

# WORKSHOP ON COMPUTATIONAL MATERIALS AND MOLECULAR ELECTRONICS



## INSTITUTE FOR THE THEORY OF ADVANCED MATERIALS IN INFORMATION TECHNOLOGY

October 20-22, 2005

INSTITUTE FOR COMPUTATIONAL ENGINEERING AND SCIENCES  
AVAYA AUDITORIUM  
UNIVERSITY OF TEXAS AT AUSTIN  
201 EAST 24TH STREET, AUSTIN, TEXAS

### **Local Organisers:**

Jim Chelikowsky, Alex Demkov, Peter Rossy (The University of Texas at Austin)  
Supratik Guha (IBM, Thomas J. Watson Research Center)

**The UT Workshop on Computational Materials and Electronics  
October 20-22, 2005  
Scientific Program**

**Thursday, October 20th**

**Welcome**

**8:50-9:00**     **Jim Chelikowsky (University of Texas)**

**Biological and Chemical Systems I**

**Alex Demkov (University of Texas), Chair**

**9:00-9:30**     Peter Rossky (University of Texas)  
*Simulation of condensed phase quantum dynamics by exploiting quantum decoherence*

**9:30-10:00**     David Beratan (Duke University)  
*Electron transfer within and between proteins*

**10:00-10:30**     Break

**Biological and Chemical Systems II**

**Peter Rossky (University of Texas), Chair**

**10:30-11:00**     Otto Sankey (Arizona State University)  
*Lessons from the simplest molecular wire system - alkane with gold contacts*

**11:00-11:30**     Alex Stuchebrukhov (UC Davis)  
*Computational studies of coupled electron and proton transfer in proteins*

**11:30-Noon**     Dima Makarov (University of Texas)  
*Translocation and unfolding of a protein pulled mechanically through a pore*

**Noon-1:30**     Lunch

**Biological and Chemical Systems III**

**Dima Makarov (University of Texas), Chair**

**1:30-2:00**     Abe Nitzan (Tel Aviv University)  
*Molecular junctions: Considerations of heat and light effects*

**2:00-2:30**     Misha Galperin (Northwestern University)  
*Inelastic effects in molecular junctions: weak and strong interaction*

**2:30-3:00**     Break

**Oxides and Semiconductor Systems I**

**Marco Nardelli (NCSU), Chair**

**3:00-3:30**     R. Ramesh (UC Berkeley)  
*Multifunctional Complex Oxide Heterostructures*

**3:30-4:00**     Fred Walker (ORNL)  
*Surface and Interface Structures of Crystalline Oxides on Silicon (COS)*

**4:00-4:30**     Charles Ahn (Yale University)  
*Chemical and electric field doping of complex oxides*

**4:30-5:00**     Yong Liang (Freescale Semiconductor)  
*Atomic Process and Fermi Level Position at the Epitaxial SrTiO<sub>3</sub>-GaAs Interface*

**Friday, October 21st**

**Oxides and Semiconductor Systems II**

**Rodney McKee, (ORNL), Chair**

- 8:30-9:00** Jean-Pierre Locquet (IBM, Zurich)  
*Epitaxial and amorphous materials for the advanced gate stack*
- 9:00-9:30** Nai Juan Wu (CAM, University of Houston)  
*Electric Pulse Induced Programmable Resistance Change in Oxide Films*
- 9:30-10:00** Marco Buongiorno Nardelli (North Carolina State University)  
*First principles theory of metal-oxide interfaces: the Schottky-Mott theory revisited*
- 10:00-10:30** Break

**Industrial Computational Materials I**

**Jim Chelikowsky (University of Texas)**

- 10:30-11:00** Sadas Shankar (Intel)  
*Fundamental Material Interactions in Nanotechnology*
- 11:00 -11:30** Doug Allan (Corning)  
*Continuum photoelastic model for permanent laser-induced optical changes in silica*
- 11:30-Noon** Cristina Thomas (3M)  
*Novel Nanosystems and Materials in the Safety, Security and Protection Industries*
- Noon-1:30** Lunch

**Industrial Computational Materials II**

**Yong Liang (Freescale Semiconductor), Chair**

- 1:30-2:00** Gaddi Haase (Texas Instruments)  
*Reliability Issues in IC Interconnect Systems*
- 2:00-2:30** Manish Jain (3M)  
*Non-Precious Metal Catalysts for PEM Fuel Cells*
- 2:30-3:00** Break

**Complex Systems in Condensed Matter: International Perspective**

**Jim Chelikowsky (University of Texas), Chair**

- 3:00-3:30** Nadia Bingeli (Trieste)  
*Exploring new phases of segregated impurities at transition-metal surfaces*
- 3:30-4:00** Jose L. Martins (Lisbon)  
*Micromagnetic Simulations*
- 4:00-4:30** Leeor Kronik (Weizmann)  
*Electronic structure of organic/inorganic interfaces*

**Saturday, October 22nd**

**CMOS Materials**

**Alex Demkov (University of Texas), Chair**

- 9:00-9:30** John Robertson (Cambridge University)  
*Calculation of Band gaps and Defect levels in Functional oxides*
- 9:30-10:00** Jose Ortega (University Autonoma, Madrid)  
*Van der Waals interactions in local-orbital DFT*
- 10:00-10:30** Break

**Materials Theory**

**G. Hwang (University of Texas), Chair**

- 10:30-11:00** Steven G. Louie (UC Berkeley)  
*Many-electron Effects in the Photo-Excited State: Nanotubes to Self-Trapped Excitons*
- 11:00-11:30** R. Wentzcovitch (University of Minnesota)  
*CoI\_xFexS2: A Tunable Source of Highly Spin-Polarized Electrons*
- 11:30-Noon** E. Kaxiras (Harvard University)  
*A new class of semiconducting nanotubes based on metal-cyanide complexes*
- Noon-1:00** Lunch

**Numerical Methods for Materials**

**Jim Chelikowsky (University of Texas), Chair**

- 1:00-1:30** Yousef Saad (University of Minnesota)  
*Diagonalization methods in PARSEC*
- 1:30-2:00** Andreas Stathopoulos (William and Mary)  
*PRIMME: Preconditioned Iterative MultiMethod Eigensolver*
- 2:00-2:30** Young Kwon (University of Massachusetts Lowell)  
*Absorption spectra and excitonic effects of nanostructured materials*
- 2:30-3:00** Break

**ITAMIT Postdoctoral Session**

**Yousef Saad (University of Minnesota), Chair**

- 3:00-3:30** Murilo Tiago (University of Minnesota)  
*Optical excitations in nanosystems*
- 3:30-4:00** Scott Beckman (University of Minnesota)  
*Investigating dislocations in semiconductors with Monte Carlo and ab initio methods*
- 4:00-4:30** Gustavo Dalpian (University of Texas)  
*Electron-induced stabilization of ferromagnetism in GaGdN*
- 4:30-5:00** Wenguang Zhu (Harvard)  
*Dopant assisted population enhancement of substitutional sites by Mn in Ge and Si*

## **Simulation of condensed phase quantum dynamics by exploiting quantum decoherence**

Peter J. Rossky  
The University of Texas at Austin

The computationally convenient description of the quantum mechanical dynamics of electronic systems and of light nuclei in condensed phases is an important goal for the accurate atomistic representation of chemical, biochemical, and materials processes. In electronic systems, the rate of decay of an excited state is influenced by the coherence among the amplitudes for the initial state and the component decay channels. For a species in a condensed phase, the dynamics of the bath can strongly dissipate this coherence and thus modify the rate of electronic evolution. For nuclear dynamics, the coherence between alternative nuclear paths has a parallel significance, and interaction with the surroundings has a similar dissipating effect. Practical approaches to simulation of these cases will be described which only require evaluation of the *classical* molecular dynamics of nuclei. The evolution of electronic excited states and the description of the dynamics of light nuclei, including the dissipative role of the environment, will be illustrated in practical cases; these include electronic excited state relaxation in solution, motion in neat liquids, and vibrational spectroscopy of liquid water.

## **Electron transfer within and between proteins**

David Beratan  
Duke University

Electron transfer through proteins proceeds via hole-mediated superexchange. I will present theoretical descriptions of these superexchange interactions that capture the differences between bond-mediated and through-space tunneling, that include the influence of protein dynamics, and that include multi-pathway interferences. The striking balance between docking energetics and superexchange coupling for inter-protein electron transfer will be explored, as will the interesting role of water at the interface between electron-transfer proteins.

## **Lessons from the simplest molecular wire system – alkane with gold contacts**

Otto F. Sankey  
Arizona State University

New opportunities for wiring molecules into novel circuits and devices lie before us. Especially attractive are opportunities with “active molecules” such as those that have an ability to change conformation due to light or other stimuli, or those that selectively dock (e.g biomolecules) with other molecules or ions in the environment. In this talk we will examine a relatively dull molecule, alkanes (with thiol/Au contacts), to benchmark our understanding, particularly concerning the theory/experiment comparison. Of particular interest is the “non-unique” result found in AFM repeated break junction experiments. We have examined different bonding sites and metal contact geometries and find large changes in the Fermi-level lineup and its relation to “Sulfur induced” states producing special i-v signatures.

**Computational studies of coupled electron and proton transfer in proteins.  
Proton pumps, cytochrome c oxidase, and biological energy transduction.**

Alexei Stuchebrukhov  
University of California, Davis

Cytochrome c oxidase is the terminal enzyme in the respiratory electron transport chain of aerobic organisms. This enzyme catalyses the reduction of atmospheric oxygen to water in our cells, and converts the free energy of oxygen reduction for the creation of the membrane proton gradient by pumping protons across the membrane. The proton gradient subsequently drives the synthesis of ATP. The details of the mechanism of this redox-driven proton pump are unknown. Computer simulations directed toward understanding proton pumping mechanism of cytochrome c oxidase described in Refs 1-3, along with more recent work on the subject, will be discussed.

1. D. M. Popovic and A. A. Stuchebrukhov, Electrostatic study of the proton pumping mechanism in bovine heart cytochrome c oxidase, *J. Am. Chem. Soc.* 126, 1858, 2004.
2. D. M. Popovic and A. A. Stuchebrukhov, Proton pumping mechanism and catalytic cycle of cytochrome c oxidase: Coulomb pump model with kinetic gating, *FEBS Lett.* 2004.
3. A.A. Stuchebrukhov, Electron transfer reactions coupled to proton translocation. Cytochrome oxidase, proton pumps, and biological energy transduction. *J. Theor. Comp. Chem.* 1, 91-118, 2003.



## **Translocation and unfolding of a protein pulled mechanically through a pore.**

Dima Makarov  
University of Texas

Many biological processes involve protein translocation through pores. For example, proteasome – a cellular machine responsible for protein degradation – unfolds proteins by pulling them mechanically through a narrow constriction. Recently, the transport of charged biopolymers driven electrophoretically across ion channel pores has been studied at a single molecule level by a number of groups. In this talk I will describe some of our group's theoretical and computational efforts to understand how the protein translocation & unfolding processes depend on the structure of the translocated proteins, the pore dimensions and the applied electric fields.

## **Molecular junctions: Considerations of heat and light effects**

Abraham Nitzan  
Tel Aviv University

We consider several thermal and optical phenomena involving molecules in biased metal-molecule-metal junctions. These include heating of current carrying molecular junctions, thermal conduction by molecular wires, heat current rectification and heat pumping in molecular junctions, current induced light emission and light induced current. Relevant experimental results are discussed when available.

## Inelastic effects in molecular junctions: weak and strong interaction

M. Galperin  
Northwestern University

Molecular electronics is an active area of research with the goal of supplementing currently available Si based electronics in further miniaturization of electronic devices. An intriguing issue in molecular junctions is the role played by nuclear motions in the conduction process. Theoretical study of electron-phonon interaction has a long history. In biased current junctions this issue raises new points for consideration. The interpretation of electronics transport in molecular junctions has so far being done in the context of multi-channel scattering problem. The influence of the contact population as well as of the electronic subsystem on the phonon dynamics is disregarded in this case. A systematic framework for describing transport phenomena of many-particle systems is based on the nonequilibrium Green's function (NEGF) formalism. We use the NEGF formalism to describe inelastic electron transport through molecular junctions for weak and strong electron-phonon interactions.

The weak interaction case corresponds to non-resonant phonon assisted electron tunneling. Theoretically it can be described by a perturbation (in interaction strength) approach on the Keldysh contour. The lowest non-zero diagrams lead to self-consistent Born approximation (SCBA) for both electron and phonon Green functions. We use the scheme to describe features (peaks, dips, lineshapes and linewidths) observed in the IETS signal,  $d^2I/dV^2$  as function of the applied bias voltage  $V$  [1, 2].

The strong electron-phonon interaction usually corresponds to the near resonant tunneling situation. Generally, perturbative consideration in this case breaks down. We investigate two possible approaches. One is based on the Born Oppenheimer approximation. The approach leads to a simple mean field model, which becomes exact in static limit. We apply the scheme to describe negative differential resistance (NDR) and hysteresis observed in molecular junctions within the same polaronic model [3]. In the second approach we try to avoid timescale limitations. This approach is based on the second order cumulant expansion and equation of motion method. We propose a self-consistent scheme on the Keldysh contour to investigate intermediate to strong electron-phonon interaction parameter region. We apply the scheme to study inelastic resonant tunneling in molecular junction [4] and compare our results to previous works.

### References

- [1] M. Galperin, M. A. Ratner, and A. Nitzan. J. Chem. Phys. 121, 11965-11979 (2004).
- [2] M. Galperin, M. A. Ratner, and A. Nitzan. Nano Letters 4, 1605-1611 (2004).
- [3] M. Galperin, M. A. Ratner, and A. Nitzan. Nano Letters 5, 125-130 (2005).
- [4] M. Galperin, A. Nitzan, and M. A. Ratner (to be published).

## **Multifunctional Complex Oxide Heterostructures**

R. Ramesh  
University of California, Berkeley

Complex perovskite oxides exhibit a rich spectrum of functional responses, including magnetism, ferroelectricity, highly correlated electron behavior, superconductivity, etc. There exists a small set of materials which exhibit multiple order parameters; these are known as multiferroics. Using our work in the field of ferroelectrics and ferromagnetics as the background, we are now exploring such materials, as epitaxial thin films as well as nanostructures. Specifically, we are studying the role of thin film growth, heteroepitaxy and processing on the basic properties as well as magnitude of the coupling between the order parameters. In single phase multiferroic perovskites, such as  $\text{BiFeO}_3$ , we have found significant enhancements in magnetism and ferroelectricity compared to bulk. Detailed measurements indicate that the enhancement in magnetism is due to a mixed  $\text{Fe}^{2+}/\text{Fe}^{3+}$  state in the films, while the ferroelectric polarization is reasonably commensurate with that predicted from first principles theory. A very exciting new development has been the discovery of the formation of spontaneously assembled nanostructures consisting of a ferromagnetic phase embedded in a ferroelectric matrix that exhibit very strong coupling between the two order parameters. This involves 3-dimensional heteroepitaxy between the substrate, the matrix perovskite phase and spinel phase that is embedded as single crystalline pillars in this matrix. This epitaxial coupling is critical and is responsible for the significantly higher magnetoelectric coupling and magnetic anisotropy in such vertical heterostructures compared to a conventional heterostructure.

This work is supported by the ONR under a MURI program.

## **Surface and Interface Structures of Crystalline Oxides on Silicon (COS)**

Fred Walker  
Oak Ridge National Laboratory

The structure of the Sr-covered Si(001) surface (the precursor to COS heteroepitaxy) is a matter of on-going scientific debate with experiment and theory casting opposing views. Real space Z-contrast imaging shows that  $\frac{1}{2}$  of the silicon atoms on the (001) surface are absent, and this has presented us with the intriguing question – “Where does the silicon go?”.

While a crystalline oxide interface with silicon has been the goal, a metallic surface termination of silicon was required in the layer-sequenced heteroepitaxy. What has been common to all experimental realizations of the layer-sequenced COS structure, is the presence of hydrogen, intrinsic to the use of alkaline earth metal sources, during the film growth. We report here that this hydrogen has inadvertently played a pivotal role in defining the silicon termination and thus the evolution of the interface structure for COS. We will describe the thermodynamic basis for this hydrogen effect along with experimental and theoretical characterization of the structural details. So we have the answer to the intriguing question and will divulge where the silicon has gone.

## **Chemical and electric field doping of complex oxides**

Charles Ahn  
Yale University

A generic feature of complex oxide materials is the sensitivity of their electronic properties to changes in the carrier concentration. Modification of the carrier density is usually carried out through chemical doping, which introduces chemical and structural disorder, potentially altering the resulting electronic properties of the system. Here, we discuss the effect of chemical and electric field doping on the anisotropic magnetoresistance (AMR) of colossal magnetoresistive oxides. While chemical doping changes the relative AMR, electric field doping leaves the relative AMR unchanged. This electric field effect approach allows one to tune the Curie temperature while maintaining a fixed value of the relative AMR.

## **Atomic Process and Fermi Level Position at the Epitaxial SrTiO<sub>3</sub>-GaAs Interface**

Yong Liang  
Freescale Semiconductor Inc.

Metal oxides possess a wide range of novel properties that make them uniquely suitable for a number of potential technologies. The combination of oxides with semiconductors provides the opportunities through which the novel properties of oxides and mature technology of semiconductors can be exploited simultaneously. The challenge of forming a well-defined oxide-semiconductor system lies in the chemical and structural dissimilarities at the oxide-semiconductor interface.

We show that the epitaxial oxide-semiconductor systems with desired properties can be achieved by proper control of interfacial chemistry. We use SrTiO<sub>3</sub>-GaAs as an example to demonstrate the importance of initial stages of growth and self-organized processes on the atomic and electronic structures of the SrTiO<sub>3</sub>-GaAs interface. A number of issues such as band alignment, Fermi level pinning, and atomic structures at the SrTiO<sub>3</sub>-GaAs interface have been examined using several surface and interface sensitive techniques. These results will be presented at the workshop.

## **Epitaxial and amorphous materials for the advanced gate stack**

Jean-Pierre Locquet  
IBM Zurich

In this talk, I will discuss progress regarding the integration of epitaxial and amorphous high K dielectrics on top of silicon. The thin layers used in this project are typically grown using molecular beam epitaxy. An outlook, towards the use of high mobility semiconductors for this application is also given.



## Electric Pulse Induced Programmable Resistance Change in Oxide Films

N. J. Wu

Texas Center for Advanced Materials & University of Houston

A novel electrical pulse induced resistance change effect (EPIR) has been identified in thin films of perovskite oxide materials, such as  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  (PCMO) which exhibits large reversible resistance changes at room temperature. Positive voltage pulses of  $< 4\text{V}$  can switch the resistance of the thin film oxide device from a high resistive state into a low resistive state, and negative voltage pulses can return the system back to the high state in times shorter than  $\sim 10\text{ns}$ . A resistance change of more than two orders of magnitude has been obtained for samples pulsed at 3 to 4 V, in an operating temperature range of  $23\text{ }^\circ\text{C}$  to  $100\text{ }^\circ\text{C}$ . It has been shown that the resistance change is non-volatile with retention times  $> 10^8\text{sec}$ . Moderate fatigue is exhibited by the effect, however, this seems to depend on film processing parameters. The mechanism underlying the EPIR effect is not yet fully understood, however, preliminary data suggests that current induced vacancy motion in the oxide nears the metallic electrical contact may be responsible for the non-volatile change in sample resistance. The device performance indicates that a two-state non-volatile resistance random access memory (RRAM) can be realized based on this EPIR effect. This would present the possibility of a new nonvolatile, high density, fast write/read, and low power-consumption memory system.

## **First principles theory of metal-oxide interfaces: the Schottky-Mott theory revisited**

Marco Buongiorno Nardelli  
North Carolina State University

Advances in the epitaxial growth of ultra-thin films and heterojunctions have made viable new classes of device applications that may sustain the semiconductor roadmap for another decade. However, this progress will require an in-depth understanding and utilization of electronic processes at the nanoscale. One of the central issues is the role of interfaces between materials, where most of the electronic properties of the system are determined. In this talk, I will discuss recent fundamental advances in our understanding of the physics of nano-scale interfaces with particular emphasis on metal-insulator systems where understanding the formation of the Schottky barrier is of paramount importance for the design of metallic gate contacts and the engineering of advanced electronic devices.

## **Fundamental Material Interactions in Nanotechnology**

Sadasivan Shankar  
Intel Corporation

Over the past 3 decades the semiconductor industry has doubled the number of transistors on integrated circuits every 2 years, following an empirical law widely known as Moore's law. The ability of the semiconductor industry to stay on Moore's law has enabled the digital revolution and now the convergence of communications and computing. However, as the size of the smallest structures decrease, this has required the introduction of many new materials and the interactions of these heterogeneous materials and processing is increasing in complexity. Due to the presence of multiple thin films and metal alloys in the process, grains, and interfaces assume more significance than before. This paper reviews some of the challenges in materials and the opportunities for using fundamental modeling and characterization techniques to enable successful management of these heterogeneous interactions. The three specific topics expected to be covered are 1) Electromigration, 2) Mechanical integrity, and 3) Interface adhesion.

## **Continuum photoelastic model for permanent laser-induced optical changes in silica**

Doug Allan  
Corning

Fused silica, when exposed to pulsed UV excimer laser light, exhibits permanent optical changes. These changes are readily observed and quantified using interferometry and/or polarimetry. The pattern of birefringence observed in polarimetry depends on the polarization of the exposing laser. This polarization induced effect has been known for several years, but has become much more important with the advent of immersion photolithography and its associated very high numerical apertures. High numerical aperture optics require controlled polarization, notably linear polarization, in order to maintain phase contrast at the image. When birefringence and wavefront changes are induced by laser exposure, the image contrast at the wafer deteriorates. We interpret the changes in optical properties in terms of permanent *anisotropic* strain induced by laser damage, and the associated strain-induced optical effects. This is accomplished using the mathematics of tensors to account for anisotropic strain and optical anisotropy, and using finite element analysis to calculate the strain fields taking the sample and exposure geometries into account. We report the relations between underlying density and strain anisotropy changes and the induced birefringence and wavefront for a given experimental sample geometry. We also report some examples of the different degree of laser damage from silica with different compositions and different processing conditions.

## **Novel Nanosystems and Materials in the Safety, Security and Protection Industries**

Cristina U. Thomas

3M

Nanosystems have shown to represent new opportunities and new possibilities for advanced materials. It is hence very important that theoretical and computational methods are developed so that the materials are designed and optimized to deliver their expected performance and benefits. Many industrial scientists are focusing on nanotechnology based on the belief and realization that nanosystems are basic and important blocks for building new businesses. As an applied scientist, who finds industrial computational experts to be at the right intersect, it is really exciting period in applied research. This intersect is right since computational technologies are distinctively capable to access understanding, to stimulate thoughts and possibilities, to run "what-if" scenarios, and to "truly" discover new nanosystems and advanced materials. This presentation will focus on describing computational methodologies that we are currently using in the area of nanocomposites. It will then follow with a discussion on the applications of IR absorbing nanoparticles to the protection of people and their property. It will finish with a look at inorganic materials for fire safety.

## **Reliability Issues in IC Interconnect Systems**

Gaddi S Haase  
Texas Instruments

Interconnect systems in modern integrated circuits carry electrical signals in typically 5-8 metal levels, with line width and line-to-line spacing falling under 100 nm, and with a total length of over 100 m. Even at the post-silicon era, molecular electronics will still need a hosting matrix and an interconnect system. The doubling of device density every 2-3 years leaves a thinner interconnect dielectric layer between the leads. The increase in speed requirements pushes for the replacement of the traditional SiO<sub>2</sub> –based insulators with lower-k materials, which are weaker both mechanically and electrically. Unlike gate oxides, process variations and additional interfaces that span between biased metal-lines and vias create weak spots, as well as pose difficulties in testing chips for the detection of defects. Accelerated tests, at elevated temperatures and voltages, are used to predict the lifetime of these systems under operating conditions. However, we need to gain a better understanding of basic degradation mechanisms to be able to construct correct models for such lifetime extrapolations.

## Non-Precious Metal Catalysts for PEM Fuel Cells

Manish Jain  
3M

We used density functional methods to examine the structural and electronic aspects of such non-precious metal catalysts. One, centered on iron, has been extensively studied experimentally in the literature [M. Lefèvre, J. P. Dodelet, and P. Bertrand, *J. Phys. Chem. B*, **104**, 11238 (2000)]. While, an atomic level description of these iron-based catalysts has not been achieved, secondary ion mass spectrometric (SIMS) studies indicated that the ion  $\text{FeN}_2\text{C}_4^+$  might be a signature of the most active catalytic site. This result has led to the suggestion that the active site might correspond to a graphene lattice into which Fe and N had been substituted; and in which the nitrogen atoms act as ligands that provide binding sites for iron. We studied the thermodynamic stability of some of these proposed catalytic centers in these materials. It is also considered that this fundamental chemistry might be carried out using continuous, vacuum sputtering deposition process technology. We also examine the possible structures formed during the vacuum vapor deposition of C-N and C-N-Fe materials using *ab initio* molecular dynamics. Combined with characterization techniques, such as EXAFS and UPS, this work provides insight into possible bonding configurations between carbon, nitrogen and a transition metal such as iron in these materials.

This research was supported in part by the U.S. Department of Energy (DOE), Cooperative Agreement No. DE-FC36-03GO13106. DOE support does not constitute an endorsement by DOE of the views expressed in this presentation.

## Exploring new phases of segregated impurities at transition-metal surfaces

N. Binggeli  
Trieste, Italy

Segregation of bulk non-metallic impurities at transition metal surfaces has an important impact on materials properties such as oxidation resistance, catalytic activity, and surface magnetism. Recently, STM experiments have revealed interesting cases of self-organized nano-scale structures of segregated impurities at Fe surfaces, giving rise to surface configurations with long-range order and peculiar electronic properties. This includes a  $c(3\sqrt{2}\times\sqrt{2})$  Fe(001) structure with self-assembled carbon zigzag chains, that have a passivation effect on the iron surface and modify its magnetic properties. Using *ab initio* pseudopotential calculations and Monte Carlo simulations, we have examined this structure and the mechanism behind its formation. In particular, our results show that the formation of the zigzag chains, observed at a C coverage of  $2/3$  monolayer, derive from repulsive interactions between the C impurities segregated at hollow sites of the Fe surface. We also find that the formation of the C chains gives rise to one-dimensional Fe surface states near to the Fermi energy. The simulation of the STM image allows us to assign the chain-like structure, observed in the STM experiments, to such one-dimensional Fe surface states laterally confined within the C zigzag stripes.

Work done in collaboration with G. Trimarchi (NREL, Golden, CO)



## **Micromagnetic Simulations**

José Luís Martins  
Técnico, Lisbon, Portugal

The detection of small magnetic fields from small elements is a key technology not only in the read heads of magnetic hard disks but can be used for memory (MRAM) or other applications. We have developed a micromagnetic simulation code that allows us to simulate multi-layered thin-film devices and established a collaboration with an experimental group. The simulations are very helpful in the interpretation of the measurements and have been used to suggest improvements in the design of the devices. We describe briefly the basic concepts of micromagnetism and our approach to the problem and present some of our recent applications of the method to the simulation of devices.

In collaboration with F. Ribeiro, T. Rocha, Y. Liu, M. Mendes.

## **Electronic structure of organic/inorganic interfaces**

Leeor Kronik  
Weizmann Institute, Israel

We present a first principles study of the electronic structure, and particularly the surface dipole, at self-assembled monolayers adsorbed on a semiconducting substrate. We provide computational evidence for long-range, cooperative behavior that highlights the role of order in controlling experimentally observed electronic properties.

## Calculation of Band gaps and Defect levels in Functional oxides

J Robertson  
Cambridge University

It is well known that first principles calculation of electronic structures of semiconductors and insulators using the local density approximation (LDA) gives good structures but leads to severe under-estimate of the band gap. This can be corrected empirically by the “scissors approximation” of rigidly raising conduction bands to get the experimental band gap, but this loses any predictive power. The error for some transparent conductive oxides like ZnO, In<sub>2</sub>O<sub>3</sub> or SnO<sub>2</sub> is 70%.

The error can be corrected by methods such as the GW approximation, but this computationally quite expensive. There are other methods which can correct the band gap such as B3LYP, self-interaction correction (SIC) or LDA+U. It can be corrected by lower cost methods such as the screened exchange (sX) method, which we and others have found to be quite accurate and reliable. However, for oxides, sX has the disadvantage of requiring the use of norm-conserving pseudopotentials. These use a cutoff energy of up to 1000 eV for oxygen, whereas the smoother ultra-soft pseudopotentials of Vanderbilt need only 350 eV. A new method, the weighted density approximation (WDA), has been introduced which allows ultra-soft pseudopotentials. A further feature of WDA and sX is that they are a density functional, not a perturbative method like GW, so that the structural energy of defects could be minimised within WDA itself.

We present calculations of the band gaps of oxides using both sX and WDA methods for a wide range of oxides. As examples, we calculate the minimum WDA band gaps as SiO<sub>2</sub> 9.2 eV, Al<sub>2</sub>O<sub>3</sub> 9.3 eV, MgO 7.7 eV, LaAlO<sub>3</sub> 6.7 eV, LaScO<sub>3</sub> 6.3 eV, SrTiO<sub>3</sub> 3.0 eV, c-ZrO<sub>2</sub> 6.0 eV, HfO<sub>2</sub> 6.1 eV, ZrSiO<sub>4</sub> 7.0 eV, SrCu<sub>2</sub>O<sub>2</sub> 4.1 eV. We are particularly interested in oxides used as high K gate oxides, ferroelectrics and transparent conducting oxides. Calculations of vacancy energy levels are also given.

The ability to use WDA in functional mode allows defect structures to be found. This is important in defect calculations where the defect level could be in the conduction band in the LDA, so that LDA could actually find the wrong structure. Thus the WDA method opens up many opportunities for supercell calculations of surfaces, interfaces and defects.

## Van der Waals interactions in local-orbital DFT

J. Ortega  
University Autonoma, Madrid

Van der Waals (vdW) forces play a fundamental role in large molecular systems of biological importance, organic chemistry, noble-gas chemistry, pharmaceutical compounds, colloidal systems, polymers, etc. However, in spite of the relevance of these interactions, the development of a practical scheme to include vdW interactions in first-principles simulations, beyond the simplest cases, remains a great theoretical challenge.

Here, we discuss how vdW interactions can be included within a local-orbital Density Functional Theory (DFT), using a local orbital-occupancy formulation. In this approach, the exchange-correlation energy as well as the van der Waals forces are written as a function of the orbital occupation numbers,  $\eta_{i\sigma}$ . We first analyze in detail the He-He and Ne-Ne cases and calculate the DFT-vdW energy,  $E^{\text{vdW}}[\eta_{i\sigma}]$ .

Our analysis also suggests an alternative approach for including van der Waals forces in the local orbital-DFT formulation, namely, to introduce an effective hopping interaction between the orbitals of both atoms. Then, we discuss how this approach can be extended for large systems, and present some results for the case of two parallel graphene layers.

[1] M.A. Basanta, Y.J. Dappe, J. Ortega and F. Flores, *Europhys. Lett.* 70, 355 (2005).

## **Many-electron Effects in the Photo-Excited State: Nanotubes to Self-Trapped Excitons**

Steven G. Louie  
University of California at Berkeley

We discuss some recent progress on first-principles study of excited-state properties, in particular the optical response of condensed matter. As examples, we present results on the optical properties of nanotubes and on the phenomenon of self-trapped excitons in  $\text{SiO}_2$ . The approach involves solving for the quasiparticle and electron-hole excitations of the interacting-electron system within the GW approximation. In the study of self-trapped excitons, calculation of forces on the atoms in the excited state is further required. Owing to their reduced dimensionality, many-electron effects qualitatively alter the optical spectra of the nanotubes. It is discovered that exciton states in the semiconducting carbon nanotubes have binding energies that are orders of magnitude larger than bulk semiconductors and hence they dominate the optical spectrum at all temperature, and that bound excitons can exist even in metallic carbon nanotubes. Similar studies show that excitonic effects are even stronger in the BN nanotubes. In  $\text{SiO}_2$ , the excited electron and hole spontaneously distort the crystal, and the exciton self traps locally to the distortion (to a lower-energy configuration in the excited state) leading to a huge Stokes shift of over 6 eV in the photoluminescence frequency. The calculations provide a microscopic picture of the trapping mechanism and geometry of the self-trapped exciton. The physics behind these phenomena is discussed.

## **Co<sub>1-x</sub>Fe<sub>x</sub>S<sub>2</sub>: A Tunable Source of Highly Spin-Polarized Electrons**

Renata M. Wentzcovitch  
University of Minnesota

In the emerging field of spin-electronics ideal ferromagnetic electron sources would not only possess a high degree of spin polarization, but would also offer control over the magnitude of this polarization. We demonstrate here that a simple scheme can be utilized to control both the magnitude and the sign of the spin polarization of ferromagnetic CoS<sub>2</sub>, which we probe with a variety of techniques. The position of the Fermi level is fine-tuned by solid solution alloying with the isostructural diamagnetic semiconductor FeS<sub>2</sub>, leading to tunable spin polarization of up to 85%.

In collaboration with: K. Umemoto, C. Leighton, and L. Wang

## **A new class of semiconducting nanotubes based on metal-cyanide complexes**

Efthimios Kaxiras  
Harvard University

We propose a new type of nanotubes made of the layer-structured cyanide compounds  $\text{Ni}(\text{CN})_2$ ,  $\text{Pd}(\text{CN})_2$  or  $\text{Pt}(\text{CN})_2$ . Using first-principles calculations, we study the electronic and mechanical properties of these materials in both a two-dimensional sheet and a one-dimensional tube form. We find that the helicity of the nanotube does not significantly affect its electronic properties, which are similar to those of the sheet form. The nanotubes are insulators with a band gap greater than 2 eV. The predicted structure involves an unusual 90-degree bent single bond that joins 3 atoms. The presence of this bond singles out nanotubes of a particular helicity as energetically more stable than others. These features may make cyanide nanotubes more amenable to mass production than present carbon nanotubes.

## **Diagonalization methods in PARSEC**

Yousef Saad  
University of Minnesota

The Pseudopotential Algorithm for Real-Space Electronic Structure calculation (PARSEC) is a package for electronic structures designed for massively parallel computers. It uses a real-space approach to discretize the Kohn-Sham equations and this results in a large sparse eigenvalue problem to solve at each self-consistent iteration. The code has constantly evolved over more than a decade as features were progressively added and the diagonalization routine, which accounts for the biggest part of a typical execution time, was upgraded several times. In this talk I will discuss the diagonalization methods which have been used in PARSEC, as well as some methods which are not yet implemented. We found that it is important to consider the problem as one of computing an invariant subspace in the non-linear context of the Kohn-Sham equations. This viewpoint leads to considerable savings as it de-emphasizes the accurate computation of individual eigenvectors and focuses instead on the subspace which they span.



**PRIMME: Preconditioned Iterative MultiMethod Eigensolver**  
**A robust, efficient and flexible Hermitian eigenvalue software**

Andreas Stathopoulos  
William and Mary

In recent years, many preconditioned eigensolvers have emerged that perform well in many, but not all applications. Moreover, in the related software, robustness has taken a secondary role behind efficiency. In view of the above, our group has developed a robust, efficient multi-method software called PRIMME. PRIMME is based on a Davidson-type main iteration, but it implements various techniques such block, locking, CG-type restarting, and adaptive inner-outer iterations, that allow it to transform to any current eigenvalue method. More than thirty features are controllable and tunable by the user, but a complete set of defaults requires only two to be set. The software runs both on parallel and sequential machines and can use the optimized BLAS and LAPACK libraries of the target machines. Additionally, PRIMME has the ability to sense both the computing environment and the problem solved, and adapt its choice of parameters accordingly.

In this talk, we present an overview of PRIMME, its robustness and efficiency, and show how JDQMR, one of the supported methods, can improve even on the Lanczos/ARPACK methods for Laplacian-type problems that are common in materials science applications.

# Absorption spectra and excitonic effects of nanostructured materials<sup>1</sup>

Young-Kyun Kwon  
University of Massachusetts Lowell

Due to their low-dimensionality, the excitonic effect becomes very important in the optical property of nanomaterials. To investigate the optical spectra and excitonic effects of nanostructured materials, we solve the Bethe-Salpeter equation of the two-particle Green's function employing one-particle input from the empirical pseudopotential method, which is computationally more efficient than using one-particle-particle input from the GW approximation, although it would be less accurate. The calculated absorption spectra and excitonic effects of nanotubes and bulk Si will be presented and compared with experiments and *ab initio* results.

<sup>1</sup> This work has been done in collaboration with Steven G. Louie (UC Berkeley), Marvin L. Cohen (UC Berkeley), and James R. Chelikowsky (U of Texas Austin), and supported by ITAMIT.

## **Optical excitations in nanosystems**

Murilo Tiago  
University of Minnesota

While the ground state of an electronic system can be easily and accurately predicted within density-functional theory (DFT), first-principles theories for excited states are considerably more complex. One such theory is based on solving the Bethe-Salpeter equation for neutral excitations. This approach has been successfully applied to solids, nanotubes and small molecules. Alternatively, time-dependent DFT can be used, often with very good results. We discuss applications of these two theories in the calculation of linear optical response of semiconductor nanocrystals and organic molecules.

## **Investigating dislocations in semiconductors with Monte Carlo and *ab initio* methods**

S. P. Beckman  
University of Minnesota

I present a model in which the complex structure of a dislocation core can be coarse grained onto a pair of interpenetrating spin chains. It is argued here that this simple model is sufficient to describe the nature of the dislocation core. The macroscopic properties of a dislocation are dictated by defects along the line such as kinks, phase interfaces, reconstruction defects, etc. The interaction of these structural excitations can be investigated within a Monte Carlo framework. The interaction energies for such a model are proposed to be investigated by *ab initio* methods. I will discuss an *ab initio* study comparing the relative energies of two phases of the reconstruction along the  $90^\circ$  partial dislocation in GaAs, Si, C, and Ge.

## **Electron-induced stabilization of ferromagnetism in GaGdN**

Gustavo Dalpian  
University of Texas

Diluted Magnetic Semiconductors (DMSs) are potential materials for the development of devices based on spintronics ideas. Many different materials have been proposed for this task, mainly focusing on transition metal(TM) doped II-VI and III-V semiconductors, where ferromagnetism is stabilized by holes. In this work we present a study on a new DMS: GaGdN. We show that the magnetic properties of GaGdN are drastically different from TM-doped GaN. The coupling between Gd atoms in the alloy is antiferromagnetic, but the ferromagnetic phase can be stabilized by introducing electrons due to the coupling between the Gd f levels and the conduction band of GaN.

## **Dopant assisted population enhancement of substitutional sites by Mn in Ge and Si**

Wenguang Zhu  
Harvard University

Dilute magnetic semiconductors (DMS) have attracted attention as promising materials for spintronic devices. Initially, III-V semiconductors doped with Mn were studied and found to exhibit ferromagnetic ordering. Recently, ferromagnetic ordering has also been observed in Mn doped Ge-based materials, offering a better opportunity for integrating magnetism with existing silicon technology. Previous studies showed that the magnetic ordering temperature,  $T_C$ , may depend sensitively on relative populations of interstitial and substitutional magnetic dopants. We investigate the influence of a p-type or n-type dopant on Mn doping in both Ge and Si bulk systems by using first-principles total energy calculations within density functional theory. With the assistance of an n-type dopant, such as P, As and Sb, a Mn atom can be incorporated easier into substitutional sites in bulk Ge. Similarly, the site preference for incorporation of the Mn dopant in bulk Si can be changed from the interstitial site to the substitutional site in the presence of a neighboring n-type dopant. Our findings point to the possibility of increasing Mn occupation of substitutional sites in semiconductor systems, making it a more effective spin carrier.