Towards Reality in Nanoscale Materials

December 10th - 12th 2007 in Levi, Finland

Summary

The overall plan for the TRNM workshop was a theoretical focus, but bringing some contributions from leading experimental groups. The main suggested topics of the workshop were as follows:

* Methods - application of first principles methods to atomistic modeling of non-ideal nanoscale materials. Including advanced approaches for studying excited states and very large systems.
* Multiscale - approaches to link first principles calculations to larger scale methods, such as kinetic Monte Carlo.
* Defects in nano-structured carbon materials - including the study of how mechanical and electronic properties of nano-structured carbon materials are influenced by defects.
* Surface chemistry at the nanoscale - particular emphasis will be placed on those systems where defects and impurities clearly dominate reactive properties.
* Defect creation - studies of doped and irradiated nanoscale materials.
* Defect control - beyond just studying and understanding the properties of defects and impurities, we wish to explore avenues of atomic scale control: charging; optical excitation; mechanical manipulation. This direction leads to the possibility of tailoring the electronic structure of nanoscale systems.

The workshop consists of invited and contributed talks as well as posters and short poster talks. In general the invited and contributed talks applied these methods to either carbon nanostructures or insulating surfaces, particularly considering their interaction with molecules, nanoparticles or the role of defects.

Scientific content and discussion

Perfectly fitting the theme of the workshop, the conference began with a multi-scale simulation talk from Michael Moseler. Focusing on Carbon he showed in his talk how a series of numerical tools - ranging from density functional theory and density functional based tight-binding, via bond order potentials to a continuum treatment- can be combined in a multiscale modeling strategy in order to understand the active physical mechanisms in carbon nanosystems. Neatly following this, Florian Banhart presented his use of energetic electron beams in an electron microscope to create defects in nanomaterials and, at the same time, to monitor the structural evolution carbon nanotubes, graphene, or fullerene-like particles demonstrate a variety of interesting transformations when exposed to electron irradiation. This is due to the unique ability of graphene to reconstruct after the formation of vacancies. The controlled formation of vacancies or interstitials is the key to 'nanoengineering'

of nanotubes or related graphitic structures.

After the break, the focus shifted from carbon to insulating materials. Clemens Barth presented highly resolved Scanning Force Microscopy studies of alkali halides, demonstrating the power of the technique in studying the role of impurities in the ionic materials in modifying the structure, composition and charge state of the surfaces which will be the focus of the talk. The theme was continued with Alexander Shluger's detailed theoretical study of electron trapping in high-k materials. This was supported by a comprehensive study of different impurities and their influence on the electronic structure, and the role of grain boundaries in defect creation and migration.

In the afternoon, there was series of excellent contributed talks building on the foundations of the morning. Leandra Liborio used ab initio thermodynamics to calculate the formation energies, at different environmental conditions, of different oxygen-defective structures in rutile. Irene Suarez-Martinez used DFT (AIMPRO) and DFTB+ codes to examine both graphene and CNTs with a variety of oxygen plasma induced defects, as well as their interaction with a variety of metal species such as Ti, Pd and Au. They further correlated their results with experimental HRTEM, XPS and X-ray and Ultraviolet photoemission spectroscopy results of both plasma- treated and non-treated CNTs. Vanja Lindberg studied the interaction of CO with metal nanoparticles and showed that the charge transfer between the nano particle and the CO molecule depends critically on the nano particle size, and that this dependence is intimately connected to the local electronic structure at the point where the molecule approaches the particle. Carsten Muller introduced a local correlation scheme called "The Method of Increments" for fast calculations of surface processes. In this method, the correlation energy is expanded in local contributions from each atom, each atom pair, and so on.

Tuesday morning began with Kai Nordlund discussing to what extent ion irradiation data can indeed be used to validate potentials. He first briefly described some measurable quantities, such as ion range profiles, ion beam mixing, sputtering yields and threshold displacement energies, and discussed what energy range of a potential each quantity relates to. He then described molecular dynamics simulations of these quantities and how they have been able to validate or discard interatomic potentials using them. David Tomanek flamboyantly presented his first principles simulations of carbon nanosystems. He introduced photo-excitations as a selective and powerful technique to purify carbon nanotubes from chemical impurities. He showed that the effciency of the underlying photo-chemical process is high due to the long lifetime of electronic excitations in nanotubes, which is comparable to phonon periods, and that depending on the energy scale, electronic excitations may play a decisive role in determining the generation of defects during sputtering by ions.

After the break, Konstantin Neyman described his modeling strategy, developed to computationally represent at a suffciently realistic level oxide-supported nanoparticles with ~ 10^3 metal atoms, which are experimentally explored as model catalysts. In this novel approach ordered three-

dimensional nanoparticles of ~ 10^2 atoms are employed with structures cut from bulk and terminated by low-index surfaces; in this size range cluster properties are scalable to the bulk. Jean-Christophe Charlier introduced his computed constant-current STM images of defects in carbon nanostructures. He showed that these defects should also play a key role in the chemical reactivity of carbon nanotubes, and expanded the study to also include the modulation of the quantum conductance due to specific molecules adsorbed at the defected nanotube surface will also be presented.

In the afternoon, a series of contributed talks showed how multiscale methods can be used to study complex systems. Tommi Jarvi introduced Kinetic lattice Monte-Carlo simulations for studying the ordering kinetics driven by thermal and athermal vacancies in metal particles. The results reveal that post-irradiation annealing of a 4 nm FePt particle with about 60 accumulated athermal vacancies does not promote long-range order as compared to the case of thermal annealing of a non-irradiated particle. Henry Pinto studied the effect of different tip structures on the computed scanning tunneling microscopy (STM) of clean and hydroxylated rutile TiO (110). Andres Ayuela reported on first-principles calculations for metallic carbon nanotube superlattices N (12, 0)/N (6, 6) with N = 1 − 4. Marcello Rosini studied the GaAs and InAs surfaces, and calculated the energy barriers between the adatom adsorption sites within a first-principles approach using a wide set of DFT, while the surface diffusion is calculated both via the solution of the master equation for the occupation probability, and by simulations through a kinetic Monte Carlo Method.

Wednesday morning was kicked off with Lev Kantorovich presenting results of his theoretical modelling of manipulation of a large molecule, the C60 fullerene, covalently bound to the Si(001) surface. In particular, he discussed its vertical manipulation and demonstrated that it is actually possible to lift this molecule from the surface employing only the tip-molecule chemical interaction, without applying bias voltage. To achieve this, however, a special manipulation protocol has to be implemented: the molecule needs to be brought first to a precursor state where its bonding to the surface is minimised. He showed that this type of manipulation is possible in STM experiments, but that in AFM experiments this mechanism would not work since the cantilever oscillation period is much longer than atomic relaxation times, and the molecule would relax from the metastable precursor state to nearest stable site. Following the SPM theme, Renald Schaub reviewed recent studies on a prototypical model oxide system - the rutile TiO_2 (110) surface - where he has exploited high-resolution, variable-temperature and time-resolved STM to study how oxygen vacancies influence surface and interface reactions. Hannu Hakkinen discussed a recent breakthrough in experimental characterization of a ~ 20 kDa thiolate-protected gold particle, for which the structure is now resolved with atomic precision by X-ray diffraction from a single crystal sample. The results confirm in part the predictions from his ealier "divide and protect" model. He then presented a recent density-functional investigation which has now unveiled the detailed electronic structure of the experimentally characterized compound, and found the reasons for the extraordinary stability. Miguel Gosalvez's talk focuses on

the presentation of two prominent examples of currently available atomistic simulation tools for evolving complex interfaces, namely Kinetic Monte Carlo (KMC) and Cellular Automata (CA) methods, showing their similarities and differences, and stressing their relative strengths and weaknesses for the simulation of an evolving complex interface.

The workshop closed with two talks looking at the influence of vacancies on electronic structure properties. Andriotis looked at the role of vacancies in the magnetic properties of C_{60} nanostructures. Zhukovskii calculated the electronic structure of AlN and BN nanotubes with varying concentrations of vacancies. The workshop was also supported by a long and vibrant poster session, with many exciting contributions.

Impact and future direction

The workshop repeatedly demonstrated a strong link between the researchers studying different materials and processes, particularly in methodology and in the role of defects and impurities. Specific links were seen in the: understanding of magnetism in carbon and oxides due to intrinsic defects and non-magnetic materials; mapping of charge distribution in high resolution of alkali halides and high-k oxides via Kelvin Probe Microscopy; testing of atomistic potentials in metals and carbon; methods for higher accuracy treatment of electron correlation; methods for treating the time-dependence of excited states. In general the participants were pleased with the format and structure of the workshop, and encouraged us to organize a similar one in the future.

Final programme

Monday

8:45 – 9:00 15 min A. Foster Introduction
9:00 – 9:45 45 min M. Moseler Understanding carbon nano-materials by multiscale simulation
9:45 – 10:30 45 min F. Banhart Defects and diffusion in carbon nanomaterials: experiments in the electron microscope
10:30 – 11:00 30 min Coffee
11:00 – 11:45 45 min C. Barth The (001) surfaces of ionic crystals under the influence of impurities: A dynamic scanning force microscopy study
11:45 – 12:30 45 min A. Shluger Electron and hole trapping in oxides: amorphous vs. crystalline materials
12:30 – 13:30 1 h Lunch
13:30 – 14:00 30 min L. Liborio Ab initio thermodynamics of oxygen defective TiO2-x: The Magneli phases
14:00 – 14:30 30 min I. Suarez-Martinez Metal decorated carbon nanotubes: towards gas sensing applications
14:30 – 15:00 30 min V. Lindberg First principles study of CO reactivity on metallic nano particles

15:00 – 15:30 30 min C. Müller Fast and accurate first principles calculations for CO adsorption on ceria
15:30 – 17:00 1 h 30 min Posters

Tuesday

9:00 – 9:45 45 min K. Nordlund Can irradiation experiments be used to validate interatomic potentials?
9:45 – 10:30 45 min D. Tománek Defect engineering of nanostructures
10:30 – 11:00 30 min Coffee
11:00 – 11:45 45 min K. Neyman Beyond the approach of single-crystal surfaces: Nano-sized metal and oxide particles as realistic models of catalytic materials
11:45 – 12:30 45 min J-C. Charlier Using defects in carbon nanotubes
12:30 – 13:30 1 h Lunch
13:30 – 14:00 30 min T. T. Järvi Enhancing chemical ordering in FePt nanoparticles by ion irradiation
14:00 – 14:30 30 min H. Pinto Modelling the effect of tip structure in STM of clean and hydroxylated rutile TiO2 (110)
14:30 – 15:00 30 min A. Ayuela First-principles calculations of carbon nanotube superlattices
15:00 – 15:30 30 min M. Rosini In adsorption and diffusion on In-rich (2x4) reconstructed InGaAs surfaces on GaAs(001)
15:30 – 17:00 1 h 30 min Posters
18:00 – 21:00 Dinner

Wednesday

9:00 – 9:45 45 min L. Kantorovich Manipulation of covalently bound molecules with STM and AFM: role of tip-molecule interaction
9:45 – 10:30 45 min R. Schaub High-resolution scanning tunneling microscopy studies of surface reactions on rutile TiO2 (110)
10:30 – 11:00 30 min Coffee
11:00 – 11:45 45 min H. Häkkinen Structure of thiolate-passivated gold nanoparticles: a breakthrough and a dream-come-true
11:45 – 12:30 45 min M. A. Gosálvez Atomistic simulation of etching
12:30 – 13:30 1 h Lunch
13:30 – 14:00 30 min A. N. Andriotis Induced magnetism in carbon-based and non-traditional inorganic molecules
14:00 – 14:30 30 min Y. Zhukovskii Influence of N vacancies on structural and electronic properties of AIN and BN nanotubes

Posters