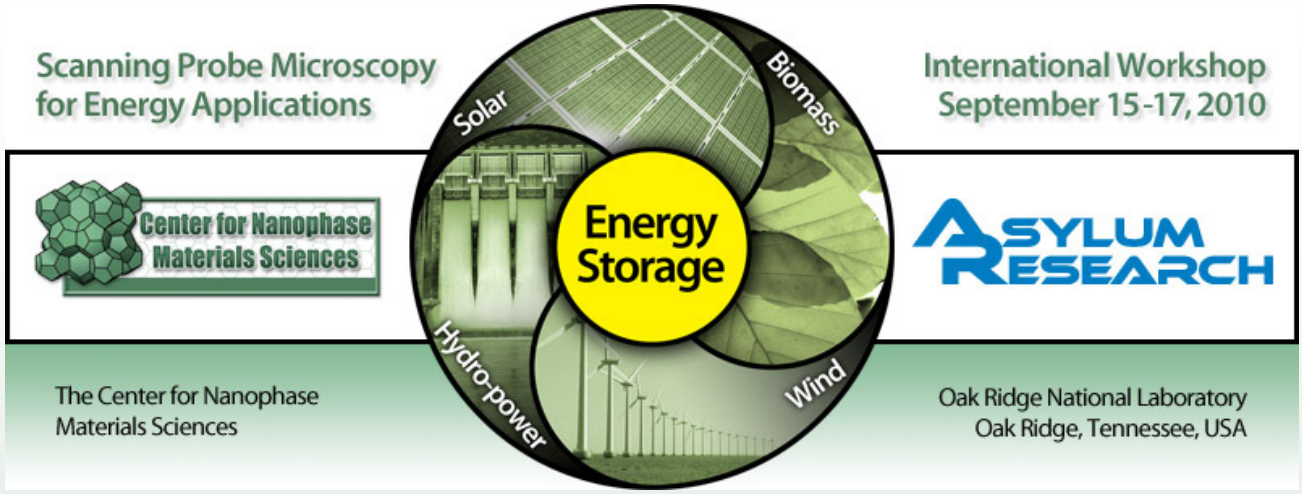

Scanning Probe Microscopy for Energy Applications

Program

Scope and Goals

Energy generation, storage, and conversion systems are an integral component of emerging green technologies, including solar power, automotive, and storage components of solar and wind energy economics. Despite the rapidly expanding manufacturing capabilities and wealth of phenomenological information on the macroscopic behaviors of energy storage and conversion systems, the microscopic mechanisms underpinning solar cell, battery and fuel cell operations in the nanometer to micron range are not well understood. Ultimately, our goal is to build a network of materials scientists centered on the applications of SPM for energy problems and to promote rapid dissemination of theoretical knowledge, experimental protocols, and novel technique development in this rapidly growing area.

Venue

Oak Ridge National Laboratory
Center for Nanophase Materials Sciences
Oak Ridge, TN 37922

Organizing Committee

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Acknowledgements

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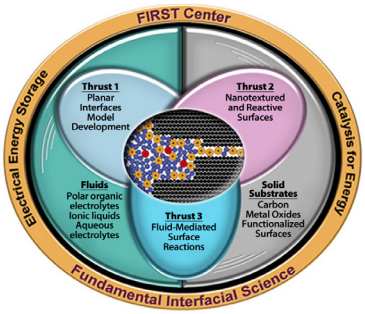
- The Center for Nanophase Materials Sciences which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy



Program

Wednesday, Sept. 15

8:00am		*Registration*
8:30	***David Ginger** Univ. of Washington	**Keynote** *Local Probing of Carrier Dynamics in Polymer Photovoltaic Materials*
9:15	***Keith Stevenson** UT Austin	*Elucidation of Electrochemical Interfaces via In Situ SPM*
10:00	***Nina Balke** ORNL	*Tracking Li-ion Diffusion on the Nanoscale*
10:45		*Break*
11:00	**C. Alan Wright** Univ. of MD	*Numerical Analysis of Sub-atomic AFM Imaging in Ultra-high Vacuum: Coupling Quantum Mechanics with Continuum Dynamics*
11:25	**Jagjit Nanda** ORNL	*Local State of Charge Mapping of Lithium Battery Electrodes*
11:50-2:00pm		*Poster Session and Lunch*
2:00	**Murti Salapaka** Univ. of MN	*Towards Quantitative Imaging in Dynamic Mode AFM*
2:25	**Claus Daniel** ORNL	*Probing Mechanical Degradation in Energy Storage Applications*
2:50	**Eyal Shafran** Univ. of UT	*Energy Transfer Between a Single Quantum Dot and a Carbon Nanotube*
3:15		*Break*
3:30	**Jeffrey Guest** Argonne Nat'l Lab	*Reversible Rectification in Sub-monolayer Molecular P-n Junctions; Towards Nanoscale Photovoltaic Studies*
3:55	***Thuc-Quyen Nguyen** UCSB	*Application of Scanning Probe Microscopy to Characterize Nanostructures in Bulk Heterojunction Organic Solar Cells*
4:40	***Steven Buratto** UCSB	*AFM and Conductive AFM of Fuel Cell Materials*
5:25		*Closing remarks*

**Invited Talk*

Thursday, Sept. 16

8:30am	***Arvind Raman** Purdue Univ.	*Understanding Energy Dissipation Between a Vibrating AFM Tip and a Solid-liquid Interface*
9:15	***Peter Maksymovych** ORNL	*Quantitative Analysis of Non-linear and Hysteretic I-V curves in Conductive Atomic Force Microscopy*
9:45	***Shashank Priya** Virginia Tech	*Multimodal Energy Harvesting Microsystems*
10:30		Break
10:45	***Stephen Jesse** ORNL	*Mapping Energy Dissipation by SPM: The Band Excitation Method*
11:15	**Nataliia Guz** Clarkson Univ.	*Atomic Force Microscopy Measures Single Electron Charges on Quantum Dots in Ambient Conditions*
11:40	**Mehmet Baykara** Yale Univ.	*Chemical Imaging and Interaction Quantification for Catalytic Materials Using High-Resolution Atomic Force Microscopy*
12:05-1:00		*Lunch*
1:00	***Alexander Tselev** Univ. of Tennessee	*Microwave Imaging of Energy Materials*
1:30	**Philippe Leclere** Univ. of Mons	*Organic Electronic Device Characterization: The Key Role of Scanning Probe Microscopies*
1:55	**Patrick Fletcher** UIUC	*Electrothermal Microcantilever with Integrated Heater for Scanning Probe Microscopy*
2:20	**Behrang Hamadani** NIST	*Imaging of Nanoscale Photogenerated Charge Transport in Organic Photovoltaic Materials*
2:45		*Break*
3:00	**Soonil Lee** Penn State Univ.	*The Role of Defects for Ferroelectric-Thermoelectric Marriage*
3:25	***Jiangyu Li** Univ. of Washington	*Probing Local Thermal Phase Transition on the Nanoscale*
4:10	***Anil Gannepalli** Asylum Research	*Multifrequency AFM*
4:55	***Robert Kostecki** Lawrence Berkeley Nat'l Lab	*In situ SPM of Local Interfacial Phenomena in Li-ion Batteries*
5:40		*Closing remarks*

Friday, Sept. 17, 9am-noon—Equipment Demonstrations

Lab 1: *Li-ion Dynamic Imaging by Electromechanical Strain Microscopy*

Lab 2: *Energy Dissipation Mapping by Multifrequency SPM*

Lab 3: *Thermal and Thermomechanical Imaging*

Lab 4: *Band Excitation MFM and PFM*

Lab 5: *Electromechanical Imaging in Ultra-high Vacuum*

Talk Abstracts

Local Probing of Carrier Dynamics in Polymer Photovoltaic Materials

David Ginger, University of Washington

Organic photovoltaics (OPV) are a potential low-cost alternative to conventional inorganic photovoltaics. The most successful organic solar cells to date rely on nanoscale phase separation between different components as the basis for their operation. Understanding and controlling this nanoscale film structure is a central challenge that affects every aspect of the field, from the optimization of new low-bandgap polymers to early efforts to scale up manufacturing. Our group has pioneered several scanning-probe methods, including time-resolved electrostatic force microscopy (trEFM) and photoconductive atomic force microscopy (pcAFM), as tools to characterize the influence of nanoscale film morphology in active organic solar cells. In this talk I will discuss lessons learned in model OPV systems so far, as well as highlight opportunities for scanning probes in other emerging energy areas such as photocatalysis. Finally I will review new opportunities for applying electrically active scanning probes to nanostructured energy conversion devices if instrumental performance can be improved.

Elucidation of Electrochemical Interfaces via *In Situ* SPM

Keith J. Stevenson, Department of Chemistry and Biochemistry, University of Texas at Austin

The development of advanced materials and technologies to efficiently convert and store energy directly into electricity or chemical fuels is of urgent importance due to increasing energy demands of an ever growing world population and decreasing energy reserves. However the tremendous scientific challenges remain before successful implementation of any number of competing energy technologies such as solar cells, fuel cells, and batteries. These materials, interfaces and device architectures currently being explored are very challenging to characterize by ensemble-averaging, bulk experimental methods since they do not exhibit long-range order or homogeneity, contain unique nano-morphological features and possess non-uniform chemical compositions and defect chemistry. The lack of fundamental understanding for charge generation, separation and transfer at these "electrochemical" interfaces provides tremendous impetus for the continued development and application of advanced scanning probe tools with increased spatial and temporal resolution. This presentation will highlight our development of several high resolution spectrolectrochemical imaging tools for studying the ion/charge transfer at model electrochemical metal oxide, polymer and nanocarbon interfaces. Hybrid scanning probe approaches will be described that combine two or more techniques such as conductive probe atomic force microscopy (CP-AFM) and Kelvin probe microscopy (KPM) integrated with Raman and UV-Vis microscopy to enable sub-ensemble functional imaging and multi-dimensional analysis of complex, interdependent processes that occur at electrodes, electrolytes, and interfaces. Information obtained from these tools provides fundamental understanding of electron and charge transfer processes and degradation mechanisms for materials utilized in energy conversion and storage technologies.

Tracking Li-ion Diffusion on the Nanoscale

Nina Balke, Oak Ridge National Laboratory

The development of the capability for probing ion transport on the nanometer scale is a key challenge for development of energy storage and generation systems including Li-ion batteries, and can potentially unravel complex interplay between structure, functionality, and performance in these systems. In the field of thin film batteries Scanning Probe Microscopy has been used to characterize solid/liquid interfaces and their change during battery operation on the nanometer scale. These measurements were usually restricted to purely topography imaging. However, the unique capability of Scanning Probe Microscopy to measure bias induced phase transitions on a local scale as it is common in other fields like ferroelectrics is not used in the field of thin film batteries. Consequently, the nanoscale mechanisms underpinning battery functionality remain unexplored, precluding developing strategies for improvement of energy and power densities and life times of these devices. The strong strain-bias coupling in electrochemical materials is used to develop the capability for mapping electrochemical reactions on the nanometer scale, and hence get insight into the mechanisms of battery operation. The developed technique, Electrochemical Strain Microscopy (ESM) is demonstrated on $LiCoO_2$ thin films as an example for cathode materials for Li-ion batteries. A high frequency periodic electric field is applied to the tip, resulting in small volume Li-ion redistribution. The associated changes in molar volume result in local surface expansion and contraction that is transferred to the Scanning Probe Microscopy probe and detected by microscope electronics. Theoretical calculations are shown to support the experimental data and to give insight into the signal generating mechanism. In addition, it will be demonstrated how ESM can be used to investigate the Li-ion flow through a $LiCoO_2$/Lipon/Si system thin film battery with a sub-10 nm resolution and correlate it directly to the microstructure of the battery. The role of defects for lithium diffusion is discussed and it is demonstrated how electrical cycling influences the battery performance. The electrical field-dependence of Li mobility is explored to determine the critical bias required for the onset of electrochemical transformation, potentially allowing to deconvolute reaction and diffusion processes in the battery system on a local scale.

Research was sponsored as part of the Fluid Interface Reactions, Structures and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number ERKCC61 and part of the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy in the projects CNMS2010-098 and CNMS2010-099.

Numerical Analysis of Sub-atomic AFM Imaging in Ultra-high Vacuum: Coupling Quantum Mechanics with Continuum Dynamics

C. Alan Wright and Santiago D. Solares, University of Maryland, College Park

Recent reports of sub-atomic resolution frequency-modulation AFM (FM-AFM) images acquired using transition metal (e.g., tungsten, platinum, palladium) tips in ultra-high vacuum (UHV) [1, 2] have sparked debate within the AFM community [3]. Nevertheless, an in-depth theoretical study of this work – one which incorporates all of the appropriate length and time scales to fully capture the system's behavior – has yet to be produced.

Our focus has been on the tungsten/graphite system investigated by Hembacher, et al. [2] in which experimental higher-harmonic images revealed features exhibiting four-leaf clover symmetry within the diameter of a single tungsten atom. The authors interpret these features as four bonding lobes of increased charge density, the existence of which has previously been demonstrated in bulk systems by plane-wave calculations of the W(001) surface [4, 5]. These lobes are thought to be the result of covalent-like bonding in the bulk, a common feature of transition metals [6]. However, two important questions arise in the context of AFM: "Are similar lobe orbitals present in non-bulk systems such as AFM tips?" and "Are the tip lobe-surface interactions sufficiently strong to produce sub-atomic contrast through higher harmonics?"

We have set out to validate or invalidate the interpretation of these higher-harmonic images through multiscale simulation methods. Specifically, we investigate the effects of various environmental and experimental

parameters as they pertain to the nature of the bonding lobes, as well as the achievable image resolution. We first develop a 3D grid of short-range force curves (1.25 – 6.00 Å) for a W(001) tip interacting with a graphite surface using density functional theory (DFT). The resulting force curves are adjusted for long-range vdW interactions and used in numerical, multi-modal FM-AFM simulations of a quartz tuning fork above a graphite surface. The probe trajectories are then filtered and Fourier processed to extract and map the higher harmonics response. So far our DFT results have confirmed the presence of the four lobes of increased electron density (see Fig. 1) protruding from the apex tungsten tip atom, as well as the ability of the short-range interactions to produce higher harmonics.

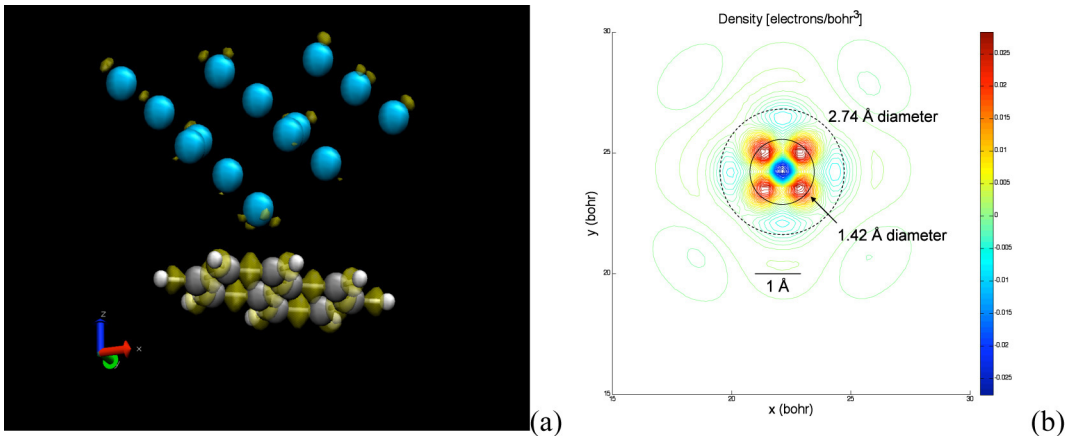


Fig. 1 (a) Change in electron density after SCF calculation. A single isosurface is shown for a 3-layer W(001) tip over two hydrogen-terminated cabon rings. (b) Density contour slice through the four lobes at the tip apex.

[1] F. J. Giessibl et al., Science 289, 422 (2000).
[2] S. Hembacher, F. J. Giessibl, and J. Mannhart, Science 305, 380 (2004).
[3] H. J. Hug et al., Science 291, 2509a (2001).
[4] M. Posternak et al., Physical Review B 21, 5601 (1980).
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[6] L. Pauling, The Nature of the Chemical Bond (Cornell Univ. Press, Ithaca, New York, 1948).

Local State of Charge Mapping of Lithium Battery Electrodes

Jagjit Nanda, Materials Science Division, Oak Ridge National Laboratory

Lithium battery electrodes are composite porous structures with a mix of active materials, polymeric binders and conductive diluents such as carbon. The electrode thickness, composition, and the particle morphologies are optimized to provide longer cycle life and performance. The Li-ion transport in such complex electrode assembly gets complicated due to local inhomogenity[1] associated with extent of carbon coverage, binder distribution and defects. In our study we have taken the unique advantages of micro-Raman spectroscopy for probing the local vibrational structure and changes associated with Li-ion battery electrodes[2] subjected to intercalation/deintercalations of lithium atoms. Specifically, we shall present the *ex-situ* state of charge (SOC) Raman mapping of electrodes subjected to charge-discharge cycles. SOC maps of charged $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ (NCA) electrodes showed a spatial non-uniformity in terms of lithium distribution[3]. The results will be discussed in terms of various kinetic and diffusion barriers that exits due to transport of Li-ion at solid as well as at solid-liquid interfaces.

1. J. Lei, F. McLarnon, and R. Kostecki, "In-situ Raman Microscopy of Individual $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ Particles in Li-ion in Battery Composite Cathode" J. Phys. Chem. B 109, pgs. 952-957 (2005).

2. Jagjit Nanda et al. "In-situ Raman microscopy on high capacity silicon-carbon composites as negative electrodes for Li-ion application", J. Electrochem. Comm. 11, 235-237 (2009).
3. Jagjit Nanda et al. "SOC Mapping of Lithium-ion Battery Electrodes", Submitted, Nature Materials (2010).

Towards Quantitative Imaging in Dynamic Mode AFM

Murti Salapaka, Pranav Agarwal, Govind Saraswat, University of Minnesota

This talk will highlight the need for quantitative imaging in dynamic mode atomic force microscopy. In the recent past, there is a renewed focus on the need for extracting sample properties other than the topography. In this talk, a new perspective to AFM based interrogation based on detection is developed. It is shown that with appropriate modeling abstraction, significant benefits can be accrued in detecting sample features. In particular, a communication channel model is extracted and it is shown that detection speeds can be increased by an order of Q where Q is the quality factor. Furthermore, the detection architecture provides a framework for providing measures on the interrogation fidelity. Exploiting the communication channel model, it will be demonstrated that significant gains can be made if, instead of deciphering feature by feature, the entire feature sequence is deciphered in a maximum likelihood setting. Implementable algorithms and proof of concept experimental results will be presented. The above framework lays the foundations for providing confidence measures on the image with controls provided to the user to select the level of compromise between false positives and missed detections.

The use of equivalent cantilever models to decipher various hypotheses will also be demonstrated to be an effective means of sensing. A novel scheme for exciting the cantilever that enables a continuous evaluation of the best equivalent cantilever model that explains the measured data is developed that will highlight the use of paradigm developed for extracting sample properties other than topography. In this method, the modified resonant frequency and quality factor of the cantilever are obtained during intermittent contact mode imaging. These real time estimates are related to conservative and dissipative components of tip-sample interaction respectively during dynamic mode operation. The method involves exciting the cantilever near its resonant frequency and two other frequencies chosen close to the resonant frequency. Methodology to choose the amplitude and frequency of sideband frequencies is outlined which ensures that the dynamic mode operation is not disturbed substantially. A recursive parameter estimation scheme is developed to estimate the instantaneous first mode response of the cantilever during dynamic mode operation. We demonstrate the application of this technique for characterizing elastic and dissipative properties of PBMA-PLMA sample, which is being researched in collaboration with the NSF funded characterization facility at University of Minnesota, Minneapolis. In addition, the application of the technique to imaging and forcespectroscopy will also be demonstrated.

The concept of adaptively estimating the parameters of the equivalent cantilever system can be suitably modified to applications in EFM and for extracting properties related to charge transport. Techniques and applications related to such studies will be elucidated.

Probing Mechanical Degradation in Energy Storage Applications

Claus Daniel[1,2], Kevin Rhodes[2,1], Sergiy Kalnaus[1], 1) Oak Ridge National Laboratory, 2) University of Tennessee

Energy storage devices, particularly batteries, are receiving more and more attention from the research community due to their potential of scalability the technology for electrification of transportation and energy storage on the electricity grid. However, for associated cycle and calendar life requirements are much more challenging than in consumer electronics and other small scale applications.

Our research group focuses on degradation mechanisms and performance limiting ion mobility kinetics associated with the mechanical behavior of active electrode materials. Recent highlights include the development of specialized acoustic emission and micro-electrode setups which can shed light on mechanical and functional degradation in energy storage devices. These methodologies combine spectroscopic with microscopic techniques and other in-situ probing tools to enable a full picture of events inside batteries. The insight provided by these new capabilities open the pathway for new microstructurally guided materials developments with much longer cycle and calendar life.

This talk will demonstrate the capabilities stemming from the combination of acoustic emission, in-situ X-ray diffraction, micro-electrode fabrication, and theoretical fracture mechanics. It will also demonstrate where scanning probe microscopy can add great value to solving the problems in energy storage devices as it is performed in starting collaborations with the Kalinin group at CNMS.

Acknowledgement
This research at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725, was sponsored by the Vehicle Technologies Program for the Office of Energy Efficiency and Renewable Energy. Parts of this research were performed at the High Temperature Materials Laboratory sponsored by the same office and the Shared Research Collaborative User Center sponsored by the Basic Energy Sciences Program for the Office of Science.

Energy Transfer Between a Single Quantum Dot and a Carbon Nanotube

E. Shafran, B. D. Mangum and J. M. Gerton, Department of Physics and Astronomy, University of Utah,*
**Presenting author e-mail: shafrane@gmail.com*

We used individual carbon nanotubes (CNTs) attached to AFM tips to probe isolated quantum dots (QDs) while measuring the fluorescence signal. Figure 1(a) shows an example of a fluorescence approach curve; the far-field-normalized fluorescence signal, S(z), is plotted as a function of the vertical separation, z, between the CNT terminus and QD surface; also shown is an x-z tomographical section [1] of a QD. The strong reduction in fluorescence was observed consistently in more than 100 measurements on >50 QDs using 6 different CNTs [2]. All data agree to high precision with energy transfer via a Förster dipole-dipole coupling between a photoexcited exciton in the QD and a resonantly-excited exciton in the CNT. However, this agreement is only achieved if the standard Förster model is modified to account for the possibility of creating an exciton above the CNT terminus. This model predicts a strong correlation between the Förster radius and the average position at which the exciton is created within the CNT, in agreement with the measurements. The model also predicts that the peak energy transfer efficiency should saturate at a value of ~0.96, which again agrees with measurements, as shown in Fig. 1(c). Importantly, this saturation seems to be independent of whether the CNT is semiconducting or metallic. In addition, the saturation value of ~0.96 is maintained even when the energy transfer must compete with faster internal relaxation of the QD (i.e., lower quantum yield), which implies that the energy transfer rate also increases to compensate. This counterintuitive result is due to the 1D nature of CNTs in that excitons are less likely to be created far from the CNT tip when the internal relaxation processes of the QD speed up. Although on very rare occasions there is some evidence of charge transfer between a QD and CNT, the overwhelming majority of measurements are consistent with energy transfer only. These results are very fundamental in nature, but they have implications for composite materials composed of QDs attached to CNTs, which are being developed for a variety of optoelectronic applications, including photovoltaics and sensing.

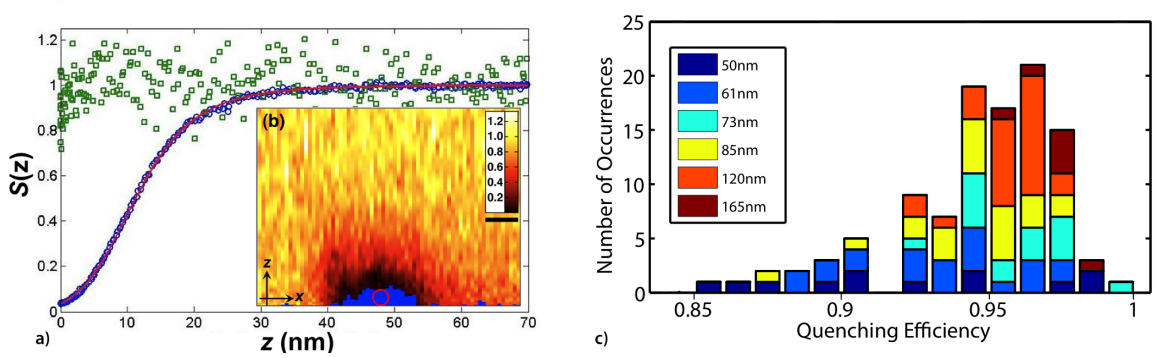

Figure 1. Energy transfer between a QD and CNT. (a) The normalized fluorescence signal is shown as a function of the vertical separation, z, between the CNT terminus and the QD surface. The blue symbols are measured data for the bright state of the QD, while the green symbols are for the dark state. The solid red line is a fit to the Förster model. (b) x–z tomographical section. The blue cutout region denotes the AFM height trace and the color scale gives the normalized fluorescence signal. The scale bar is 10 nm. (c) Histogram of the peak energy transfer efficiencies at QD–CNT contact. The data are color–coded according to the length of each CNT used.

References
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[2] E. Shafran, B. D. Mangum, and J. M. Gerton, arXiv:1004.5143 (2010).

Reversible Rectification in Sub-monolayer Molecular P-n Junctions; Towards Nanoscale Photovoltaic Studies

Jeffrey R. Guest[1], Joe A. Smerdon[1], Noel C. Giebink[1], Matthias Bode[2], Nathan P. Guisinger[1]
1 Center for Nanoscale Materials, Argonne National Laboratory
2 Physikalisches Institut, Univ. Wuerzburg, Germany

Since the original demonstration the photovoltaic effect in an organic p-n heterojunction (C. W. Tang, Appl. Phys. Lett. 48, 148 (1986)), molecular heterostructures have made steady progress towards their promise of providing low-cost solar power devices. The interfaces between the components are critical to their functioning; however, developing a deeper understanding and optimizing the morphology of these interfaces has proven extremely challenging because they are buried in device scale structures. In order to gain insight into correlations between structure and function, we have prepared model-scale p-n junctions with a prototypical acceptor-donor system – C_{60} and pentacene – in ultrahigh vacuum (UHV) and performed scanning tunneling microscopy and spectroscopy (STM/STS) measurements. STM reveals that submonolayer structures of pentacene on close-packed C_{60} (on Cu(111)) – shown in Fig. 1A – forms an upright close-packed arrangement. I-V curves obtained on this heterojunction (Fig. 1B) show rectification of the current between the tip and substrate in the direction expected for this donor-acceptor orientation. By reversing the orientation with C_{60} on pentacene (Fig. 1C), the direction of rectification is also reversed as expected. A rate equation-based model reproduces the qualitative behavior observed in our studies. In order to correlate photophysical function with structure, we are working towards performing these measurements under laser excitation. The challenge in these measurements rests with extracting the weak photoresponse of these structures from current changes due to laser heating of the tip-sample junction. In order to mitigate these effects, we have developed a laser-STM with integrated high numerical aperture (NA) optics behind the sample (as indicated in Fig. 1E and 1F) to provide a small (~1 micron) and stable laser spot.

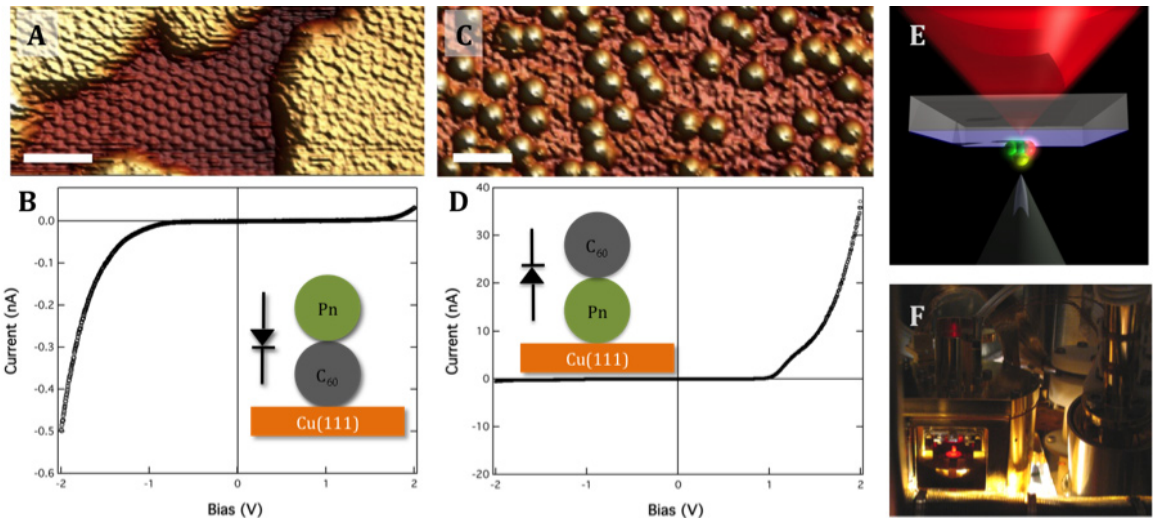

Fig. 1: Reversible sub-monolayer molecular p-n heterojunction. Scale bars in A and C are 5 nm. A) STM topography image of a sub-monolayer of pentacene standing upright on a close-packed monolayer of a C_{60} on Cu(111). B) I-V curve recorded on the pentacene; a schematic for the molecular diode is shown in the inset. C) STM topography image of a sub-monolayer of C_{60} on a pentacene monolayer on Cu(111). D) I-V curve recorded on a single C_{60}; a schematic for the molecular diode is shown in the inset. E) Schematic of our approach to laser-assisted STM, where the laser is focused to a small spot at the tip-sample junction. F) Photograph of the microscope.

Application of Scanning Probe Microscopy to Characterize Nanostructures in Bulk Heterojunction Organic Solar Cells

Thuc-Quyen Nguyen, Center for Polymers and Organic Solids and Department of Chemistry and Biochemistry, University of California, quyen@chem.ucsb.edu

Organic solar cells have obtained much attention in both academia and industry because they have the potential to produce low-cost plastic devices for alternative energy sources. In these devices, the performance depends strongly on the nanoscale film morphology and optoelectronic properties; therefore, it is important to control the nanoscale morphology and to probe these properties and correlate to the bulk measurements. In this talk, I will give a summary of our group effort on applying various forms of scanning probe microscopy (SPM) such as atomic force microscopy (AFM), conductive and photoconductive AFM (c-AFM and pc-AFM) to characterize organic solar cells. Important information can be obtained using SPM including film morphology, vertical and lateral phase separation, assigning phase domains to the donor and the acceptor components, nanoscale charge generation and transport, and external quantum efficiency (EQE = the collected charge carriers/the incident photons). For example, we combine dark and photoconductive atomic force microscopy (pc-AFM) to study nanoscale morphology and optoelectronic properties of bulk heterojunction solar cells. The effect of processing conditions including additives, solvents, and thermal annealing on nanoscale morphology, charge generation and the device performance is also investigated. Often, we find strong correlation between nanoscale and bulk measurements. Our results demonstrate that SPM is a powerful technique to characterize solar cell materials and can be used to understand the bulk performance.

AFM and Conductive AFM of Fuel Cell Materials

Steven K. Buratto, James R. O'Dea, David A. Bussian, and Horia Metiu, Department of Chemistry and Biochemistry University of California, Santa Barbara

A technique to map surface domains responsible for proton transport in PEM fuel cells has been developed. Specifically, this technique couples two operating modes of atomic force microscopy—dynamic and contact modes—to determine the distribution and relative electrochemical activity of proton transport domains.

In dynamic mode, a cantilever is driven to oscillate near its resonance frequency either just above or making intermittent contact with the surface of a proton exchange membrane. Operating in this mode yields both topography and phase images, where contrast in latter arises from different probe-sample interactions. In membranes whose proton transport is governed by aqueous domains, phase contrast is caused by different forces exerted on the probe by aqueous and non-aqueous domains. In perfluorosulfonic acid type polymer membranes, aqueous domains are associated with sulfonic acid groups and non-aqueous domains with fluorocarbon groups. Through dynamic mode imaging we obtain a map of the aqueous domains with spatial resolution approaching 1 nm and in the limit of a single aqueous channel.

Current derived from the reduction of oxygen is visualized in contact mode, in which the Pt coated AFM tip acts as a nanoscale cathode as it scans the surface of the membrane whose opposite side has been hot pressed with a gas diffusion electrode and is continuously exposed to hydrogen gas. These current images allow for direct visualization of the electrochemical activity at the surface of the membrane. We have been successful in imaging Nafion® membranes with spatial resolution of a single channel, and have measured the conductance of a single channel.

Furthermore, overlaying phase images taken in dynamic mode with current images taken in contact mode reveals that approximately half of the aqueous surface domains of a Nafion membrane are not electrochemically active (i.e. not all aqueous domains facilitate proton transport and contribute to fuel cell performance). Initial work has focused on Nafion membranes and commercially available electrode materials imaged under ambient conditions, while changes in electrode fabrication and membrane preparation have also been explored. Controlled variations in membrane water content and chemical structure may elucidate additional properties of the ion transport channels. We will report on the progress of these experiments.

Support for this work has been provided by the Army Research Office Multi-disciplinary University Research Initiative.

Understanding Energy Dissipation Between a Vibrating AFM Tip and a Solid-liquid Interface

Arvind Raman, Purdue University

The dynamic Atomic Force Microscope is a model system for studying friction and energy dissipation between an oscillating single asperity and a solid-liquid interface. In this talk we will review some fundamentals of AFM cantilever dynamics in liquids on both hard (inorganic) and soft biological samples. Issues such as energy propagation to higher harmonics, interpretation of phase contrast in liquids, role of solvation layers will be discussed.

Quantitative Analysis of Non-linear and Hysteretic I-V Curves in Conductive Atomic Force Microscopy

Peter Maksymovych[1], Minghu Pan[1], Pu Yu[2], Ramamoorthy Ramesh[2], Arthur P. Baddorf[1], Sergei V. Kalinin[1]*
1 Center for Nanophase Materials Science, Oak Ridge National Laboratory
2 Department of Materials Sciences and Engineering and Department of Physics, University of California Berkeley

Many future applications can rely on unique phenomena that arise in wide-bandgap oxides and organic semiconductors when electron transport is coupled to rich oxygen vacancy chemistry, one or several coexisting order parameters and ionic conductivity. Conductive Atomic Force Microscopy (cAFM) is emerging as a potent probe of such properties, due to its ability to differentate between intrinsic and defect-mediated behaviors. Yet, interpretation of cAFM data is almost always complicated by uncertainties in the tip-surface junction, material parameters and a limited range of accessible electric field and temperature. We will discuss three novel approaches to the analysis of non-linear and hysteretic I-V spectra obtained on the surfaces of epitaxial thin films of $Pb(Zr_{0.2}Ti_{0.8})O_3$ (PZT) and $BiFeO_3$ (BFO). Both materials are excellent ferroelectrics and both exhibit rectifying I-V curves and a pronounced polarization-mediated electroresistance [1].

In the first approach we utilized the bias- and temperature dependence of current normalized differential conductance as a descriptor of the transport mechanism. In contrast to traditional methods of shape analysis of I-V curves and temperature dependence, this method was found provide a conclusive differentiation between candidate transport mechanisms. The I-V curves were found to be determined by both interfacially (Fowler-Nordheim tunneling) and bulk-limited (Poole-Frenkel) transport mechanisms, depending on the bias-range and measurement temeperature [2].

The second approach involves spatially resolved analysis of the variations within individual I-V curves, uniquely enabled by sub-10 nm spatial resolution of cAFM in vacuum. When applied to PZT, this analysis revealed a crossover between two limiting transport mechanisms, manifested in the change of both the strength and spatial distribution of the disorder. Thus arises an intriguing opportunity to spatially resolve the electronic properties of the tip-surface junction as well as the bulk, and even bottom interface [2].

Finally, the third methodology relies on the use of a non-linear bias-waveform to acquire the I-V curve. When applied to I-V hystereses, found in resistive switching and memristors, the measurement can decouple the bias-dependence of the transport mechanism from the field-induced changes of the electronic state of the material. The three approaches complement each other. When applied to polarization-controlled transport in PZT and BFO [3], the conductive measurement yield unprecendented new insight not only into electron transport but also the dynamics of the order parameters.

Research conducted at Center for Nanophase Materials Sciences, sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. DOE.

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Scaling of Multimodal Mechanical to Electrical Conversion Systems

Shashank Priya, Center for Energy Harvesting Materials and Systems (CEHMS), Virginia Tech

Scaling of mechanical to electrical energy conversion devices has several challenges both at the level of materials and overall system architecture. In this presentation, we will provide an overview of various reported devices and prototypes covering broad spectrum of energy conversion mechanisms. The prime goal of this review being identification of the current stage of energy conversion devices and evaluation in terms of magnitude of output power and specific power density, detailing the spread of technology over varying dimensions. We will also conduct an comparative analysis of the various transduction mechanisms. Next, we present concepts that combine multiple modalities into unified broadband energy harvesting structures. Analytical modeling and FEM results will be presented to illustrate the concept of multimodal conversion. Experimental results based on bulk-structures will be used to validate the models which will then be used to make scaling predictions. Once the multimodal energy conversion structures have been designed, there remains challenge in printing heterogeneous materials on the same platform with nanometer precision in complex configurations. These challenges include embedding the ceramic with metal layers, rapid-annealing of the printed materials in real-time to achieve desired microstructure, and fabrication of large arrays with in-phase response. We provide our ideas on addressing these issues and show preliminary results.

Mapping Energy Dissipation by SPM: The Band Excitation Method

Stephen Jesse , Oak Ridge National Laboratory

Mapping energy transformation pathways and energy dissipation on the nanometer scale and understanding the role of local structure on dissipative behavior is a grand challenge for nanoscale imaging in areas ranging from electronics and information technologies to efficient energy production and use. To date, dissipation measurements are primarily based on either phase and amplitude detection in constant frequency mode, or as amplitude detection in frequency-tracking mode. Sampling of a single frequency in the Fourier domain of the system allows only two out of three parameters (amplitude, resonance, and Q) to be determined independently. The analysis in both cases implicitly assumes that amplitude is inversely proportional to the Q-factor and is not applicable when the driving force is position dependent, as is the case for virtually all SPM measurements.

Here, we developed and implemented a new approach for SPM detection based on the excitation and detection of a signal having a finite amplitude over a selected region in the Fourier domain. The detected signal is Fourier transformed and fitted by appropriate model. This data acquisition scheme substitutes standard lock-in or PLL detection. This band excitation (BE) SPM allows very rapid acquisition of the full frequency response at each point in an image and in particular enables the direct measurement of energy dissipation through the determination of the Q-factor of the cantilever-sample system. This band excitation method allows acquisition of the local spectral response at a ~10ms/pixel rate, compatible with fast imaging. We demonstrate this tech¬nique with electromechanical imaging, the investigation of dissipative defects in magnetic force microscopy, nanomechanical and thermomechanical properties, and in force-distance spectroscopy. The strategies for data analysis and visualization in BE based on functional fits and multivariate statistical methods are discussed. The BE method thus represents a new paradigm in SPM, beyond traditional single-frequency excitation and is applicable as an extension to many existing SPM techniques.

Research was supported by the U.S. Department of Energy Office of Basic Energy Sciences Division of Scientific User Instruments and was performed at Oak Ridge National Laboratory which is operated by UT-Battelle, LLC.

Atomic Force Microscopy Measures Single Electron Charges on Quantum Dots in Ambient Conditions

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Here we describe a method to measure electrical charges accumulated on cadmium selenide (CdSe) quantum dots with the help of Atomic Force Microscopy (AFM). The sensitivity of the method allows detecting charges up to the single electron value even in ambient conditions. Quantum dots capped with tri-n-octylphosphine oxide (TOPO) were charged by using photon excitation with green laser and the action of a conductive AFM probe. After the charging, the AFM was switched to the Lift mode with AC (resonance oscillating) scanning while using multiple lift heights [1]. This allows measuring the shift of the resonance frequency which is proportional to the gradient of force acting between the AFM probe and individual dots. This force occurs due to induction of the mirror charge in the conducting volume of the AFM probe. Simple electrostatic model is used here to find the value of the charge on the dot. Using the presented method, we are able to measure single electron charges on the quantum dots dispersed from toluene solution onto graphite film (graphene). Fig.1 shows the results of measurements for a number of quantum dots, the resonance frequency shift as a function of the probe-dot distance. Solid lines show theoretical dependences corresponding to one and two electron charges.

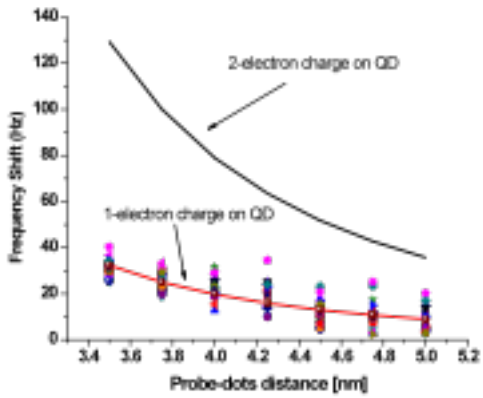

Figure 1. Measurements of the charges on quantum dots and comparison with theory.

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Chemical Imaging and Interaction Quantification for Catalytic Materials Using High-Resolution Atomic Force Microscopy

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Developing a fundamental understanding of catalytic reactions is of very high importance for a number of energy related issues. Such reactions are often triggered by the presence of surfaces, where chemical forces extending into the vacuum enable these reactions to happen by modifying the involved energy barriers. Therefore, it would be useful to map and quantify the interactions between a catalytically active surface and a probe with atomic resolution in order to study the role and effectiveness of various surface defects such as vacancies, impurities, steps, kinks, and domain boundaries as active sites. An ability to discriminate between different chemical species on the sample surface would offer further insight.

In this talk, we will show with the example of an oxygen-reconstructed copper (100) surface that much of this information can be derived from combining the new method of three-dimensional atomic force microscopy (3D-AFM) [1,2], a variant of noncontact atomic force microscopy, with scanning tunneling microscopy. The surface oxide layer of Cu(100) features domain boundaries and a distinct structure of the Cu and O sublattices that is ideally suited for such model investigations. While different tips show different chemical contrasts, 3D data sets enable the site-specific quantification of force interactions and tunneling currents. Most interestingly, the high resolution achieved allows the direct characterization of subtle modifications in local interaction strength caused by the presence of surface defects.

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[2] M. Z. Baykara et al., Advanced Materials, DOI: 10.1002/adma.200903909 (published online 4-9-10)

Microwave Imaging of Energy Materials

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Development and optimization of new materials for energy applications, including solar cells and Solid Oxide Fuel Cells (SOFC), demand characterization tools capable to track processes occurring in this materials at various stages of their life with a nanometer-scale detail. In particular, alterations of the electrical conductivity, which are sensitive both to microstructure and composition of materials, require simple and non-invasive techniques for local probing and characterization of the electrical properties at the nanoscale. Recently developed AFM-platform-based Scanning Near-field Microwave Microscopy is an ideal tool for addressing this demand. The principle of the technique is based on the dependence of the microwave impedance of the probe on the electrical properties of the material in the direct probe vicinity. It the system, a solid wire cantilever tip is connected to a coaxial cable (transmission line) through a matching network and then to a vector network analyzer. Amplitude and phase of the microwave signal reflected from the tip are measured while scanning over the sample surface in contact AFM mode. The system is realized on an Asylum Research MFP-3D AFM platform. The imaging can be performed in a frequency range from 1 GHz to 12 GHz. The advantage of microwave imaging over conducting AFM (c-AFM) is that it does not require fabrication of electrodes over the sample because the electrical circuit is complete through displacement currents between the AFM tip, sample, and outer conductor of the microwave line. The microwave signal carries information about conductivity of the materials directly under the tip apex. The very same tip is used for simultaneous contact AFM topography imaging. We demonstrate mapping of material conductivity with a resolution of about 20 nm, which is limited by the probe tip radius, using as model systems homogeneous bulk ceramic materials, graphene as well as heterophase domain structures appearing during metal-insulator transition in VO2 microcrystals (nanoplatelets). Research at ORNL's CNMS was sponsored by the Division of Scientific User Facilities, BES, U.S. DOE

Organic Electronic Device Characterization: The Key Role of Scanning Probe Microscopies

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Well-defined conjugated materials play an important role in organic electronics because of their precise chemical structure and architecture. This give rise to well-defined functional properties and facilitate control over their supramolecular organization. The solid-state properties of organic electronic materials are determined not only by those of individual molecules but also by those of ensembles of molecules. This ability to control the building of nanoscopic and mesoscopic architectures represents a starting point for the construction of (supra)molecular organic electronic devices with nanometer-sized semiconducting objects.

The role of self-assembling processes in these systems is demonstrated here for thiophene-, phenylene-, phenylenevinylene-, and fluorene-based conjugated oligomer (and polymer) linear and branched systems. It appears that the presence of bulky side chains, or chiral centers, or hydrogen bonding groups is drastically affecting the final morphology.

During these processes, the interplay between the conjugated molecules, the solvent, the substrate surface, is the main key-parameter governing the formation of these supramolecular assemblies. Depending on these interactions, one-dimensional (nanowires) or two-dimensional (platelets) objects can be generated. Atomic Force Microscopy (AFM) is used to investigate the morphologies of self assembled conjugated systems starting from molecularly dissolved solutions or from aggregates already formed in solution. Moreover, molecular modelling calculations are essential in this field of research for a better understanding on how the molecules are organized within these nano-structures and therefore rationalize the experimental data.

By using AFM-derived techniques (such as Conducting AFM, Kelvin Probe Force Microscopy - KPFM), electrical properties can be measured at the local scale (together with the morphological characterization of the samples) helping the optimization of the device performances. For instance, for photovoltaic organic devices, we spatially resolve by KPFM under ultrahigh vacuum (UHV) the surface photo-voltage in high efficiency nanoscale phase segregated photovoltaic blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PC61BM). The spatial resolution achieved, represents a tenfold improvement over previous KPFM reports on organic solar cells. By combining the damping contrast to the topographic data in non contact AFM under UHV, surface morphologies of the interpenetrated networks are clearly revealed. We show how the lateral resolution in KPFM can be significantly enhanced, allowing a direct visualization of the carrier generation at the donor-acceptor interfaces and their transport through the percolation pathways in the nanometer range. Some other practical examples such as field effect transistors and white-light emitting diodes will be also discussed.

Electrothermal Microcantilever with Integrated Heater for Scanning Probe Microscopy

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This paper reports the development of an atomic force microscope (AFM) cantilever whose tip temperature and tip electric potential can be simultaneously and independently controlled. The electrothermal (ET) cantilever can self-heat to over 400°C while the tip voltage can be measured or controlled independent of tip temperature, up to ± 10 volts.

Figure 1 shows micrographs of a fabricated cantilever and cantilever tip. The microcantilever is made of doped single-crystal silicon and has three legs serving as electrical paths to the cantilever free end. The free end has a resistive N-type heater, N+-type tip, and region of P+-doped silicon that electrically isolates these two functional regions by forming an NPN junction. While the heater and electrode are electrically isolated, heat conduction between the two regions facilitates tip temperature control. Breakdown voltages across the NPN isolation region are ± 10 volts, indicated by a sudden increase in diode leakage current. Laser Raman spectroscopy [1] was used to calibrate tip temperature. The heater temperature can be controlled over the range 25 - 400°C.

Figure 2 shows preliminary results where an ET cantilever was operated in Kelvin probe mode [2] to measure the spatial work function on a conductive substrate at various tip temperatures. It has been suggested that a thermal gradient from tip to substrate increases contact potential difference [3]. Indeed, work function contrast and resolution were improved with increasing scanning tip temperature.

The ET cantilever combines the functions of heated and electrically conductive AFM cantilevers. Such a device facilitates combined nanoscale electronic and thermal measurements. Such measurements are essential for understanding the nanometer-scale properties of energy conversion materials, ferroelectrics, and batteries.

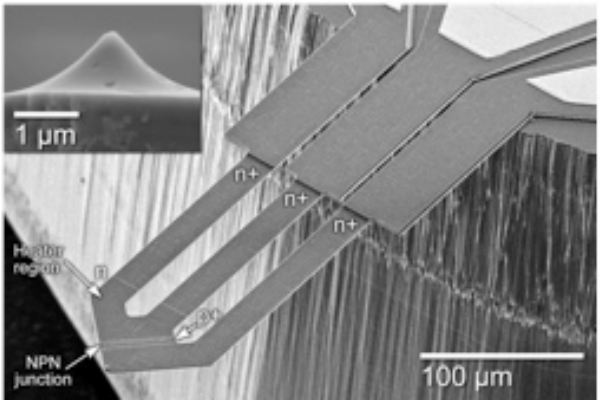

Fig 1.

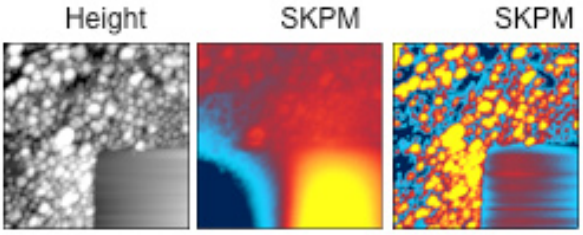

Fig. 2

Figure 1. Single-crystal doped silicon microcantilever with integrated solid state heater and electrode using NPN doping to form back-to-back diodes. Figure 2. Temperature dependent scanning Kelvin probe microscopy using electrothermal cantilever. An ET cantilever measured topography of a conductive substrate (left) and the contact potential with the tip at room temperature (center) and at 157°C (right).

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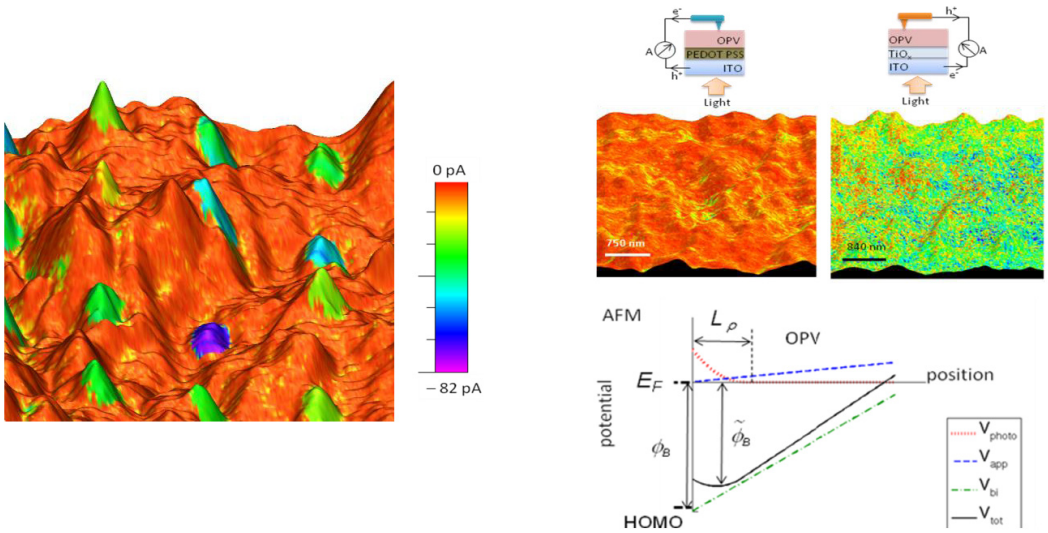
Imaging of Nanoscale Photogenerated Charge Transport in Organic Photovoltaic Materials

Behrang Hamadani, Hua Xu, Paul Haney and Nikolai Zhitenev, Center for Nanoscale Science and Technology, National Institute of Standards and Technology, Gaithersburg, MD

The efficiency of photovoltaic devices based on inorganic thin-films or organic polymer blends is often determined by the nanoscale structure and properties of internal and contact interfaces. Measurements of local photoconductivity, along with other scanning probe based measurements, can link the structural properties to the performance providing the desired feedback for the device optimization. However, the nature of the tip-to-sample contact can be quite different from contact interfaces in devices strongly affecting the injection and collection of charge carriers and complicating the data analysis. Here, we present the characterization of photoconductive channels in a model bulk heterojunction organic solar cell based on a p-type polymer and n-type small molecule, either directly with a conductive AFM tip or from patterned nanocontacts on the surface of the active layer [1]. Photo generated charge transport in bulk heterojunction solar cells is strongly dependent on the film nanomorphology resulting from phase segregation and connectivity of the donor and acceptor regions. We directly compare the properties of the tip-to-sample interface to the nanocontact interface, and further explore the nanoscale photocurrent response on two complementary device architectures using conductive tips suitable for the appropriate charge (i.e., electrons vs. holes) collection. We then consider the role of the film/tip contact on the local current voltage characteristics of these structures and present a physical model based on principles of drift and diffusion and further incorporating interfacial states at the tip contact that qualitatively describes the data [2]. In addition to the measurements at the top surface, we examine the response from the bulk of the film using novel sectioning technique. Our results provide significant insight into the origin of nanoscale variations in photoresponse and nanoscale morphology of such materials.



(Left) 3-D topography and the local Photocurrent response of Ag nanodots patterned on the surface of an organic active layer and probed by a CAFM tip under light, showing significant local variations related to material morphology.

(Top right) By choosing the appropriate tip, we can selectively collected photogenerated electrons (left) or holes (right) during the tip scan on the surface of the organic film.

(Bottom right) Band diagram schematics of our model of drift and diffusion, incorporating interface states at the tip contact to explain the local current voltage data.

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The Role of Defects for Ferroelectric-Thermoelectric Marriage

Soonil Lee and Clive A. Randall, Center for Dielectric Studies, Materials Research Institute, The Pennsylvania State University

Thermoelectric materials can be used to convert thermal energy to electrical energy by exposing one side of the thermoelectric material to high temperature and can, therefore, potentially be a means to harvest heat energy, the biggest source. Up to date, the dominant thermoelectric materials are semiconductor alloys. Through controlling the density of state, charge carrier concentration, and carrier mobility, the thermoelectric properties such as thermopower, electrical conductivity, and thermal conductivity have been developed. In this paper, considering many benefits of oxide thermoelectrics, such as low cost, nontoxic raw materials, high temperature stability, sustainability, etc., we have attempted to control the charge carrier properties in ferroelectric perovskite and tungsten-bronze oxides by inducing defects in their complex structures. Thermopower anomalies are observed in and around the paraelectric-ferroelectric and ferroelectric-ferroelectric phase transition temperatures and the nature of these trends was found to depend on the degree of reduction, indicating a coupling between the thermoelectric effect and the ferroelectric phase transition. The coupling in single crystals also depends on the crystal anisotropy. The nature of the reduction from the low oxygen partial pressure anneals is heterogeneous; clusters of defects ~3 nm wide meander through the crystallites. This may give rise to a decoupling between thermopower and electrical conductivity. Some of the reduced ferroelectrics showed attractive figure of merit with high power factor. The complex nature of the thermochemical reduction and its associated nanostructure near the Metal-Insulator transition will challenge simple physical models for oxide thermoelectrics.

Probing Local Thermal Phase Transitions on the Nanoscale

Jiangyu Li, University of Washington

Single crystalline strontium barium niobate (SBN) exhibits large piezoelectric, electrooptic, nonlinear optic and pyroelectric coefficients, and is promising for applications in second-harmonic generation, optical parametric oscillation, microelectromechanical system, and thermal energy harvesting. Micro- and nanoscale domain engineering of SBN single crystal is particularly exciting, because the operation of such ferroelectric and optic devices relies on the patterned domain configurations. In this work, we engineer the domain configuration of SBN crystal using AFM based nanolithography, by patterned poling of the SBN crystal through a large voltage applied via the AFM tip. Piezoresponse force microscopy is then applied to image the engineered domain configurations, and measure the resulted hysteresis loop and butterfly loop. The response of SBN at different temperatures below and above its Curie temperature is investigated, revealing the stability of domains at elevated temperature and the nucleation of ferroelectric phase below the Curie temperature. Other ferroelectric materials, such as P(VDF-TrFE) copolymers, have also been studied using this approach, and related systems, such as thermoelectric oxides, have also been investigated.

Multifrequency AFM

Anil Gannepalli, Asylum Research

Compositional mapping of materials at the nanoscale using an AFM is an extremely important technique for characterizing nanostructured composites being researched for a variety of energy applications. Multiple frequency AFM techniques probe the tip-sample interactions at multiple frequencies, thereby increasing the amount of information many fold without any penalty in terms of time requirements. In this talk, we will review some of the latest developments and results using multifrequency AFM techniques. These will include bimodal techniques [1] where multiple resonances are excited and the cantilever is operated in a primarily intermittent-contact mode, showing compositional contrast [2-3], separation of long and short-ranged forces [4-5] and very high resolution. In another instance using two frequencies about a single resonance can be used to track the tip-sample contact resonance [6]. In this technique, called Dual AC Resonance Tracking (DART), the information at two frequencies allows the determination of the conservative and dissipative nature of the tip-sample contact. This technique has been applied to piezoresponse force microscopy (PFM), Atomic Force Acoustic Microscopy (AFAM) and Ultrasonic Force Microscopy (UFM) contact resonance measurements and to high resolution localized melting transition measurements using heated cantilevers down to the single molecule level.

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In Situ SPM of Local Interfacial Phenomena in Li-ion Batteries

Robert Kostecki, Lawrence Berkeley National Laboratory

Li-ion batteries are complex multicomponent electrochemical systems that incorporate widely dissimilar phases in physical and electrical contact. Electron and ionic transfer across solid-solid, solid-liquid interfaces and within each of constituent phases determine the behavior of the composite electrodes and the electrochemical performance of the entire battery system. The gradual degradation of lithium-ion batteries often limits the performance of portable electronic devices and presents a significant barrier for vehicular applications. The continuous charge-discharge and/or prolonged storage of Li-ion batteries invariably leads to performance degradation caused by irreversible changes in the structure, morphology, topology, and composition of the materials, the nature and mechanism of which has not yet been fully identified. The impedance growth that is observed at both electrodes is associated with slow side-reactions at electrode surfaces that consume solvents and salt and form an ion-blocking surface film as well as an electronically insulating barrier within the electrode. The resistances to both ion and electron transfer constitute the overall charge transfer impedance and contribute to the overall electrode impedance. In contrast to the anode, the cathode SEI layer is so thin that its presence has not been confirmed until recently. Adequate surface sensitive techniques must be used to detect, monitor and analyze surface layers on composite electrodes [1,2,3,4].

Interfacial phenomena and structural changes in composite electrodes in Li-ion battery systems occur and often manifest themselves at nano- or micro-scales. These effects can be detected and characterized only by techniques of suitable sensitivity, selectivity and resolution. The development and application of *in situ* non-destructive photon- and particle based spectroscopic, microscopic, and scattering techniques capable of the highest sensitivity, structural and elemental specificity, and temporal resolution is crucial to gaining a fundamental understanding of the mechanism of chemical and electrochemical processes, which are responsible for the Li-ion battery electrochemical performance [5].

Ex situ Raman mapping of cathodes and anodes from tested high-power Li-ion cells, showed that the state of charge (SOC) of active material particles on the cathode surface was highly non-uniform despite deep discharge of the Li-ion cells at the end of the test. *In situ* Raman microprobe monitoring of the SOC of individual oxide particles in the composite cathode revealed that the charge/discharge rate varied with time and location [4]. SPM images of aged composite electrodes revealed surface deposits and significant morphology changes. Surface analysis revealed that surface decomposition products originate from $LiPF_6$ decomposition and oxygen, water, and C-O-H, -C=O surface functional groups adsorbed at carbon additives catalyze and/or react with the electrolyte. These surface reaction products create electronic barriers within the composite electrode, which lead to inconsistent kinetic behavior of individual oxide particles and contribute to the overall impedance of the electrodes.

This work presents an overview of the selected published work that illustrate an effective use of advanced *in situ* and *ex situ* SPM characterization techniques to sense and monitor physico-chemical properties of the electrode/electrolyte interface and within the active material phase, and provide unique insight into the mechanism of chemical and electrochemical processes, which contribute to the complex Li-ion system chemistry. Recent results of *in situ* spectroscopic and microscopic investigations of intermetallic anodes will be discussed.

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Poster Abstracts

1. Probing Complex Oxide Interfaces

TeYu Chien, Nathan P. Guisinger, John W. Freeland, Argonne National Laboratory

Recently, interfaces between novel oxide materials have become a playground for manipulation of new functionalities. At interfaces, the broken symmetry and modified local interactions have been shown to generate wholly new electronic phases (e.g. magnetism, metallicity, superconductivity etc.) distinct from the composite bulk materials. However, to date our understanding of these interface driven phases is still limited. While there exist powerful spatially resolved tools for visualizing the chemical and magnetic structure of an interface, a direct observation of electronic behavior across the interface presents a major experimental challenge.

After the success of creating flat fractured surfaces on Nb-doped $SrTiO_3$ (Nb:STO) accessible to scanning tunneling microscopy (STM)[1-3], we further harness the high-sensitivity to electronic local density of states (LDOS) of the scanning tunneling spectroscopy (STS) in cross-sectional geometry to visualize complex oxide interface electronic properties. By extending XSTM to the interface between colossal magnetoresistant manganite $La_{2/3}Ca_{1/3}MnO_3$ (LCMO) and semiconducting Nb-doped $SrTiO_3$, we were able to map the LDOS across the boundary, unambiguously visualize the interface by the location of the valence band, and elucidate the fundamental issue of band alignment at a complex oxide heterointerface[4].

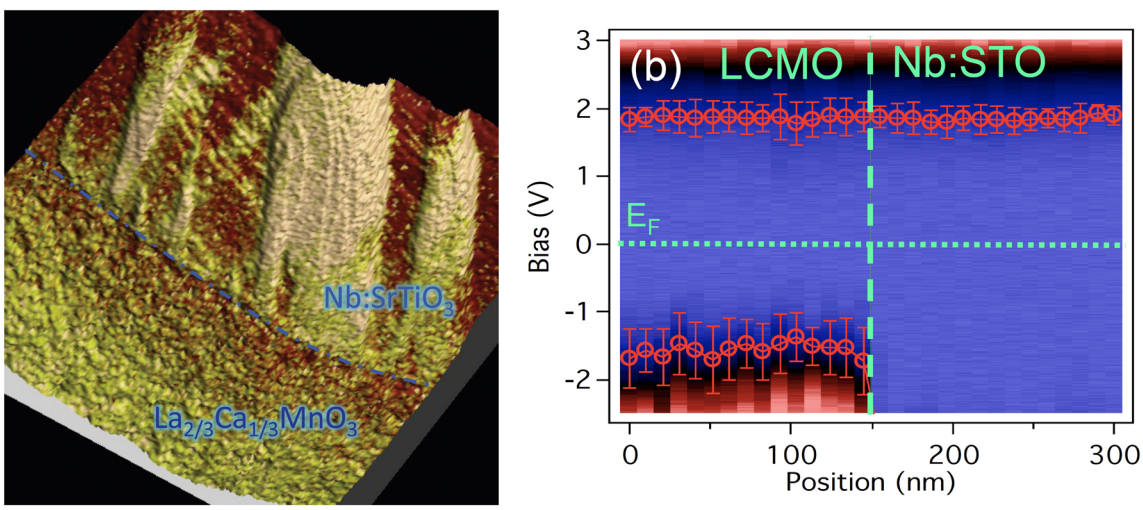

Figure 1: The left figure shows the morphology near LCMO/Nb:STO interface overlaid with LDOS at +3V (white color represents high contrast against brown color). The right figure shows the measured spectrum as function of the distance to the interface. The conduction band alignment is observed across the interface.

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2. Thermoelectric Properties Characterization of a Single Electrospun $NaCo_2O_4$ Nanofiber Using Scanning Probe Microscopy

Feiyue Ma, Jiangyu Li, Department of Mechanical Engineering, University of Washington

Nanostructured thermoelectric materials are promising for high efficiency thermoelectric conversion. While thermoelectric properties characterization of these nanostructured materials is very challenging, especially for one dimensional thermoelectric material such as nanofibers and nanorods. In this work, $NaCo_2O_4$ thermoelectric nanofibers with a diameter around 200 nm and gain size as small as 10 nm are fabricated by sol-gel based electro-

spinning technique. The thermoelectric properties of a single electrospun $NaCo_2O_4$ nanofiber are characterized by a series of scanning probe microscopy (SPM) studies. Conductive atomic force microscopy (cAFM) is carried out to measure the electric conduction in the nanofiber, and the thermoelectric effect is characterized using a novel thermal probing technique that induces large temperature gradient in the nanofiber. This characterization technique is universal and can be tested on other one dimensional thermoelectric materials.

3. BNT-BT Ceramic Preparation, Structure and Properties

Sungwook Mhin, Isaac Krull, Humberto Foronda, Jennifer S. Forrester and Jacob L. Jones, Department of Materials Science and Engineering, University of Florida

Lead-free piezoelectric materials have been under intense research as potential substitutes for conventional lead zirconate titanate (PZT)-based solid solution, $Pb(Zr_xTi_{1-x}O_3)$. Among possible lead-free alternatives, $Bi_{0.5}Na_{0.5}TiO_3$ or bismuth sodium titanate (BNT)-based solid solution is praised as one of the excellent candidates which shows a high Curie temperature (T_c= 320˚C), remnant polarization (P_r= 38μC/cm^2) and coercive field (E_c=73kV/cm). Of particular focus is the solid solution of rhombohedral phase BNT with tetragonal perovskite phase $BaTiO_3$ (BNT-BT) which exhibits a rhombohedral – tetragonal morphotropic phase boundary (MPB) at approximately 7% $BaTiO_3$. BNT-BT in the region of the MPB can be used for many applications because it exhibits low permittivity (see poster for equation), high electromechanical coupling factor (k_t or k_{33}) and high mechanical strength (σ), as well as an effective piezoelectric activity by poling. In this study, solid state ceramic processing of BNT and modified BNT, $(Bi_{0.5}Na_{0.5})_{0.93}Ba_{0.7}TiO_3$ (BNT-7BT) was synthesizes and the structure between BNT and BNT-7BT were analyzed using the Rietveld refinement method. Also, the ferroelectric and piezoelectric properties of BNT and BNT-7BT such as permittivity, piezoelectric constant (d), polarization hysteresis loop and strain hysteresis loop were measured.

4. Study of Ferroelectric Domain Structures of $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ Near the Morphotropic Phase Boundary

Jianjun Yao, Wenwei Ge, Yaodong Yang, Li Yan, Jiefang Li, and D.Viehland, Department of Materials Science and Engineering, Virginia Tech; Qinhui Zhang, Haosu Luo. Shanghai Institute of Ceramics, Chinese Academy of Science

Piezoelectric constants of d_{33}≈500pC/N have been reported in the $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ (NBB near the morphotropic phase boundary (MPB). Here, the domain structures of NBBT and 1 at.% Mn-doped $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ (Mn-NBBT) near the MPB were carefully investigated by polarized light (PLM) and piezo-response (PFM) microscopies both at room temperature and on heating. Stripe-like domains oriented along {110} were both for both two crystals in the zero-field state. Poling resulted in the formation of tetragonal macro-domain platelets, where the orientation of the stripe-like domains was changed from {110} to {100}. For Mn-NBBT, the size of the stripe-like domains was much finer and remained aligned along {110}. The evolution of the macro-domain platelets and ferroelectric stripe-like domains was studied on heating to 250˚C was studied using PFM.

5. Local Two-way Magnetoelectric Couplings in Multiferroic Composites via Scanning Probe Microscopy

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Local two-way magnetoelectric (ME) couplings of a multiferroic composite have been characterized at nanoscale using novel scanning probe microscopy techniques we developed. A bilayer multiferroic composite consisting of lead zirconate titanate (PZT) and TbDyFe (TDF) has been fabricated, and the evolution of ferroelectric domains in PZT induced by an external magnetic field is observed by piezoresponse force microscopy (PFM), while the evolution of magnetic domains in TDF induced by an external electric field is observed by magnetic force microscopy (MFM),

confirming the two-way ME couplings in the multiferroic composite. The technique will be useful in characterizing nanoscale ME couplings in a wide range of multiferroic composites.

6. Interaction Between Gold and Barium Titanate

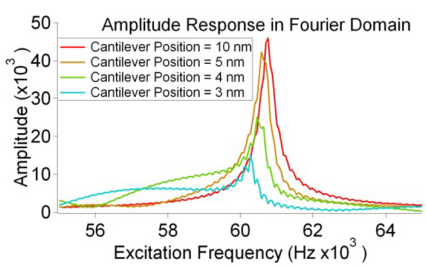
Yaodong Yang, Jianjun Yao, Jiefang Li and Dwight Viehland, Department of Materials Science and Engineering, Virginia Tech

In our study, we find that perovskite $BaTiO_3$ (BTO) has unusual orientation distributions when deposited on (100) and (110) oriented $SrTiO_3$ or STO single crystal substrates that have predeposited patterned Au regions by pulsed laser deposition. BTO areas deposited on gold islands were found to have a (111) orientation, whereas those deposited directly on STO had the same orientation as the substrate. The piezoelectric properties of different orientations are quite different. Based on this result, we can pattern a single BTO film that has different orientations and subsequently control the property distribution. We also found on a (111) oriented STO single crystal substrate that predeposited Au seed layers can affect the BTO grain size. Our results provide new understanding into the relationship between metal (Au) and ceramic (BTO) which could help in new device development.

7. Numerical Analysis of the Band Excitation AFM Method

Adam Kareem, Stephen Jesse, Sergei Kalinin and Santiago Solares

The objective of this work is to provide a numerical simulation framework for the Band Excitation method developed by Jesse and coworkers [1], whereby the AFM microcantilever is excited with a signal that contains a continuum band of frequencies, in contrast to the common discrete frequency approaches. This method allows the user to simultaneously observe the system's response to an entire range of frequencies without having to perform a frequency sweep, which in turn provides rapid insight into the elastic and dissipative properties of the tip-sample interaction. In our simulations the dynamics of the microcantilever beam are modeled using the first three eigenmode solutions of the Bernoulli-Euler beam equation of motion with all eigenmodes being coupled through the tip-sample interaction force. As is customary, the tip-sample force is modeled using the Hamaker equation for the long-range van der Waals attractive force and the Derjaguin-Muller-Toporov (DMT) equation for the short-range contact force. The cantilever tip trajectories and simulated photodetector readings (which differ from the actual trajectories due to differences in the tip slope among the various eigenmodes) are analyzed in real space and also Fourier transformed to obtain the transfer function, as in the experimental method. With this setup we have so far performed single-point simulations, either approaching the surface using a constant band excitation amplitude or keeping the cantilever at a fixed height while increasing the band excitation amplitude. Typical results are shown in Figure 1 for the constant excitation case, and in Figure 2 for the constant height case.



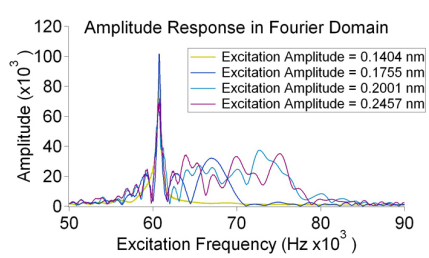


Figure 1 (left): Typical transfer functions obtained for constant band excitation surface approach for a 10-nm-radius silicon tip tapping on a Si(100) surface. Figure 2 (right): Typical transfer functions obtained for constant-height/variable band excitation simulations for a 10-nm-radius silicon tip tapping on a Si(100) surface.

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8. Measuring Oxygen Reduction Reaction in Fuel Cells

A. Kumar, S. V. Kalinin, S. Jesse, Oak Ridge National Laboratory

Electrochemical energy conversion systems based on gas-solid interactions such as solid oxide fuel cells (SOFC) and Li-air batteries are one of integral components of current and future energy technologies. The energy conversion in these systems is underpinned by a series of complex mechanisms like ion and vacancy diffusion, electronic transport and solid-gas and solid-liquid reactions at surfaces and triple phase junctions. One of the critical steps in the SOFC and Li-air battery operation leading to large overpotentials and charge-discharge hysteresis was the kinetics of the oxygen oxidation reaction (ORR). While it is well-recognized that ORR efficiency can be greatly enhanced by catalytic particles or morphologies, the mechanisms beyond this enhancement remain elusive, largely due to the lack of experimental techniques capable of probing ORR on the nanoscale.

Here, we explore an alternative approach for probing of ion diffusivity and electrochemical reactivity on the nanometer length scales on the free electrochemically active surfaces and packaged devices, providing insight into the energy conversion and storage device operation on a level of single structural element with ~10 nm resolution.

The Scanning Probe Microscopy (SPM) tip concentrates an electric field in a nanoscale volume of material, resulting in gas-solid or liquid-solid reactions, oxygen vacancy or proton injection, and ionic and vacancy diffusion. The vacancy movement and ion mobility results in localized strain under the tip which in turn can be probed by strain-bias coupling. We demonstrate local strain generation on the nanometer scale and correlate it directly to local oxygen ion diffusivity as well as the localized oxygen reduction for a LSC/GDC/YSZ system. These results are then compared to those obtained using classical characterization methods like electrochemical impedance spectroscopy which have already revealed markedly increased ORR activity up to two orders of magnitude on the epitaxial LSC surface in comparison to bulk, which may be attributed to increased oxygen vacancy concentrations in the films. The electrical field-dependence of ionic mobility is explored to determine the critical bias required for the onset of electrochemical transformation, potentially allowing to deconvolute reaction and diffusion processes in the fuel cell system on a local scale.

This material is based upon work supported by research division of Materials Science and Engineering, Office of basic energy sciences, DOE.

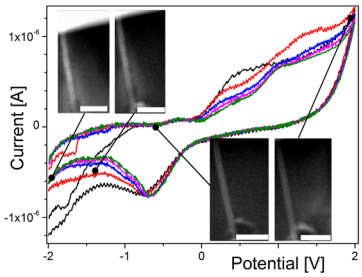
9. A Device for *In-situ* SEM Observation of Solid - Electrolyte Interface during Electrochemical Reactions at the Surface of Individual Metal Oxide Nanowire

Joshua Cothren and Andrei Kolmakov, Physics Department, Southern Illinois University Carbondale

Nanoscale materials are considered as a highly prospective platform for the next generation of energy storage devices. Specifically, metal oxide nanostructures in the form of belts, wires and tubes are nearly ideal media for battery electrodes due to their well defined morphology, single crystallinity (and therefore well defined properties) and high surface to bulk ratio. The complete understanding of processes like physical and chemical sorption, intercalation and electrochemical reactions requires a combination of microscopic and spectroscopic techniques which may be applied to the individual model nanostructures. Therefore currently, there is a strong demand for in situ spectro- microscopy studies of the processes taking place at the solid-electrolyte interface of these new materials under the realistic reaction conditions. In this article we report on the design and fist tests of multi-electrode micro-electrochemical cell compatible with common scanning electron microscopes. The main features of the cell include:

(i) a modified commercially available electronic package capable of holding 70 μL of electrolyte
(ii) a single nanowire as a working electrode placed over the electron transparent 50 nm thick silicon nitride window
(iii) working and reference electrodes fabricated on the SiN chip and/or ceramic package.
(iv) optically transparent back window for the optical microscopy/spectroscopy studies.

The tests included the verification of vacuum integrity of the cell, the mechanical and chemical robustness of the SiN membrane and preliminary cyclic voltammometry measurements in 10-3 M $AgNO_3$ as a model electrolyte solution. The first results and capabilities will be presented.



Exemplary voltammograms of SnO2 nanowire as a working electrode in 10-3 M AgNO3 electrolyte in combination with corresponding SEM images taken in situ.

10. Modeling and Characterization of $LiCoO_2$ Through Scanning Probe Microscopy Method

Ding-Wen Chung and R. Edwin García Purdue University, *redwing@purdue.edu*

The macroscopic characteristics of energy storage materials has been well studied in the past decade. However, the electrode behavior at the micron and nano levels are not well understood. Scanning Probe Microscopy (SPM) which allows sub-nm strain detection opens a field of research on single structural element characterization in energy storage materials research. This technique imposes a periodic voltage bias and drives ion redistribution into the probed electrode. The strong coupling between ion intercalation and change in molar volume allows localized characterization of the electrode at sub-nm scale. In this paper, we propose a numerical technique, based on the Finite Element method, to study the SPM actuation process on a $LiCoO_2$ electrode.

To investigate the effects of thickness and microstructure two sets of calculations were performed. One, where the effect of frequencies (frequency spectrum) for fixed thickness and crystallographic orientation, and a second one to access the effects of crystallographic grain orientation on the electromechanical hysteresis response. Measurable quantities and contributions from grains, grain boundaries, are assessed, and implications on battery life and performance are discussed. This material is based upon work support by Oak Ridge National Laboratory (ORNL). D. Chung acknowledges S. V. Kalilin and N. Balke for the financial and intellectual support.

11. Self-organized Synthesis and Characterization of Multi-functional Nanocomposite Materials with Plasmonic and Ferromagnetic Properties

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Magneto-plasmonic nanomaterials exhibit characteristics of ferromagnetism, and localized surface plasmon resonance (LSPR), with potential for resonant magneto-optical responses. Due to this capability to simultaneously control the polarization state and current of photons and electrons, these multi-functional materials could impact many applications, including high density magneto-optical recording, energy harvesting , biological sensing, and information processing. Here we present the synthesis and characterization of nanocomposites of Ag and Co by pulsed laserinduced self-organization. Bilayer films of Ag and Co in various combinations of thickness were deposited on SiO_2 substrate. Pulsed laser irradiation in self-organization resulted films into nanoparticle composites with well defined size, spacing and compositions. The composition dependent plasmonic and ferromagnetic behavior was investigated.

Substantial shifts in the LSPR location as well as magnetic saturation and coercivity with composition and size were observed by optical spectroscopy and surface magneto-optic Kerr effect measurements. Magnetic force microscopy revealed single domain magnetic behavior for the nanoparticles, with magnetic anisotropy dependent on composition and particle size. These investigations reveal that laser self-organization can be used to synthesize controllable plasmonic-ferromagnetic nanocomposites.

This was work supported by NSF grants CAREER DMI-0449258, CMMI-0855949, and DMR-0805258.

12. Surface Self-assembly of Pyridyl-substituted Porphyrins on Au(111) Investigated Using *In Situ* Scanning Probe Microscopy and Nanolithography

Zorabel Mallorca LeJeune, Matt McKenzie, Stephanie Robert, M. Graca H Vicente, Bin Chen and Jayne C. Garno, Department of Chemistry, Louisiana State University*

Molecular-level investigations of the surface assembly of pyridyl porphyrins formed on Au(111) were investigated using scanning probe microscopy (SPM) and scanning probe lithography. Mechanistic details of the surface assembly of porphyrins over time were revealed with high resolution SPM images acquired in liquids. The unconstrained assembly of pyridyl-functionalized porphyrins from solution produced two distinct configurations on the surface, a mixture of upright and co-planar islands. However, for nanografted patterns produced within an *n*-alkanethiol matrix on Au(111) formed under spatially constrained conditions, an upright configuration was observed exclusively for pyridyl-porphyrins. For nanografting, small confined areas of freshly exposed gold are produced while scanning the probe under an elevated force. The conditions of spatial confinement when nanografting are known to generate a different pathway for molecular assembly. The process of nanografting alters the assembly of pyridyl porphyrins to directly adapt an upright configuration, attached to the surface by nitrogen-gold chemisorption. During nanografting, there is not sufficient space on the local areas of the surface for a lying-down phase to form. Unlike the well-studied assembly mechanism of n-alkanethiols, the surface assembly for porphyrins is more complex, and is influenced by intermolecular interactions such as pi-pi stacking between macrocycles and binding interactions between the peripheral groups. Patterns created using nanoshaving and nanografting were used as molecular rulers for local height measurements of films of pyridyl porphyrins. Car-Parrinello Molecular Dynamics (CPMD) simulations were used to obtain energy minimized structural models that correlate with experimental results. Understanding the self-organization and interfacial assembly of porphyrins will contribute to rational designs of porphyrins for electronic and photonic devices.

13. Horizontally Aligned Single Wall Carbon Nanotubes (HA-SWNTs): Observation of Short Disordered Nanotubes Near the Catalyst Edge

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Realizing the full potential of SWNTs in electronics, optoelectronics, and sensing requires control of the alignment and position at the nanoscale. Directed growth to produce horizontally aligned carbon nanotubes has recently been demonstrated by numerous groups. We have investigated the growth of SWNTs with Fe as the catalyst, ethanol as the carbon source, and with varying concentrations of H2O. With the introduction of water we observed a decreased density of disordered and smaller diameter nanotubes next to the catalyst edge. This lead to a higher fraction of the tubes aligning at 10 and 100 um from the catalyst edge.

14. The Impact of Surface Modification on Oxygen Reduction Kinetics: Study of Patterned Electrodes by Scanning Kelvin Probe Microscopy

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Cathode polarization due to oxygen reduction contributes the largest to the energy loss in a solid oxide fuel cell (SOFC). Surface modification has been used to enhance the performance of SOFC cathodes [1, 2]; however, the mechanism of performance enhancement is yet to be determined. In this study, we fabricated test cells with patterned electrodes of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3\pm d}$ (LSCF), and subsequently modified the surface of LSCF by

a variety of catalysts to enhance the surface catalytic properties. In particular, it found that a thin coating of GDC significantly decreased the polarization resistance, as shown in Figure 1. Analysis of the data suggests that the entire surface of the patterned electrodes is active. Thus, the improvement in electrode performance can be attributed to the enhancement of oxygen reduction kinetics.

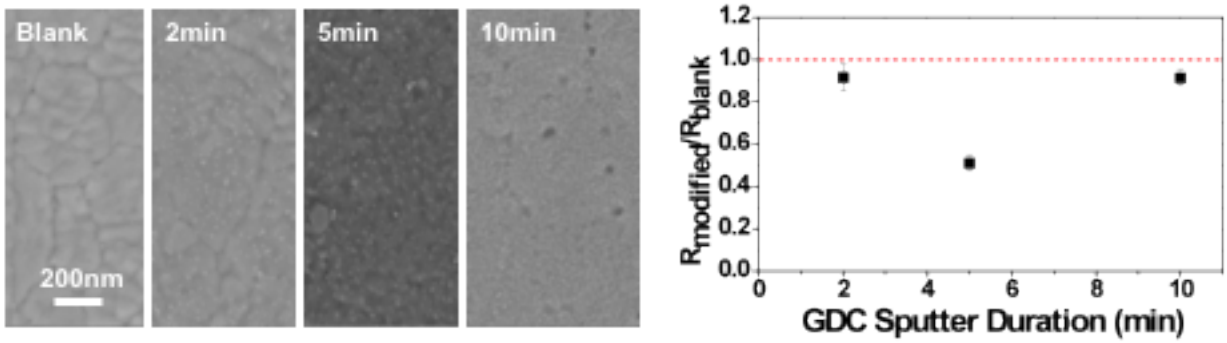

Figure 1 Left, SEM images of a blank LSCF film modified with GDC by sputtering for different periods of time. Right, polarization resistances (Rp) of the GDC modified LSCF films (data points), benchmarked by that of the original blank LSCF film without GDC modification (dashed line).

To further understand the mechanistic details of the electrode reactions, we propose to perform scanning Kelvin probe microscopy (SKPM), which is sensitive to surface physical properties such as potential variation[3] over electrode surfaces. Since the intermediate oxygen species will incur a surface space charge[4], the profile of the surface charge may change if there are hot spots for oxygen reduction. By probing the surface potential of patterned electrodes with well controlled geometries, we may be able to identify the hot spots, for example, along the electrode edge, or around the modification particles. The proposed experiments are schematically shown in Figure 2.

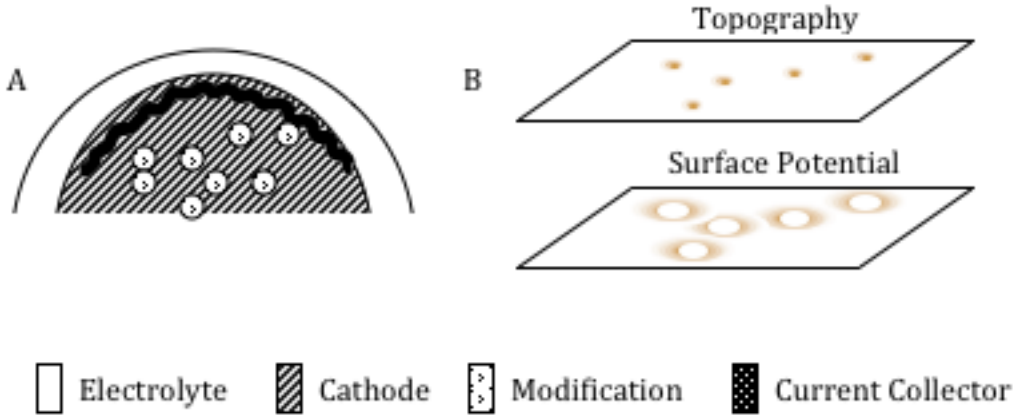

Figure 2: Proposed experiments and expected response. (A): Modification materials on the electrodes. (B): the possible correspondence of topography (by AFM) and surface potential mapping (by SKPM).

By probing and mapping the physical properties of electrode surfaces and their correlation with the electrochemical performance, we may be able to gain some important insight into the mechanism of electrode reactions, potentially providing guidelines for rational design of better electrode materials for SOFCs, oxygen permeation membranes, and other oxygen reduction catalysts.

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15. High Temperature Chemical, Electronic and Nanostructure Dynamics on Perovskite Thin-Film Surfaces

Yan Chen, Helia Jalili, Zhuhua Cai, Yener Kuru, and Bilge Yildiz, MIT

Reducing the operation temperature of Solid Oxide Fuel Cells from 800°C to 700-500°C to improve their durability and decrease their cost is of technological importance. These temperatures, however, present difficulties for the electrochemical efficiency of ceramic oxide cathodes because of the high activation energies in their catalytic activity. In order to overcome these difficulties, the underlying ORR mechanisms involving electronic and ionic charge transport and the impact of different metal cations on the catalytic properties of the cathode surfaces need to be elucidated. Furthermore, the electronic and chemical states of the cathode surfaces evolve with temperature and oxygen pressure, requiring the capability to probe their surfaces *in situ*. Our objective is to uncover the evolution of the electronic and chemical state on cathode surfaces with high spatial resolution and relate them to oxygen reduction kinetics at the atomic level. Our approach integrates surface characterization methods under extreme conditions (i.e. high temperature and high oxygen pressure), in particular using *in situ* Scanning Tunneling Microscopy and Spectroscopy (STM/STS) and *ex situ* X-ray Photoelectron Spectroscopy (XPS). We demonstrated the capability to probe the electronic structure of oxide films with high spatial resolution at the nanoscale in the presence of structural inhomogeneities using STM/STS at ambient and at high temperatures in oxygen gas environment. We will present our results on perovskite-type mixed ionic-electronic conductor (MIEC) thin film oxides, including $La_{0.7}Sr_{0.3}MnO_3$ (LSM), $(La,Sr)CoO_3$ (LSC) and $Sr(Ti,Fe)O_3$ (STF), grown by Pulsed Laser Deposition (PLD). Correlation of electron tunneling properties to the heterogeneities such as grain boundaries, hetero-interfaces and segregates, and to the surface chemical state as a function of temperature and oxygen pressure will be discussed.

16. Structural Origins of the Large Electric Field Induced Strain in the Lead-free $(1\text{-}x)BiFeO_3\text{-}xBaTiO_3$ Solid Solution

Serhiy O. Leontsev, Richard E. Eitel, Department of Chemical and Materials Engineering, University of Kentucky

In ferroelectric ceramics, the piezoelectric response and hysteretic behavior are inherently related to the crystal structure and domain configuration. Understanding the mechanisms underlying the observed strain-field dynamics and the origin of ferroelectric ordering in lead-free $(1\text{-}x)BiFeO_3\text{-}xBaTiO_3$ (BFBT) piezoelectric ceramics is important to optimize electro-mechanical properties in this material. Piezoelectric Rayleigh studies conducted under DC bias suggest structural complexity and strain contributions beyond typical ferroelectric/MPB phenomena. In order to investigate the structural origins of field induced changes in BFBT ceramics the microstructures of unpoled and poled samples were compared using diffraction contrast TEM imaging. In unpoled BFBT with 33 mol% $BaTiO_3$ composition, a highly frustrated nanoscale domain structure is observed. In poled samples, a transition from frustrated nanoscale domain patterns to long-range ordered bands of uniform polarization is observed. Extrapolation of Rayleigh and TEM results suggests the field dependence of the piezoelectric response in BFBT compositions near the MPB (x~0.33) could be explained through a field-induced phase transformation into an ordered ferroelectric state at large DC bias fields.

17. Exploring the Effects of New Processing Methods on the Nanoscale Morphology and Photocurrents in Organic Photovoltaics

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Bulk heterojunction (BHJ) polymer photovoltaics (PVs), containing a thin film blend of a hole transporting polymer and an electron transporting material, show promise in the search of new energy resources. One of the key challenges to achieve better power conversion efficiency in the BHJ PVs is the control of the three-dimensional

morphology of the thin film blend as it plays the central role in the charge separation and transport processes. Herein we explore a novel low temperature processing strategy to control the morphology of polythiophene based polymer/[6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) blends and investigate how the nanoscale morphology and structure affect and the local charge transport properties using an atomic force microscope.

18. Combining Acoustic Emission and XRD for *In Situ* Characterization of Lithium Ion Batteries

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1 Department of Materials Science and Engineering, University of Tennessee, Knoxville
2 Materials Science and Technology Division, Oak Ridge National Laboratory

The deployment of an electrical vehicle fleet requires the development of a safe, reliable, and affordable portable energy source. Lithium ion batteries (LIB) are a prime candidate for this role and their potential has already been amply demonstrated by their success in portable electronic devices. However, some issues must be addressed before LIB's can be scaled up to transportation applications. As lithium intercalates and de-intercalates active electrode materials, stress and strain develop in many active electrode materials which can lead to fracture and degradation. This manifests as a drop in cell capacity and a shortening of a LIB's operating lifetime.

Acoustic emission (AE) is nondestructive technique capable of recording ultrasonic sounds that may arise from events such as cracking or bubbling. AE has been applied to the in situ study of battery materials as they are cycled. This technique provides a time resolved picture of when and to what extent different events occur. In order to correlate lattice parameters and phase composition with the onset of fracture detection a novel in situ method that combines AE and X-ray diffraction (XRD) has been developed. Mylar disks sputtered with a thin layer of copper were laminated with a silicon composite electrode and assembled in a coin cell versus lithium foil. The coin cell hardware was modified to include a hole were X-ray could penetrate the Mylar disk to the active material.

This research at Oak Ridge National Laboratory, managed by UT Battelle, LLC, for the U.S. Department of Energy under contract DE-AC05-00OR22725, was sponsored by the Vehicle Technologies Program for the Office of Energy Efficiency and Renewable Energy. Parts of this research were performed at the High Temperature Materials Laboratory, a National User Facility sponsored by the same office.

19. Scrutinization of Electrochemical and Optical Properties of CdSe Nanocomposites to Design Optimal Devices

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CdSe nanocomposites of water soluble mercaptopropanoate anion-passivated CdSe nanoparticles (CdSe-MPA– NPs) and water/tetrahydrofuran (THF) (70/30) soluble sexithiophene bolaform amphiphiles (6TN) were fabricated on different substrates such as gold (Au), silicon (Si) wafer, and indium tin oxide (ITO)-coated glass via electrostatic layer-by-layer (ELBL) self assembly method. The electrochemical and optical properties of the CdSe nanocomposites were studied in detail to investigate self-assembly of bi-continuous CdSe-MPA– NPs and 6TN via ELBL, nanomorphology, thermodynamic cascade of charges at donor (6TN)-acceptor (CdSe-MPA– NPs) interface for possible applications of photovoltaic devices (PVs) and light-emitting diodes (LEDs). UV-visible absorption spectroscopy of glass/ITO/APS^+/$(CdSe\text{-}MPA\text{–}\ NPs/6TN)_{10}$ showed linear increase of absorbance intensities of 6TN (λ_{max} = 426 nm) and CdSe-MPA– NPs (λ_{max} = 563 nm) with increasing number of layers and a blue shift of absorption of 6TN compared to 6TN in water/THF (70/30) solution (λ_{max} = 445 nm to 426 nm) indicated π-π stacking or H-aggregates on the CdSe nanocomposites. Ellipsometry measurements of Si wafer/APS^+/$(CdSe\text{-}MPA\text{–}\ NPs/6TN)_{10}$ showed ~ 3.2 nm thickness of the first CdSe-MPA– NPs layer on the substrate indicating uniform deposition of nanoparticles and after the first layer self assembly of double layer $(6TN/CdSe\text{-}MPA\text{–}\ NPs)_1$ increased gradually giving an average thickness of 1.4 nm. Tilted Nyquist plot of Au/MPS–/$(6TN/CdSe\text{-}MPA\text{–}\ NPs)_1$ compared to that of Au/MPS–/$(6TN/\text{polystyrene sulfonate (PSS)})_1$ obtained from electrochemical impedance spectroscopy indicated improper surface coverage of CdSe nanocomposite on the substrate. Surface roughness and larger domains on AFM images of glass/ITO/APS^+/$(CdSe\text{-}MPA\text{–}\ NPs/6TN)_{10}$ compared to glass/ITO/APS^+/$(PSS/6TN)_{10}$ further confirmed the results from impedance spectroscopy. Correlation of electrochemical and optical data depicted staggered energy levels at 6TN-CdSe-MPA– NPs interface (type II bulk heterojunction interface).

Emission spectra of 6TN on glass/ITO/APS+/(6TN/CdSe-MPA– NPs)$_{10}$ at the excitation wavelength of 420 nm quenched compared to that of glass/ITO/APS^{+}/(PSS/6TN)$_{10}$ indicating photo-induced charge transfer in the presence of CdSe-MPA– NPs. H-aggregates, average double layer thickness, 1.4 nm, which is less than the size of CdSe-MPA– NPs, and results of impedance spectroscopy and AFM studies concluded deposition of CdSe-MPA– NPs only on 6TN modified areas to preserve the electrostatic attractions giving significant interdigitation and necessity of using higher concentration of CdSe MPA– NPs compared to 6TN in ELBL self assembly method to minimize H-aggregates. Photo-excited charge transfer and the type II bulk heterojunction interface suggested CdSe nanocomposites appropriate to design optimal PVs using Au as the cathode. The absence of charge transfer from 6TN to CdSe-MPA– NPs in Au/MPS–/(6TN/CdSe-MPA–)$_{7}$ under an influence of a voltage indicates that Au cathode needs to be replaced with Al in order to design CdSe nanocomposites for optimal LEDs.

20. Subsurface Characterization of Polymer Carbon Nanotube Composites via AFM Optimal Devices

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Polymer-carbon nanotube (CNT) composite materials are gaining increased interest for their potential use in solar cells, supercapacitors, Li-ion batteries, and fuel cells [1]. This study focuses on the subsurface characterization of polymer carbon nanotube composites through the use of dynamic, attractive regime AFM. Two sample types are analyzed: CNTs grown directly on a silicon substrate covered with a spun-coat polymer, and a polymer-CNT blend spun-coated directly onto the substrate [2], creating a 3D CNT network. In particular, we use the method of scanning polarization microscopy [3] to study the sub-surface structure of CNT networks in polymer nanocomposites. The CNT's polarize in the presence of an external bias voltage and change the local dielectric constant of the material relative to that of the polymer alone. This difference creates a noticeable phase contrast in the images

Current efforts are focused on the possibility of (a) identification of electrical contact between CNT's in the composite, and (b) depth sensitive tomography of CNT networks.

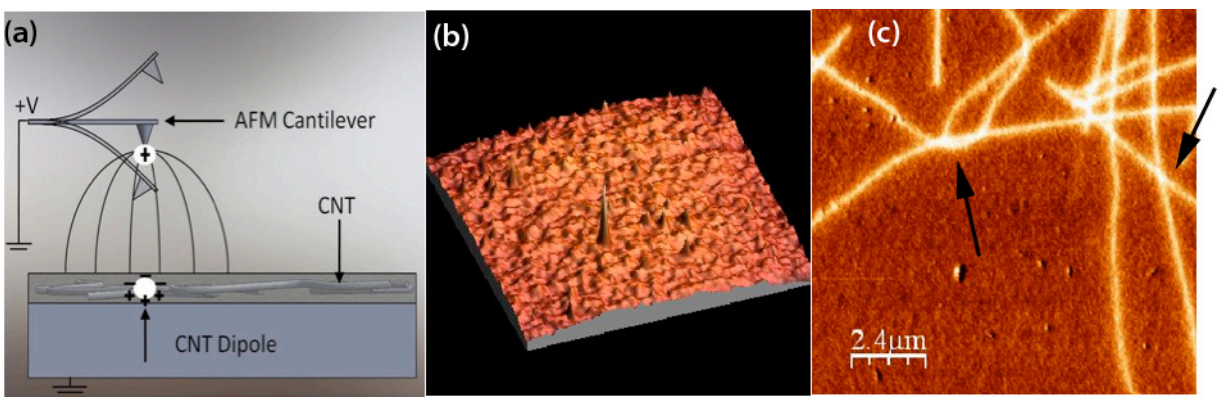

Fig. 1: (a) 2D model of AFM cantilver over CNT-pymer sample, emphasizing dipole created at CNT. (b) and (c) 12 µm x 12 µm 2V AFM images. (b) Topography and (c) Phase image. Please note that the CNTs are visible in the phase lag image, highlight with black arrows, but do not appear in the topography.

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21. STM for Energy Applications: Tip Enhanced Optical Studies at the Single Molecule Level

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Charge transfer at organic/inorganic interfaces underlies many applications in solar energy conversion and photo-induced membrane separations. The broad absorption spectrum of oligothiophenes incorporating metal-metal quadruple bonds, for instance, renders them ideal for photovoltaic applications [i]. It has also been suggested that C_{60} incorporation into zeolites could yield highly efficient photo-induced separation of O_2 and N_2 [ii]. Little is known, however, about the nanoscale chemistry and physics that occurs at the interface between these molecules and proximal materials. To develop a better understanding of energy related chemical processes at the single molecule/atom level, we have designed and constructed a novel low temperature scanning tunneling microscope (LT STM) optimized for tip-enhanced Raman spectroscopy (TERS). This instrument utilizes an atomically sharp, optically active metallic tip onto which polarized laser light is focused by means of a maneuverable, in situ sapphire lens. The resulting enhanced Raman signal from molecular species localized within the tip-sample junction is collected via a homebuilt confocal Raman microscope. Design considerations, including optical access to and alignment of a high numerical aperture objective lens in close proximity (< 1 cm) with the tunnel junction, will be discussed. Electrochemical etching recipes for and characterization of suitable Ag and Au STM tips with < 20 nm apex diameters will also be addressed. To our knowledge, this STM is the first worldwide that implements TERS in a cryogenic (4 K), ultrahigh vacuum (UHV) environment.

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ii. Dutta, P., private communication.

22. Thermophotovoltaic Energy Conversion and Near-field Enhancement of Thermal Radiative Transfer

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Thermophotovoltaic (TPV) systems convert thermal radiation from a neighboring heat source directly into electricity using a thermophotovoltaic cell, just as solar cells convert solar energy into electricity. TPV systems offer several advantages over other heat conversion devices as they can be used to reprocess waste heat from industries and they also do not have any moving parts affording quieter operation and low maintenance. However, these systems experience low power throughput since the power radiated by the emitter is limited to the black body radiation. By placing the heat source in the proximity of the cell, the phenomenon of thermal radiative enhancement due to near-field effects can be adequately used to increase the throughput of the system.

In order to facilitate the use of near-field radiative transfer in TPV systems, the mechanism by which the near-field transfer takes place when the gap between the bodies is in the nanometer scale needs to be understood thoroughly. While the theory of near-field enhancement between planar surfaces is well developed, experimental confirmation at nanometer gaps has proven to be elusive because of difficulties in maintaining a constant gap across two dirt-free surfaces. To overcome this constraint, we have developed an experimental technique to measure radiative transfer between a microsphere attached to a bi-material atomic force microscope cantilever and a substrate by measuring the deflection of the cantilever. A silica microsphere is attached to the tip of the cantilever, a laser beam is focused onto the reflective side of the microcantilever, and the reflected laser beam is detected by a position sensitive detector. As the substrate approaches the microsphere, the temperature of the microsphere decreases and causes a deflection of the cantilever due to the mismatch in coefficients of thermal expansion of the two materials that comprise the cantilever. Since theoretical or numerical studies of near-field radiative transfer involving microspheres is lacking, we have analyzed near-field transfer between two spheres using fluctuational electrodynamics and have shown that the radiative transfer scales as R/d as $d/R \rightarrow 0$ and $\ln(d/R)$ for larger gaps till the far-field limit.

23. Investigation of the Magnetoelectric Coupling in Ceramic Bilayered Nanocomposites by Magnetic Field-Assisted Piezoelectric Force Microscopy

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Here we report on our recent measurements of the magnetoelectric coupling in bilayered ceramic nanocomposites obtained by a soft-solution technique. Highly uniform polycrystalline layers of PbTiO3 and a spinel ferrite (both cubic, that is cobalt (CFO) and nickel (NFO) ferrite and hexagonal, that is BaFe12O19) with a thickness of 210 nm were deposited in aqueous solutions at temperatures as low as 45 oC. A sequential deposition of the metal oxide layers onto LaNiO3-buferred (001) Si (conductivity <0.05 Ω.cm) allowed the design of spinel-perovskite bilayered structures in a capacitor geometry with the magnetostrictive layer on top of the structure. A detailed structural, morphological and compositional characterization of the pristine perovskite and spinel phases, as well as the layered nanocomposites revealed that they are formed by densely packed spheroïdal particles with diameters comprised between 20 and 60 nm depending on the composition of the film. Magnetization vs. field measurements at room temperature indicated that the coercivity of the spinel phase decreases by 8.5% in the PTO-CFO bilayered structure as compared to that of the magnetic film deposited onto bare Si. Piezoelectric force microscopy measurements evidenced a robust piezoelectric signal in the pristine perovskite films. Magnetic field-assisted Raman spectroscopy indicated a shift to higher wave numbers of the soft phonon modes E(1TO) and A(1TO) when a magnetic field is applied in the plane of the film. Such a hardening of the soft-phonon modes is ascribed to a change in the ferroelectric domain structure of the perovskite layer as a result of the stress generated in the spinel film (negative magnetostriction coefficient for the cobalt ferrite). Magnetic field-assisted PFM measurements furthermore confirmed the existence of a strong coupling between the perovskite and spinel phases in these bilayered structures. As seen in Figure 1the slope of the amplitude-voltage curves in the case of the ceramic bilayered structures changes significantly when a static magnetic field is applied in the plane of the film. For the PTO-CFO bilayered structure the static value of the d33 piezoelectric coefficient was found to increase from 7.4 to 11.2 pm/V, whereas for the PTO-Ba-M structure d33 increased 2.59 to 2.71 pm/V when the magnetic field varied from 0 to 1500 Oe. Interestingly, the amplitude of the butterfly loop increases with the magnetic field in the case of the PTO-CFO layered nanocomposites, whereas and opposite trend was observed in the case where the top layer was a hexagonal ferrite. This effect was presumably ascribed to the opposite sign of the magnetostriction coefficient of the hexagonal ferrite as compared to that of the spinel ferrite.

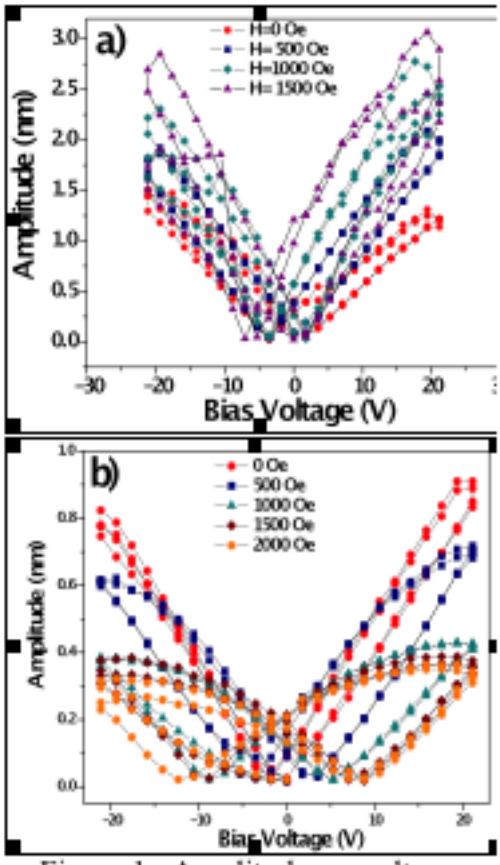

Figure 1. Amplitude vs. voltage measurements of perovskite ($PbTiO_3$)-spinel ($Co_{0.32}Fe_{0.68}O_4$ (a) and $PbTiO_3$-$BaFe_{12}O_{19}$ (b)) bilayered structures under different magnetic