient  $S$ , and thermal conductivity  $\kappa$ . The aim is to have a material with as high  $Z$  as possible. While deceptively simple, the realization of high  $Z$ -values is exceedingly difficult because of the interdependence of the transport parameters. A family of semiconductors called skutterudites is of interest for TE applications because of their excellent electronic properties that make the numerator in the above expression large. The trick is to find ways to make the denominator small; in other words, ensure a very low thermal conductivity. The skutterudite lattice contains structural voids and these can be filled with foreign species such as rare earths or alkaline earth atoms forming what is known as filled skutterudites. The filler species are rather loosely bonded to the matrix and act as independent oscillators ("rattlers") that scatter heat-carrying phonons (quantized lattice vibrations) and thus degrade the thermal conductivity. During the past

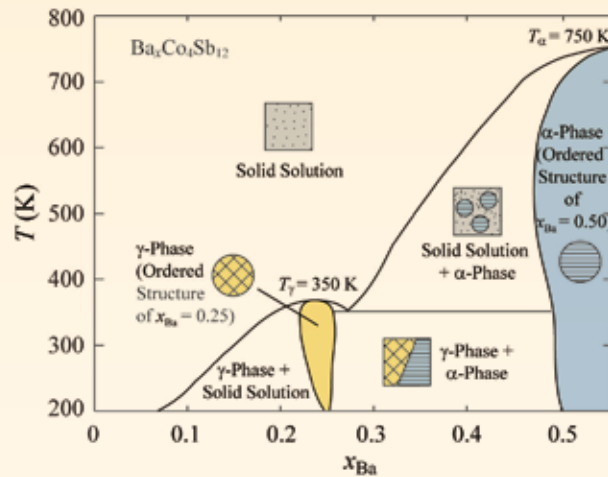


Figure 1: The solid-state phase diagram of  $\text{Ba}_x\text{Co}_4\text{Sb}_{12}$  as a function of Ba content and temperature, which shows the boundaries of the disordered solid solution phases and the order-disorder transition temperatures ( $T_\alpha$  and  $T_\gamma$ ) for the two ordered phases. The positions of the ordered phases show that, for  $x$  less than 0.25, phonon scattering is by point defects, while for  $x$  between 0.25 and 0.5, two-phase (interfacial) phonon scattering occurs.

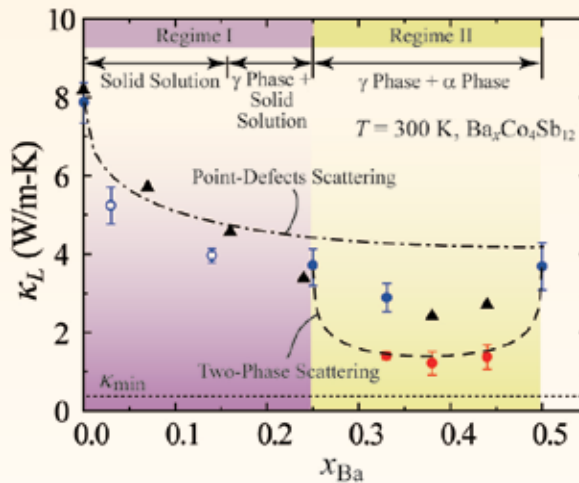


Figure 2. Dependence of the predicted lattice thermal conductivity of  $\text{Ba}_x\text{Co}_4\text{Sb}_{12}$  on the Ba concentration at 300 K. The development of the phase diagram in Figure 1 allowed delineation of the regions where the two different analytical models for calculating  $\kappa_L$  can be applied—the dashed line (two-phase scattering) and dash-dotted line (point-defects scattering). The trend in the two-phase scattering model follows that of the experimental data, supporting the presence of the ordered phases and suggesting the mechanism for the drop in thermal conductivity.

## Molecular Dynamics/Green-Kubo Results

- Solid Solution
- Single-Phase
- Two-Phase Mixture
- ▲ Experiment
- Two-Phase Scattering
- Point-Defects Scattering

# CSTEC Cosponsors ICEL 2010

decade, while focusing on identifying the filler species that are most effective in suppressing the thermal conductivity, scientists ignored the possibility that the filler atoms might order on the available lattice sites. Ordering refers to a condition in which one atom is found in a constant ratio with another type of atom (or atoms) and is also located in the same, repeatable location in the crystal lattice. Ordering is dissimilar from a situation in which atoms are found in random locations, also known as a solid solution.

CSTEC researchers have addressed this problem by inquiring into the ordering of Ba in the void sites of  $\text{CoSb}_3$ , the archetypal skutterudite material. *Ab initio* calculations, cluster expansion, and Monte Carlo simulations were used to construct the temperature-composition phase diagram that describes configuration patterns of barium as a function of its concentration and temperature (Figure 1). The phase diagram exhibits prominent ordered phases of Ba compositions: the  $\gamma$ -phase with  $x = 0.25$  and the  $\alpha$ -phase with  $x = 0.5$ . They next calculated the lattice thermal conductivity across the phase space of Ba concentrations provided by the phase diagram and found that while phonon scattering in the solution phase is noticeable, it is even more dramatic in the two-phase regime where the  $\gamma$  and  $\alpha$  phases coexist (Figure 2). The results show that the two-phase mixture has very low lattice thermal conductivity. It is only slightly higher than the predicted minimum thermal conductivity  $\kappa_{\min}$

for an amorphous phase (the so-called “glass-like” thermal conductivity). The authors’ atomic-level investigation indicates that the search for high-performance TE skutterudites can greatly benefit from the presence of order-disorder phase transitions of the filler species, which leads to the two-phase coexistence and low lattice thermal conductivity.

This research project was conducted by Hyoungchul Kim and Professor Massoud Kaviani of mechanical engineering, John C. Thomas and Professor Anton van der Ven of materials science and engineering, and Professor Ctirad Uher of the physics department. Baoling Huang, from the Hong Kong University of Science and Technology, also collaborated.

More details of this work may be found in:

*H. Kim, M. Kaviani, J. C. Thomas, A. van der Ven, C. Uher, and B. L. Huang, “Structural Order-Disorder Transitions and Phonon Conductivity of Partially Filled Skutterudites,” Phys. Rev. Lett. 105, 265901 (2010).*

The University of Michigan was host to the 8th International Conference on Electroluminescence & Organic Optoelectronics (ICEL 2010—[www.icel2010.org](http://www.icel2010.org)). This conference (co-chaired by CSTEC principle investigators Stephen R. Forrest and Max Shtein) is the leading international forum for scientists to discuss research in and applications of organic-based materials and devices, including light-emitting devices, field effect transistors, lasers, photovoltaic devices, memory, and sensors. The conference was attended by 175 people from countries in each of the continents; and featured excellent plenary, invited, and contributed talks, as well as posters spanning three and one-half days. The greatest number of submitted abstracts were on the topic of organic photovoltaic materials, devices, and associated issues. There was also a special session devoted to work done in U-M’s and USC’s Energy Frontier Research Centers (EFRCs). Sponsors of the conference included Angstrom Engineering, Universal Display Corporation, Global Photonic Energy Corporation, Aixtron AG, Applied Materials, USC EFRC, U-M EFRC, U-M College of Engineering, U-M Office of the Vice President for Research, and Michigan Memorial Phoenix Energy Institute. The feedback from attendees has been overwhelmingly positive. We are very much looking forward to the next edition of the conference, which is scheduled for summer of 2012 in Fukuoka, Japan.

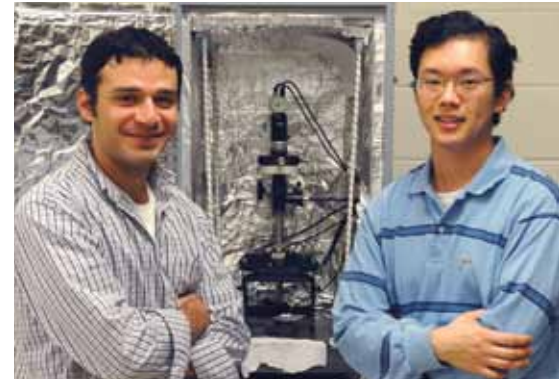
# Nanoscale Thermal Imaging

The ability to probe temperature with nanoscale resolution is essential to understanding not only the novel thermal transport phenomena that arise at the nanoscale but also the dissipation of energy in a variety of nanoscale electronic and photonic devices. This is critical to the development of novel energy conversion and computing devices.

In this project, an Atomic Force Microscope (AFM) based technique (Figure 1) that is capable of mapping thermal fields with <100 nm spatial resolution and ~10 mK temperature resolution is achieved. Although previously demonstrated AFM-based techniques are capable of comparable resolutions, their use is limited by the need to micro/nano fabricate special

probes or the need for a high vacuum environment. The method developed in this project (Figure 2) overcomes these challenging constraints by allowing direct measurement of the temperature field of a metallic surface with ~50 nm resolution at ambient conditions without using specially fabricated scanning temperature-probes.

Given the simple elegance of this technique, we believe that it will be widely used in a variety of important studies in nanoscale energy transport and dissipation in nanoelectronic devices and will be of broad interest to a variety of researchers. In fact, we are currently using this technique to characterize temperature differentials in nanoscale gaps that will be used to study the relationship between electronic struc-

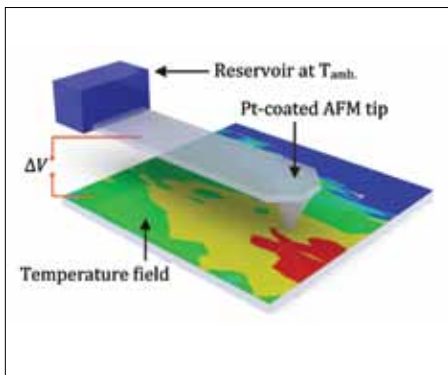


**Seid Sadat and Aaron Tan flank the nanoscale thermo-imaging AFM in the lab of Professor Pramod Reddy.**

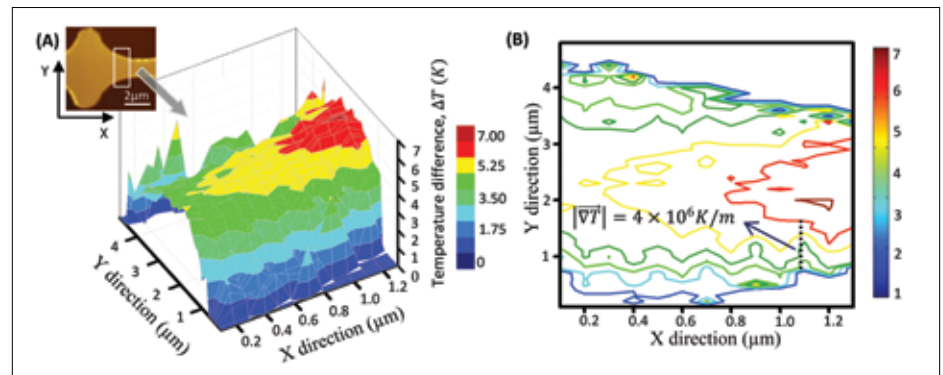
ture and thermoelectric properties.

For more information, see:

*S. Sadat, A. Tan, Y. J. Chua, P. Reddy. "Nanoscale Thermometry Using Point Contact Thermocouples," Nano Lett. 10, 2613 (2010).*



**Figure 1. Schematic view of the nanoscale point contact thermocouple setup used to determine the temperature of metallic surfaces with nanometer resolution.**



**Figure 2. (A) Nanoscale thermal image of a heated metal line (inset shows the metal line). (B) Contour map of the thermal field in the metal line: Thermal gradients as large as  $4 \times 10^6$  K/m can be detected.**



# Engineering Pathways for Enhanced Energy Transmission through Device Electrodes

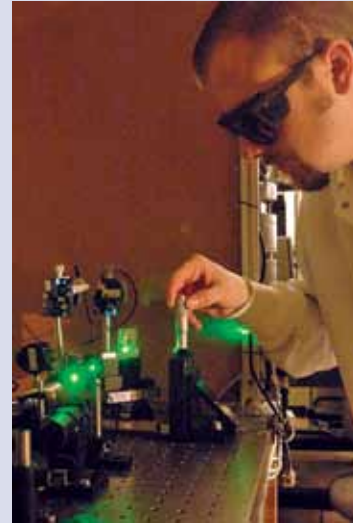
When designing the electrodes used for solar cell applications, engineers typically consider the tradeoff between light transmission, which requires a thin electrode, and electrical conductance, which requires a thick electrode. Because organic-based solar cells are usually thin with respect to the dominant range of wavelengths emitted by the sun, new strategies need to be developed for engineering new ways to convey light energy through the electrodes. One strategy being pursued is to resonantly transfer light energy to waves of free electrons known as surface plasmon polaritons (SPPs). By using the SPPs to transport the energy through the electrode rather than passing light through it, thicker electrodes can potentially be used, resulting in higher solar cell efficiency. Since this SPP-mediated energy transmission pathway is reversible (i.e., it can be used to transport light either into or out of a device), organic light-emitting diodes (OLEDs) were used for experimental convenience to demonstrate the pathway and characterize its efficiency.

A series of OLEDs were first capped with organic films containing a thin fluorescent dye layer precisely located at one of two different distances from the silver cathode. These were then evaluated based on their ability to transfer light energy from within the OLED through the cathode. The cathode thickness was chosen to maximize coupling between these SPP modes and thus form an efficient pathway for energy transmission out of the device. Devices in which the fluorescent dye layer was located 4 nm above the cathode showed a factor of 6.5 greater fluorescent emission than those in which the dye layer was located farther away at 112 nm above the cathode, in agreement with simulations. This significant 6.5-fold enhancement indicates the efficiency of the energy transfer pathway through the cathode and the potential performance improvements to be gained in optimizing this energy transfer mechanism for organic solar cells.

Research on the SPPs was conducted in the labs of Professors Kevin Pipe (mechanical engineering) and Max Shtein (materials science and engineering) by graduate student Kwang Hyup An.

Details of this work can be found in:

*K. H. An, M. Shtein, and K. P. Pipe, "Surface Plasmon Mediated Energy Transfer of Electrically-Pumped Excitons," Optics Express 18, 4041 (2010).*



**Matt Sykes measures the extent of useful light capture in organic photovoltaic structures attributable to surface plasmon resonance, in an effort to understand the fundamental limits of plasmon-exciton coupling in organic semiconductor materials and nanostructures.**

# Highly Mismatched Alloys for Energy Conversion: New Insight into the Role of Clusters

Most materials are only able to absorb light and heat of a certain limited range of wavelengths. Thus, the most efficient solar cells are made of multiple materials that together can capture a greater portion of the electromagnetic radiation in sunlight. The best solar cells today are still missing a material that can make use of a portion of the sun's infrared light. In addition, the conversion of heat to electricity is limited by the ability of electrons to do work within the material. It has been suggested that alloy films composed of highly immiscible solute atoms in a solvent, termed "highly mismatched alloys" (HMAs), are promising for energy conversion devices due to their ability to efficiently absorb light and heat, and to subsequently transport charge carriers.

The properties of HMAs are often described with a model focusing on the influence of individual solute atoms, assuming that all solute atoms "see" the same atomic environment. This simple picture, termed the "band anti-crossing" (BAC) model, is widely utilized but does not quantitatively explain several extraordinary optical and electronic properties of HMAs. For example, the addition of a sprinkle of one element drastically changes the material's ability to absorb light and to convert heat to electricity. Furthermore, in earlier work on gallium arsenide nitride, a highly mismatched alloy that is spiked with nitrogen, we revealed a substantial fraction of N pairs, and their influence on electronic

transport properties. Since many of the solute atoms "see" a variety of atomic environments, as shown in the figure, we hypothesized that these would need to be included in descriptions of fundamental alloy properties. Perhaps the most important fundamental property is the mass that electrons seem to carry as they travel through the alloy films, often termed the "effective mass."

Here, our international team of researchers from Michigan and Ireland report new experimental evidence for the significant impact of atomic clusters on the electronic properties of alloy films. As the alloy films are deposited, we add trace amounts of solute atoms, tens of parts per million at a time. We then measure the film's ability to convert heat into electricity, and determine the electron effective mass. Interestingly, as the concentration of solute atoms increases, the effective mass first increases, then decreases, and then increases again. Although these trends are not predicted by the BAC model, they are consistent with the predictions of alternative models, which consider that solute atoms can have a variety of atomic environments. We are currently in the process of identifying and controlling the atomic environments of solute atoms, in order to enhance the material's ability to convert light and heat to electricity.

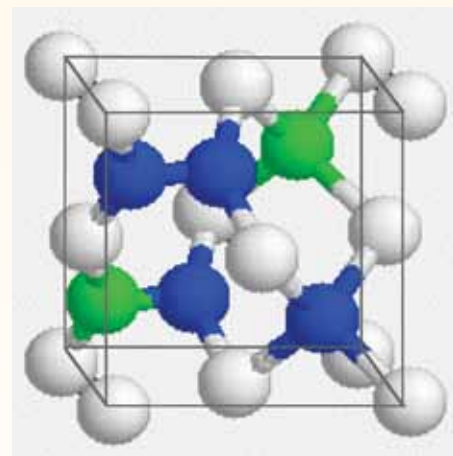
In the long run, understanding the influence of solute atom clusters on the electronic properties of HMAs pro-

vides an opportunity for a new paradigm in band structure engineering. For example, predictive models that take into account solute atom clusters would enable the design of new materials with tailored functionalities.

The researchers on this project include PhD students Tassilo Dannecker (University College Cork), Yu Jin (U-M), Hailing Chen (U-M), and John Bruckeridge (U-M); undergraduate student Charlie Gorman (U-M); UCC professor Stephen Fahy; and U-M professors Ctirad Uher, Cagliyan Kurdak, and Rachel Goldman.

For more information, please see:

*T. Dannecker, Y. Jin, H. Cheng, C. F. Gorman, J. Bruckeridge, C. Uher, S. Fahy, C. Kurdak, and R. S. Goldman, "Nitrogen Composition Dependence of Electron Effective Mass in GaAs<sub>1-x</sub>N<sub>x</sub>," Phys. Rev. B **82**, 125203 (2010).*



**Figure 1. Ball and stick model for GaAsN with substitutional N, N-As split interstitial, and N-N split interstitial. The grey, green, and blue spheres represent Ga, As, and N, respectively.**

# Atomic-Scale Mapping of Quantum Dot Structures for Energy Harvesting

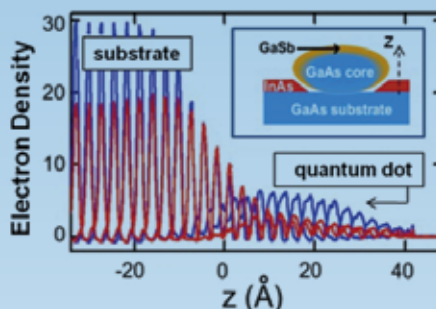
One of the most intriguing developments in nanotechnology is the use of tiny specks of matter known as “quantum dots” to form tunable electronic states much like the discrete energy levels that exist in atoms, except with potentially much greater flexibility and control. Quantum dots can be used to make highly efficient lasers, and sensors, and have potential for energy harvesting applications. As with the explorers of old, mapping the *terra incognita*

of quantum dots, in this case at the atomic level, is an essential step in realizing these novel applications. Work done by CSTEC researchers has done just that—determining for the first time the structural and

chemical makeup of semiconductor quantum dots made by the “drop-let” epitaxy approach. The results are both surprising and promising for the formation of a wide variety of complex quantum dot structures, “designer dots,” so to speak. In Figure 1, each peak represents a particular atom, distinguished by its x-ray scattering power measured at two different x-ray energies: at the



**CSTEC PI Roy Clarke, contemplating complex oxides.**



**Figure 1. Slice through a line of Ga atoms in the structure of GaAs/GaSb quantum dots (inset) as a function of distance,  $z$ , from the dot-substrate interface.**

Ga absorption edge (blue curve), and at the As-edge (red curve). This differential contrast provides detailed quantitative information on the chemical composition distribution within the quantum dots and at their interface with the substrate. The ability to map nanostructures in this way is especially important for applications to inorganic photovoltaic materials because key quantities like solar absorption, quantum efficiency, and charge capture depend critically on control of the dots’ composition, strain, and shape.

This research was conducted by Roy Clarke, professor of physics; Dr. Divine Kumah, a recent U-M graduate student, who is now a post-doctoral scholar at Yale; and visiting scholar Professor Yizhak Yacoby from Hebrew University, Jerusalem.

## 2010–11 Seminar Series

- Sept. 23 **Zhaohui Zhong**, University of Michigan, Electrical Engineering and Computer Science
- Oct. 22 **Yi Luo**, Carnegie Mellon, Electrical and Computer Engineering
- Oct. 29 **John Rogers**, University of Illinois, Materials Science and Engineering
- Nov. 11 **Richard Laine**, University of Michigan, Materials Science and Engineering
- Nov. 12 **Rama Venkatasubramanian**, RTI International, Materials Science and Engineering
- Dec. 9 **Akram Boukai**, University of Michigan, Materials Science and Engineering
- Jan. 27 **Massoud Kaviani**, University of Michigan, Mechanical Engineering
- Feb. 25 **Nick Melosh**, Stanford University, Materials Science and Engineering
- Mar. 15 **Donald Morelli**, Michigan State University, Chemical Engineering and Materials Science
- April 22 **Tonio Buonassisi**, Massachusetts Institute of Technology, Mechanical Engineering

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## Awards

### Professional Society Awards

Massoud Kaviany received the James Harry Potter Gold Medal (Science of Thermodynamics) from the American Society of Mechanical Engineers. The James Harry Potter Gold Medal recognizes eminent achievement or distin-



guished service in the science of thermodynamics in mechanical engineering. The annual prize is awarded based on contributions

involving the teaching, appreciation, or utilization of thermodynamic principles in research, development, and design in mechanical engineering. Massoud was recognized based on his work on the thermodynamics of porous media.

Roy Clarke was awarded a Royal Society Visiting Professorship, which provides support for an international collaboration among New Zealand, the United Kingdom, and the United States.

### Foundation Award

Anne McNeil was awarded a Sloan Research Fellowship. The Sloan Foundation provides grants to scientists who have made valuable early contributions to their areas of expertise and demonstrated the potential for producing exceptional discoveries in the future. Anne's research in CSTEC

focuses on tailoring the properties of unique organic materials by altering the copolymer sequence in gradient copolymers that have donor and acceptor co-monomers.

### Agency Awards

Ted Goodson was named a 2010 recipient of the NSF American Competitiveness and Innovation Fellowship—Division of Materials Research.

P. C. Ku won a Young Faculty Award from the Defense Advanced Research Project Agency.

### Internal Awards

Ctirad Uher was named the C. Willbur Peters Collegiate Professor of Physics.

Joanna Mirecki Millunchick received the John F. Ulrich Education Excellence Award from U-M's College of Engineering.

Rachel Goldman received the Department of Materials Science and Engineering's annual Outstanding Achievement Award.

### Student Awards

Simon Huang was selected as a finalist for the fourth Taiwan Semiconductor Manufacturing Company (TSMC) Outstanding Student Research Award. TSMC holds this prestigious competition to foster and reward excellent research in the areas of semiconductors and renewable energy.



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