Friday Morning, November 1, 2013

Advanced Surface Engineering
Room: 203 C - Session SE+EN-FrM

Surface Engineering for Energy Conversion and Harvesting
Moderator: A.A. Voevodin, Air Force Research Laboratory, M. Stüber, Karlsruhe Institute of Technology, Germany

8:20am **SE+EN-FrM1 Nanoscale Thermal Transport**, *G. Mahan*, Penn State University **INVITED**
Nanoscale materials and devices are usually composed of materials whose bulk thermal conductivity has been measured and is well understood. However, new effects arise when they are components of nanoscale materials: (i) The thermal boundary (Kapitza) resistance at each interface is often the largest component of the thermal resistance of the nanomaterial. Experimental and theoretical values for these boundary resistances are scarce; (ii) Phonon mean-free-paths are also nanometers, and diffraction effects from the nanostructure are important. (ii) The interfaces and nanostructures themselves will have new phonon modes. We briefly review recent work on this field. We also discuss some of our own work on calculations of Kapitza resistances at two kinds of boundaries: (i) metal-insulator, and (ii) liquid solid.

1) G.D. Mahan, Nanoscale and Microscale Therm. Eng. 12, 294 (2008)

2) G.D. Mahan, Phys. Rev. B79, 075408 (2009)

3) G.D. Mahan, Appl. Phys. Lett. 98, 132106 (2011)

4) S. Neogi and G.D. Mahan, in press

9:00am **SE+EN-FrM3 Electrical and Thermal Properties and Understanding Interface Chemistry and Structure of Metal-Pnictogen Chalcogenide Interfaces**, *F. Devender, T. Borca-Tasciuc, G. Ramanath, I. Seshadri*, Rensselaer Polytechnic Institute
Thermoelectric materials are attractive for realizing eco-friendly solid-state refrigeration, and waste heat recovery and harvesting [1]. In addition to obtaining materials with high thermoelectric figure of merit ZT, it is key to tailor the electrical and thermal properties of interfaces of these materials with metals through control of interface structure and chemistry for high performance device applications [2]. Here, we describe the properties of interfaces comprised of two high figure-of-merit pnictogen chalcogenides, namely, n-Bi_2Te_3 and p-Sb_2Te_3 and Cu, Ni, Ti and Ta. Our results show that the thermal interface conductance of structures is insensitive to the majority charge carrier type. Cu shows the highest thermal conductance, which is about tenfold higher than that of the other interfaces studied. However, we find that interfaces of Ni and Ta with p-type materials show more than tenfold higher electrical conductivities than their interfaces with n-type materials. In order to understand these trends, we embarked on a study of the interface chemistry and structure using a combination of Rutherford Backscattering Spectrometry (RBS) and X-Ray Diffractometry (XRD). Our results from XRD analysis show that all the four metals studied tend to form interfacial phase with Tellurium in different stoichiometric amounts. RBS analysis show that just after 150 ºC annealing for 30 minutes Cu diffuses significantly in both n-Bi_2Te_3 and p-Sb_2Te_3, whereas Ni shows significant compositional changes in p-Sb_2Te_3 while retaining the multilayer structure with n-Bi_2Te_3. Ti and Ta maintain multilayer structure with both n-Bi_2Te_3 and p-Sb_2Te_3. We will discuss our findings and our inferences of the interface chemistry/structure property relationships. Our results will be important for designing metal contacts to any thermoelectric material based device and especially for applications like spot cooling in electronics chips where interfacial properties have become the bottleneck for realizing high-efficiency thermoelectric cooling.

References

1) S.B. Riffat, and X.L. Ma, "Thermoelectrics: A review of present and potential applications," Applied Thermal Engineering, vol. 23, 2003, pp. 913-935.

2) G. Chen, M.S. Dresselhaus, G. Dresselhaus, J.P. Fleurial, and T. Caillat, "Recent developments in thermoelectric materials," International Materials Reviews, vol. 48, 2003, pp. 45-66.

9:20am **SE+EN-FrM4 Imaging of Electron-Phonon Interaction on the Atomic Scale**, *A.A. Voevodin, I. Altfeder*, Air Force Research Laboratory, *K.A. Matveev*, Argonne National Laboratory
The control of thermal transport through coupled metal and non-metal interfaces is critical for many applications, including electronic device operation, photovoltaic power generation, sensors, and many others. For design and engineering of such interfaces, the energy coupling between electrons and phonons for heat transfer needs be assessed. An atomic level thermometer was developed to experimentally study interfacial thermal conductivity on a single molecular scale using an inelastic electron tunneling spectroscopy (IETS) combined with scanning tunneling microscopy (STM). The IETS-STM had led to a discovery of vacuum phonon tunneling across nanometer contact gaps as it can probe electron-phonon coupling at atomic scale [1]. The further development of the STM-based spectroscopic imaging technique discussed here provides direct real-space imaging of electron-phonon coupling parameter [2]. This is demonstrated using the combination of STM and IETS for thin Pb islands epitaxially grown on 7x7 reconstructed Si(111). Electron-phonon interaction increases when the electron scattering at the Pb/Si(111) interface is diffuse and decreases when the electron scattering becomes specular. The effect is driven by transverse redistribution of the electron density inside a quantum well.

References:

[1] I. Altfeder, A. A. Voevodin, A. K. Roy, Physical Review Letters, 105 (2010) 166101.

[2] Igor Altfeder, K. A.Matveev, A. A. Voevodin, Physical Review Letters 109, 166402 (2012).

9:40am **SE+EN-FrM5 Generation of Cu_2S Nanoparticles via Cluster Beam Deposition for Bulk Heterojunction Photovoltaics**, *M.W. Majeski, I. Bolotin, L. Hanley*, University of Illinois at Chicago
Hybrid inorganic-organic based nanocomposite films are prepared by cluster beam deposition for photovoltaic applications (F.D. Pleticha, *et al.*, J. Phys. Chem. C 116: 2012, 21693). Semiconducting copper(I) sulfide (Cu_2S) nanoparticles are co-deposited into an organic matrix, pentacene, to create a bulk heterojunction where p-type Cu_2S is expected to behave as an electron acceptor and pentacene behaves as a donor. Generation of Cu_2S nanoparticles are achieved by pulsed DC reactive magnetron sputtering of a Cu target with argon while forming compound clusters via introduction of reactive hydrogen sulfide gas. Reactive sputtering occurs in a gas aggregation source in which Cu_2S nanoclusters are allowed to nucleate and grow for subsequent deposition onto a substrate. Pulsing the DC power at 20 kHz allows for stable process parameters with an absence of arcing and has been shown previously to improve the quality of the deposited films. Finally, Cu_2S-pentacene nanocomposite films are also prepared with low energy acetylene ion assisted deposition. Film properties and nanoparticle stoichiometry are analyzed with X-ray photoelectron spectroscopy, transmission electron microscopy, and high angle annular dark field scanning transmission microscopy. Photovoltaic properties of these Cu_2S-pentacene nanocomposite films will be discussed.

10:00am **SE+EN-FrM6 Fabrication of Water-Splitting Photocatalytic Electrodes by "Particle-Transfer" Processing**, *T. Minegishi, T. Yamada, N. Nishimura, J. Kubota, K. Domen*, The University of Tokyo, Japan
We developed a process of fabricating planer electrodes from photocatalytic powder, and observed a high photo-electrocatalytic activity of $LaTiO_2N$ for H_2O splitting in aqueous solutions. This technology, hereafter we call the "particle transfer (PT) method", is applicable for various kinds of photoactive semiconducting powder catalysts. We first prepare powder catalysts with a maximum grain size of a few µm. A thin layer of the powder (thickness < 0.5 mm) is spread on a planer substrate using a suspension in organic solvent. Then this layer is over-coated with a thin Nb layer and then a thick Ti layer by means of radio-frequency magnetron sputtering. The metallic Nb layer makes a good mechanical and electric contact between the grains and the Ti layer, which serves a a good electric conductor. Finally this multilayer is peeled off onto another glass substrate using an adhesive (such as epoxy resin), and a conductive electrode covered by the catalytic grains is completed. In this work we used $LaTiO_2N$ powder loaded with 5 wt% IrO_2. The $LaTiO_2N$ powder was synthesized by NH3 flow gas treatment at 1223 K on $La_2Ti_2O_7$ prepared by a molten salt method [1]. The purity of $LaTiO_2N$ was checked by X-ray diffraction. This material exhibits absorption of visible light shorter than 600 nm and can potentially utilize about a half of the solar energy. The cross sectional view of this electrode by EDX-aided scanning electron microscopy indicates the left-over grains of $LaTiO_2N$ mostly in firm contact with the Nb layer laminating

the Ti conducting layer. The grains formed monolayer in most of places, laterally interlocking one another.

This electrode was subjected to potential-versus-current measurement in 1 M Na_2SO_4 solution (pH 13.5) under illumination of AM 1.5D solar simulator. The anodic photocurrent reached ~ 2 mA cm^{-2} at 1.0 V vs RHE, which is ~ 100 times higher than that on a $LaTiO_2N$ powder-coated conductive glass substrate [2]. This is attributed to the well-controlled grain-substrate contact by the Nb layer. Similar effects were observed by replacing Nb with Ta, Zr or Ti. Furthermore, the gas products (O_2 from this electrode, H_2 from the counter Pt electrode) was detected in two-vessel electrochemical system separated by a glass filter. From the PT $LaTiO_2N$ electrode, O_2 gas bubbled out at a rate (~ 0.1 μmol cm^{-2} min^{-1}) exactly matching the photo-anodic current. Evidently, the PT method makes a breakthrough in the efficiency of solar hydrogen generation in water splitting, making use of the diversity of semiconductor powder catalysts.

[1] P. A. Fuiere et al., *J. Am. Ceram. Soc.* **74** (1991) 2876.

[2] H. Hashiguchi et al., *Bull. Chem. Soc. Jpn.* **82** (2009) 401.

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