

**Joint Chemical & Semiconductor Industry Research Needs  
for Modeling of Nanomaterials**

**Chemical Industry Vision 2020**

**&**

**Semiconductor Research Corporation/ SNB Consultative WG 2**

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## Executive Summary

In 2003, the US Chemical Industry Vision2020 published a nanotechnology research needs roadmap<sup>1</sup>, and in 2004 the US Semiconductor Industry independently published a nanotechnology research needs document. While many of the research needs identified in these roadmaps were very different, both industry groups identified the need for fundamental understanding and modeling of synthesis and material properties that can integrate from the atomic scale through the macroscale and over multiple timescales. In 2005, a work group between the Chemical and Semiconductor Industries was formed to identify common research needs.

On May 24-25, 2006, the Chemical Industry Vision 2020, and Semiconductor Research Corporation held a meeting at the National Institute of Standards and Technology (NIST) with university, national laboratory and industrial researchers to identify the critical needs for developing improved nanomaterial models for predicting structure, composition and properties.

High-performance materials applications require simultaneous optimization of multiple properties such as electronic, mechanical, surface chemical reactivity, and others. Some nanomaterials possess unique properties that make them candidates to enhance or replace conventional materials and approaches, but the need for optimization of multiple properties requires models that correlate nanostructure to properties.

Examples of these joint needs to optimize multiple properties include low dielectric constant materials for chip level interconnect isolation, chemicals and polymers with improved control of purity and properties, and controlling chemical reactivity of carbon nanotubes. Our industries are seeking an ultra low dielectric constant material with high mechanical strength, no water absorption, and excellent adhesion to multiple surfaces. Similarly, the semiconductor industry needs organic molecules and polymers with tighter control of properties and the chemical industry uses nanostructured catalyst to control the molecular weight of polymers and the purity of organic chemicals. While these examples represent a few of the common nanomaterial needs, the modeling capabilities identified in this document could be used for many joint nanomaterials, and for optimizing nanomaterials for many other applications in each industry.

Both industries agree that predictive models are needed for: optimization of the *synthesis of nanoparticles, surface chemical reactivity, electronic and transport properties, nanomechanical properties, and properties of self-assembled materials*. These modeling needs are discussed in more detail in the following document.

*Cross Cutting Modeling Needs:* Several common themes cross all model areas:

1. Innovative algorithms to model over multiple length and timescales for realistic system sizes
  - More foundational long term algorithm development is needed
2. Close collaboration between modelers and experimentalists to design experiments and validate models
3. Systematic experiments that develop fundamental understanding
  - Experiments that are on a scale that models can duplicate
  - Metrology to characterize structure and properties of materials at the nanometer scale with analysis to decouple probe-sample interactions
4. Modelers need increased access to high speed computing capabilities
5. Guidelines to improve portability of models on existing operating systems and hardware platforms

**Projected Benefits:** Robust models of the fundamental scientific principles operating at the nanoscale, including interdependent structure-property relationships will enable cost-effective design, synthesis, and scale-up of materials that deliver optimized properties, allowing industry to focus on the *requirements for specific applications* as the primary drivers of the design process. The capability will accelerate nanomaterial development, moving the field from today's discovery-based science and product development to application-based problem solving in the future.

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<sup>1</sup> *Chemical Industry R&D Roadmap for Nanomaterials by Design: from Fundamentals to Function*, December 2003; available at [http://www.chemicalvision2020.org/pdfs/nano\\_roadmap.pdf](http://www.chemicalvision2020.org/pdfs/nano_roadmap.pdf)

## Nanoparticle Synthesis

**Goal:** Development of integrated modeling systems that predict nanotube structure and growth rate from nucleation to full size as a function of process conditions. Nanostructure includes number of walls, diameter, chirality, number of tubes, growth direction and defects. These models will be experimentally validated on a set of well characterized experiments and be capable of predicting growth of nanoparticles under new conditions. Development of this predictive capability would enable modeling of synthesis of other covalently bonded nanotubes and nano-particles, including boron-nitride and other yet to be identified nanostructures.

**Motivation and potential applications:** Control of carbon nanotube properties is identified by both industries as important because of their potential applications and because control of their synthesis poses a number of cross-cutting modeling issues that can be translated to other materials. The semiconductor industry is exploring the potential application of carbon nanotubes as devices and interconnects and will need materials with tight control of electronic properties, which means tight control of nanostructure. Similarly, the chemical industry will need reproducible control of nanostructure to provide high-purity materials to the semiconductor or electronics industry for other applications. Thus, both industries need models that predict nanotube structure as a function of catalyst composition and nanostructure, temperature, gas composition, applied fields, and growth conditions to enable control of properties.

**Research Needs:** Current *ab initio*-based molecular dynamics modeling programs are limited to simulating structures with less than 100 catalyst atoms and with picosecond time scales, while most experiments are performed on larger catalysts and with much longer-time sampling of the growth phenomena, which limits experimental validation of models. Further, models are currently unable to seamlessly bridge the processes of nanotube synthesis over the full range of time and length scales and to accurately predict reaction energetics, kinetics, and nanostructure.

*Innovative Algorithms:* Research is needed on innovative algorithms to model nanotube growth, with models that comprehend the full reaction system, from nucleation at the nanometer scale, to much longer length and timescales.

*Model Validation:* Modelers and experimentalist need to closely collaborate to design experiments and simulations that can validate kinetic-based models and provide insight to the fundamental mechanisms of the growth process.

- Experiments need to be performed that are compatible with modeling capability, the number of atoms in the catalyst and nanostructure, etc.
- Experiments need to be designed such that they enable quantitative characterization of chemical reactions, intermediate states, catalyst nanostructure, surface chemistry, growth mechanisms and their effect on structure, morphology and physical properties.
- Application of a multitude of spectroscopic and microscopy techniques may need to be applied to monitor *in situ* nucleation and growth of nanotubes.
- Results will need to be reproduced with a **statistically significant number of experiments** to ensure validity of energetics, kinetics and mechanisms for the models.

**Projected Benefits:** These improved models would potentially enable design of catalysts and processes to control nanotube structure as well as exploration of new nanoparticle compositions and structures. Nanotubes have many potential applications, but many need control of electronic properties and this could enable design of growth processes to control these.

## Surface Chemical Reactivity

**Goal:** To develop validated modeling and simulation methods to improve the design, development, and manufacture of nanoscale structures with desirable surface, characteristics and reactivity, and to link these properties with macroscopic performance.

**Motivation and potential applications:** Understanding and controlling surface chemical reactivity is critical in both the chemical and semiconductor industries for design and development of catalysts, sensors, high reliability interfaces and coatings, nanocomposites, and devices fabricated by surface growth processes.

**Research Needs:** Both the chemical and the semiconductor industries have the need to link the nanoscale with the reactor scale, particularly for catalysis and film growth applications.

*Improved models of electronic states, interactions, and reactions:* The key challenges for modeling surface chemistry using periodic DFT are methods that scale faster than conventional  $N^3$  approaches (preferably  $N \log(N)$  or less), include long-range dispersion (van der Waals), handle strongly correlated electrons, excited states (including band gaps), and predict kinetic barrier heights. More effective bridging of physical phenomena over multiple length scales will require faster semiempirical methods, hybrid quantum/classical approaches, and methods to bridge the fundamental physics at the atomistic regime with continuum models seamlessly. To bridge time scales, improvements in dynamics and Kinetic Monte Carlo methods are essential.

*Design of experiments for model validation:* Development of validated models to capture essential features and physics of multiscale systems requires time-resolved atomistic experiments and detailed characterization of reactant streams, products, evolving surface structures, and particle phases. It is critical that experimental and modeling teams collaborate in identifying reactions and characterization capabilities that will enable validation of the structure of reaction surfaces and the intermediate steps in reactions. Selection of one or two classes of model systems to focus this diverse experimental and theoretical work would be invaluable.

*Systematic characterization of reactions:* Experimental characterization of surface structure, properties, and chemistry at the nanoscale is exceedingly difficult. No single technique is universally applicable; combinations of complementary structural, microscopy and spectroscopic techniques are frequently required to characterize a single surface. As reactions proceed, surface structure, molecular species, and intermediate states must be monitored to identify the reactions occurring. Since the reaction rate depends exponentially on the kinetic barrier height, identifying and validating the rate-limiting step in a reaction is critical to understanding the mechanism and energetics. Additional difficulties arise at the nanoscale because it becomes more difficult to obtain statistics, probes perturb the sample, and the presence of defects can dominate or destroy performance. Hence, there is a need for careful, systematic, repetitive measurements to characterize surfaces and species at different stages of reactions. Experimental teams need to work closely with theoreticians and modelers to ensure the right questions are being asked, and to aid in interpretation of experiments on a relevant time scale.

*New metrology with quantitative analysis:* To enable quantitative monitoring of structure and reactions at surfaces, a high priority is the development of both experimental and theoretical methods to extract chemical information from scanning microscopy experiments.

**Projected benefits:** Many of the unique and desirable properties of nanostructures are a function of the surface structure, properties, and chemistry. It is necessary to have available a range of flexible, validated tools to address specific questions as they arise. The enabling benefits of modeling include the examination and evaluation of factors that result in fundamental mechanistic understanding at the atomic level; shortened product development cycles; an improvement in the sophistication of our interpretation of experimental data; and ultimately play a stronger role in the discovery and design of surfaces with optimized or new properties.

## Nanomechanical and Interfacial Properties

**Goal:** Development of integrated modeling systems that predict mechanical and interfacial properties for nanostructured materials in macroscale structures that are experimentally validated on a well characterized set of experiments. These models must simulate material system behavior and make predictions that are quantitatively accurate.

**Motivation and Potential Applications:** The chemical and semiconductor industries need high-performance materials with new properties, but these must have improved mechanical and interfacial performance to be reliable through their application life. Integrated circuit packaging materials for future technologies will need to maintain the silicon in a low-stress state through many years of temperature cycling and operation. Addition of nanomaterials to polymers may improve properties. Similarly, new self-assembled nanomaterials may find application in lithography or as nanoporous dielectrics, but they must have stable mechanical and interface properties during harsh process and use conditions.

### Research Needs:

Innovative computational algorithms must be developed and validated against well characterized experiments to provide guiding principles for the design of nanomaterials with required mechanical and interfacial properties. Also, new metrology capabilities are required to create basic understanding and knowledge to enable development of better nanostructured materials.

*Algorithm Development:* The algorithms must couple long range thermodynamic and mechanical state fields with time-dependent changes in structure, incorporating short time effects, such as bond breakage as well as long time effects such as diffusion.

- Self-consistent linkages between different physical regimes (long range, macroscopic to nanometer scale)
- In some cases, complex phases can exist at interfaces between nanostructured materials and the bulk matrix material; models need to predict structure and properties.

*Model Validation:* Validate models on a suite of well characterized nanomechanical and interfacial samples and disseminate standard reference simulations.

- Nanomaterial building blocks
- Nanocomposite materials
- Ultra-thin films & interfaces

*Nanometrology Capabilities:* New metrology tools are needed to characterize:

- Anisotropic properties of nanostructured materials
- Mechanical properties of embedded interfaces and ultra-thin films
- Electronic, chemical, and physical properties as a function of stress state
- Analysis to decouple probe-sample interactions and enable property extraction
- Residual material stress characterization

*Nanomechanical Calibration:* Nanomechanical force calibration standards and reference samples are needed to enable correlation between experiments.

**Projected Benefits:** Developing these models would enable both the evaluation of mechanical and interfacial properties of nanomaterials, and thus their viable design, for a wide range of applications. This should dramatically reduce experimental characterization and reliability testing of new materials that require optimization of multiple properties.

## Electronic Properties and Electronic Transport

**Goal:** The goal of this research initiative is to develop quantitatively accurate approaches, validated by experiment, to calculate the electronic properties and electronic transport of nanomaterials in integrated applications.

**Motivation and potential applications:** The electronic properties of materials determine almost all of their behavior, including electrical, optical, mechanical and chemical including catalytic. At the nanoscale, size effects can dramatically change the electronic structure; for example, the bandgap of carbon nanotubes and nanoparticle energy levels depend sensitively on their diameter. This control over the electronic structure provides unique opportunities for the Chemical and Semiconductor industries. For example, nanowire or nanotube electronic devices may have applications in integrated circuits or sensors, other nanoparticles may have value in light-emitting devices, energy conversion, or radical information processing device elements. In all of these cases, harnessing the ultimate potential of nanomaterials will require a detailed understanding of their electronic and electronic transport properties.

**Key research challenges:**

*Improved physical models:* Existing *ab initio* modeling approaches (Density Functional Theory in the Local Density Approximation) are inaccurate for excited states, which are critical for electronic and electronic transport properties. Thus, research efforts are needed to develop many-body approaches for calculating accurately the electronic structure of nanomaterials. Development of semi-empirical models is also needed to simulate complex systems, such as devices with nanostructures as the active elements.

*Development of new computational algorithms:* *Ab initio* modeling of the electronic properties in complex nanostructures (> 1000 atoms) is far beyond the computational capability of existing approaches, and if more accurate many-body approaches are used, this will become even more challenging. Research is needed into new more computationally efficient numerical algorithms, which may require teams of mathematicians, modelers, and computer scientists to work together on this common goal.

*Validation of models on well characterized experiments:* To develop quantitatively accurate models, it will be critical to benchmark their accuracy on a number of well characterized nanostructured materials. Modeling of electronic and transport properties of nanostructured materials requires a detailed understanding of the structure of the material, interfaces, disorder and defects, and many techniques may need to be applied for an accurate determination. Characterization of the transport mechanism may also require application of multiple diagnostic techniques to correlate the transport path to the physical structure. Since atomistic details can dramatically change electronic and transport properties, detailed experiments are needed to systematically identify and validate the nanostructure properties. Thus, there is a need for statistically significant, reproducible experiments by multiple researchers with careful validation of properties and mechanisms with multiple techniques; and detailed, atomistic level characterization of structure, composition and interfaces.

**Potential Benefits:** Accurate methods to calculate the electronic properties and electronic transport of nanomaterials would enable the design and fundamental understanding of novel devices based on nanostructures. Such devices will be required to enable continuation of integrated circuit technology toward nanometer scale device technologies and enable novel higher-performance, low-cost devices for new applications.

## Self-Assembled Nanomaterials

**Goal:** Predictive modeling methods that enable the design of self-assembled nanoscale materials, at specified locations, with controlled macroscopic properties, functionality, and dynamics.

**Motivation and potential applications:** The Chemical and Semiconductor industries share common interest in being able to design self-assembled materials with predictable electronic, mechanical and surface and chemical properties. Examples include nanoporous low- $\kappa$  dielectrics and directed self-assembling materials for patterning applications, where dimensional control, mechanical stability, chemical stability, and functionality are essential. Additionally, new families of ordered nanoscopic structures are sought that exhibit novel properties, such as self-healing behaviors or anisotropic properties not observed in amorphous bulk systems.

**Key self-assembly modeling research challenges:** Current algorithms are not sufficient to predict nanostructure, composition, and the resulting electronic, mechanical, and surface chemical reactivity self consistently. Furthermore, multiple properties of self-assembled nanomaterials are not characterized; in some cases metrology does not exist to measure anisotropic properties of these materials at the nanometer scale.

Specific studies are needed in the following areas:

- *Property Modeling:* While methods are emerging to model self-assembled structures, the current state-of-the-art models are limited in their **ability to predict properties, design, and synthesize materials with desired behaviors**. Coordinated modeling and experimental initiatives are needed that explore and develop the foundational theory, guiding design principles, modes, and limits of self-organizing systems. Currently, only structures are calculated and there is limited ability to model properties from nanostructure and composition for smaller structures.
- *Experiments Designed for Fundamental Understanding of the Structure Property Relationship:* Currently few properties of self assembled structures are characterized; even in self assembly of block co-polymers, currently only isotropic mechanical properties can be measured. For more complex self-assembled structures, systematic characterization of structure with electronic, chemical and mechanical properties is needed. This characterization should include other structural properties, including local bonding, defects, interface roughness, surface structure and local composition. Experiments should correlate thermodynamic and kinetic properties, such as annealing, diffusion, phase, and packing behaviors; and degree of dimensional and positional control to nanometer- and macro-scale properties.
- **Access to sufficiently large-scale and high-speed computational resources** is needed that enables the development of suitable, thermodynamically consistent coarse-grain models and non-equilibrium methods for polymeric systems.
- **Atomic and nanoscale in-situ characterization and monitoring capabilities:** Metrology is needed to characterize local structure and bonding in these highly anisotropic structures and to characterize 3D mechanical, electronic and chemical attributes at the nanometer scale.

**Potential Benefits:** The proposed modeling and infrastructure improvements would stimulate the design and discovery of new families of self-assembling materials that exhibit useful and predictable properties. Breakthrough advances in these material systems would enable many potential applications, create new and competitive fabrication methods, and open new markets in useful and functional nanomaterials for the chemical and semiconductor industries.

## **Nanomaterial Modeling Research Needs**

## Nanoparticle Synthesis

### Status of Modeling:

Current *ab initio*-based molecular dynamics modeling programs are limited to simulating nanotube growth with less than 100 catalyst atoms and with picosecond timescales, while most actual growth experiments are performed with larger catalyst and with much longer time steps. These *ab initio* models depend on models of electronic interaction potentials and significant improvements have been made in Density Function Theory. Alternate approaches, such as reactive force field modeling or tight-binding molecular dynamics are able to model larger structures over longer time scales, but require significant use of parameterized models and these need significant improvement and testing to enable predictability for a wide range of materials. Thus, *ab initio* models to study nucleation and growth of nanoparticles are limited to catalyst < 100 atoms, and timescales on the order of  $10^{-12}$  to  $10^{-9}$  seconds while experiments can characterize growth on the  $10^{-6}$  to  $10^3$  sec time scale for catalyst with several thousand atoms. With current algorithms, increased computing power alone will not enable modeling of growth effects at current experimental length and timescales in the foreseeable future.

There has been limited application of statistical methods, such as kinetic Monte-Carlo, and continuum approaches, e.g., conservation equation approaches. Initial results from these studies are limited in atomistic detail or material specificity, but interesting in that they can address experimental length and time scales.

### Modeling Research Needs

1. Research is needed to develop innovative multi-scale algorithms to enable modeling of larger structures over longer timescales with computing capabilities that will be available in the next 5-10 years.
  - a. May require collaboration between experimentalist, modelers, computer scientists and mathematicians.
2. Research into novel algorithms for self-consistent coupling continuum descriptions of the growth process to statistical and atomistic descriptions.
3. Continue to improve the accuracy of models for the chemical bonding interactions in the simulators.
4. Improve models of local thermal transport
5. Expand or develop models to include non-bonding interactions (van der Waal's, electric fields, etc)
6. Increased access of modelers to high speed computers to accelerate algorithm development and model validation.
7. Design and execute experiments that enable validation of models and physical understanding
  - a. Catalyst size and structure compatible with model capabilities (<100 atoms)
    - i. Determine the minimum catalyst size for nanotube growth
  - b. Physical, chemical & electronic state of the catalyst
    - i. Liquid, solid, crystalline, amorphous
    - ii. Catalyst nanostructure
    - iii. Metallic, oxide, carbide, etc.
    - iv. Energy levels of the catalyst & surface
  - c. Arrangement of atoms on the catalyst prior to and during growth
    - i. How do surface atoms rearrange?
    - ii. Determine energy levels of different states
  - d. Role of chemical precursors
    - i. Chemical and electronic energy state of precursors in the gas phase
    - ii. Chemical, electronic and kinetic states of precursors in and on the catalyst
      1. Role of other species in kinetics (H, O, etc)
    - iii. Presence of any species on or in the catalyst (C, H, O, etc)
  - e. Fundamental nature of the nanoparticle-carbon nanotube growth interface and the carbon segregation process from the catalyst particle.

- f. Experiments with homogeneous and heterogeneous catalysts to understand effects on reactions
  - g. Sub nanometer scale characterization of thermal and phonon effects
  - h. Characterization of substrate effect on catalyst, kinetics & growth
8. Increased interaction with the surface science and catalyst research communities may be required to accelerate characterization of surface chemical reactions

Algorithm Development: With current *ab initio* calculations requiring significant computation time to simulate several picoseconds of growth, it is not reasonable to extend these to calculating growth of structures or thin films. New computational algorithms are needed to model growth from nucleation to full tube growth over minutes of time. The development of algorithms to model over multiple length and timescales and improvement of models will require increased access to high performance computing capabilities and may require increased interaction between mathematical researchers, modelers, computer scientists, and experimentalists. Research is needed into novel algorithms for self-consistent coupling continuum descriptions of the growth process to statistical and atomistic descriptions.

For model improvement, close collaboration will be needed between modelers and experimentalists to design experiments that can effectively validate models. Current *ab initio* modeling can be only done at timescales many orders of magnitude smaller than can be experimentally captured, so experiments must be designed to validate and improve models. Initial experiments are needed to understand nanotube growth on catalysts with a size and composition compatible with modeling. Furthermore, experiments are needed to characterize growth of nanotubes with a range of nanostructures. Characterization of the kinetics of nanotube growth may require engagement with the surface chemical research community and application of a broad range of *in situ* characterization techniques.

Many fundamental issues on the role of the catalyst in nanotube growth are unresolved, and multiple *in situ* characterization techniques may need to be used simultaneously to understand this. It is critical to understand the structure of the catalyst whether it is solid, liquid or amorphous, whether the carbon is dissolved in the catalyst or is only on the surface in nucleation and growth. Furthermore, the surface structure of the catalyst may be critical in the nucleation process and the role of surface structure in the growth of nanotubes. Since the growth is complex with many interactions occurring, validation of model predictions of catalyst structure and role during growth is critical.

Similarly, understanding the interactions of the precursors with the surface and with the catalyst and each other is critical to understanding the mechanisms. This will require modelers to work with surface chemist to devise experiments to monitor the states of gas species above the surface of the catalyst and as they adsorb onto the catalyst. It is known that the presence of some gases, such as H<sub>2</sub>O can dramatically increase growth rates, so it is important to understand its role in the growth process. It will be critical to understand and find ways to monitor any potential intermediate species as a function of temperature and partial pressures to develop valid kinetic models of the growth process.

As reactions occur on the nanometer scale catalysts, modelers need to understand whether the adsorption and growth processes change the local phonon spectrum and generate sub nm scale heating effects. Local heating could result in dramatic changes in reaction kinetics, so this may need to be studied.

Understanding the role of the catalyst and its nanostructure on the resulting nanotube may enable design of catalyst with improved control of diameter and chirality. This would be a major breakthrough in the ability to grow nanotubes with predetermined properties.

Developing this understanding will require a range of experimental capabilities be applied to the characterization of the nanostructure and kinetics. Since many of these effects may be coupled, experiments will need to be designed to deconvolve factors. Critical experiments need to be repeated multiple times by multiple groups to develop statistically significant information on reaction mechanisms and kinetics.

## Surface Chemical Reactivity

### **Status of Modeling:**

Surface chemical reactivity is essentially an electronic interaction, so modeling depends heavily on the accuracy of the electronic models including the ground and excited energy levels. Furthermore, the surface chemical reactivity of a nanomaterial also depends on the structure of the surface prior to the interaction. Modeling of surface interactions works reasonably well with finite cluster Quantum Chemistry modeling of covalently bonded materials, periodic Density Function Theory for modeling crystalline materials without charge transfer, photochemistry, and many-body effects, while the Embedded Cluster method is good for metals and ionic crystals. Modeling of chemical reaction rates is very challenging because it depends exponentially on the energy barrier height, and often the barrier heights are not well characterized experimentally, and the rate limiting step is not well established with intermediate kinetics. Thus, improvement in surface chemical reactivity modeling will require improved modeling of electronic energy levels in nanomaterials, improved understanding of the surface structure prior to and in a reaction and improved understanding of kinetics of a number of chemical reactions.

**Research Needs:** Both the chemical and the semiconductor industries have the need to link the nanoscale with the reactor scale, particularly for catalysis and film growth applications self consistently.

*Improved models of electronic states, interactions, and reactions:* While a number of surface reactions can be modeled well, the key challenges for modeling surface chemistry using periodic DFT are methods that scale faster than conventional  $N^3$  approaches, include long range dispersion (van der Waals), handle materials with strongly correlated electrons, excited states (including band gaps) for materials with many body effects, and accurate calculation of kinetic barrier heights.

*Design of experiments for model validation:* Development of validated models to capture essential features and physics of the multiscale system requires time-resolved atomistic experiments and detailed characterization of reactant streams, products, evolving surface structures, and particle phases. It is critical that experimental and modeling teams collaborate in identifying reactions and characterization capabilities that will enable validation of the structure of reaction surfaces and the intermediate steps in reactions. Selection of one or two classes of model systems to focus this diverse experimental and theoretical work would be invaluable.

*Systematic characterization of reactions:* Experimental characterization of surface structure, properties, and chemistry at the nanoscale is exceedingly difficult. No single technique is universally applicable; combinations of complementary structural, microscopy and spectroscopic techniques are frequently required to characterize a single surface. As reactions begin, surface structure, molecular species, intermediate states must be monitored to identify the kinetic reactions occurring. Since the reaction rate depends exponentially on the kinetic barrier height, identifying and validating the rate limiting step in a reaction is critical to understanding the mechanism and energetics. Additional difficulties arise at the nanoscale because it becomes more difficult to get statistics, probes perturb the sample, and the presence of defects can dominate or destroy performance. Thus, there is a need for careful, systematic, repetitive measurements to characterize surfaces and species at different stages of reactions. Experimental teams need to work closely with theoreticians and modelers to ensure the right questions are being asked, and to aid in interpretation of experiments on a relevant time-scale.

*New metrology with quantitative analysis:* To enable quantitative monitoring of structure and reactions at surfaces, a high priority is the development of both experimental and theoretical methods to use phase contrast and extract chemical information from scanning microscopy experiments.

**Projected benefits:** Many of the unique and desirable properties of nanostructures are a function of the surface structure, properties, and chemistry. It is necessary to have available a range of flexible, validated tools to address specific questions as they arise. The enabling benefits of modeling include the examination and evaluation of factors that result in fundamental mechanistic understanding at the atomic

level; shortened product development cycles; an improvement in the sophistication of our interpretation of experimental data; and ultimately play a stronger role in the discovery and design of surfaces with optimized or new properties.

## **Nanomechanical and Interfacial Properties**

### Goal:

Experimentally validated models of nanostructured materials which accurately predict mechanical and interfacial material properties are sought. Models must simulate material system behavior and make predictions that are both qualitatively correct (predicting the correct mechanisms) and quantitatively accurate (with known uncertainties). Models must address the long-term feedback loop between the stresses within the system, structural and thermodynamic states within the system and the mechanical response. Models must be applicable during the full life cycle of a material as it is involved in device fabrication, packaging and product use.

### Motivation:

The chemical and semiconductor industries are constantly facing the need to develop materials with improved mechanical and interfacial performance to stay competitive and provide sustained growth. Improvements in materials performance based on nanotechnology may comprise novel structures, for example based on composite inclusions, ultrathin films, hierarchical structures, designer shapes and multiple phases. Improved material technologies typically also require enhanced functionality, multiple-material compatibility requirements and increased ultimate performance levels of several properties simultaneously. The discovery and design of such materials technologies will require unprecedented levels of understanding and control of compositional, structural and interfacial properties. Therefore there is a strategic and common goal for both industries to develop experimental and theoretical tools to achieve the necessary knowledge to develop new materials.

There are several basic properties that must be measured or predicted and coupled to multiple phase systems. Such properties include: linear, small strain shear and bulk moduli; time and temperature dependent creeping and aging; large strain plasticity; yield; ultimate fracture and failure; adhesion, bonding and weld strengths; coupled responses to electrical, optical and magnetic stimuli; as well as correlations with thermodynamic state descriptors such as internal and Gibbs energies. Instrumental hardware for measuring nanomechanical and interfacial properties with high accuracy and resolution are still lacking, particularly for materials with moduli under 10 GPa. Calibration procedures are largely absent in the current literature. Thus reliable experimental results for comparing to computational models are widely unavailable. State-of-the-art theory and computational modeling methods can currently compute stress tensors and thermodynamic state descriptors for limited types of homogeneous, bulk materials. However even the best current methods are unable to model over multiple length scales and time scales, as required to compute the aforementioned properties for nanostructured materials. Furthermore there have been very few studies in which computational models and experimental data compared and validated for consistency and accuracy for all materials of interest. To overcome these vast deficits in knowledge, there must be well-coordinated, new developments in experimental tools, theory and computational models.

### Research Needs: Experimental Challenges

New experimental tools are required to create basic understanding and knowledge to develop new and better nanostructured materials. Guiding principles must be developed for the design of bulk monoliths, films, wires, , ropes and other shaped materials as well as the selection of their composition and means of fabrication with the properties required for an application. Applications may use nanostructured materials as either basic building blocks for micromechanical devices or for bulk, high-performance engineering materials. Control of interfacial properties is often critical. Materials in the forms of ultrathin films, nanoparticles, nanoporous and other nanostructured composites must be able to be synthesized reproducibly. Instrumental hardware is required for measuring nanomechanical and interfacial properties. In many nanostructured materials the characterization of buried interfaces is critical to understand interfacial properties. The hardware must be fabricated so that standardizable measurements become more commonly available and facile while having the required resolution for both

soft and hard materials. Such hardware must be accompanied by calibration and certification procedures. Standardized test materials and data analysis procedures must be developed. The analysis of data must be able to quantify standard properties as well as provide mechanistic understanding. Specifically, it is necessary to understand the roles of diffusive, transient changes in molecular structure on time-dependent properties. Many nanomechanical tests comprise underlying stochastic processes that must be determined to interpret best the inherent property measurement noise and variation observed. Furthermore measurement and characterization methods must provide insight into how chemical impurities and defects affect thermomechanical properties. Finally, experimental characterizations must be sufficiently well understood to permit direct comparison to theoretical and computational models.

### Research Needs: Modeling Challenges

There is considerable support for research to develop theory, computational models and foundational knowledge bases that correlate and predict interfacial adhesion and mechanical properties of nanostructured materials. Such research efforts must contribute to the design of materials, prediction of material properties of specified nanostructures as well as the prediction of material performance during a material's application lifetime. Lifetime application assessment most frequently requires the analysis of coupling between mechanical and other material properties. The great complexity in this challenge arises from the underlying coupling between molecular structure, mesoscale structure and mechanical response. Since the salient physical processes occur over a multitude of length scales and time scales, new methods must be developed to enable modeling across these scales. Multiple time and length scale models must appropriately incorporate boundary conditions between scales since long range effects can affect short range behavior. The role of friction across all length scales must be addressed. Ultimately modeling methodology must be benchmarked for accuracy and compatibility with experimental measurements. Models are further needed to assist the interpretation of experimental data and quantify experimental characterization. Thus the models must be further analyzed for sensitivity to experimental parameters and the influence of stochastic processes present in experiments. Predictive models are needed to determine when unusual, new phenomena or unexpected, unique property enhancements can occur due directly from nanoscale physics. Computational models must be efficiently implemented on both common research computers as well as supercomputer resources.

#### Recommendations:

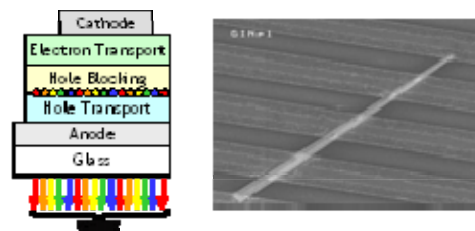
The following recommendations are proposed to facilitate direct and meaningful comparisons between experimental characterizations and predictive computational models.

- Select a few well-controlled experimental geometries
- Carefully characterize experimental system with statistical analysis
- Incorporate all relevant experimental data into models
- Model multi-scale system and compare iteratively with experimental results
- Develop and disseminate standard reference simulations: a complete set of experimentally-validated boundary conditions for a multi-scale model of an experiment

Substantial modeling infrastructure development will be necessary for ensuring robust model evaluation, comparison, and benchmarking against experimental results. A critical mass of computational resources is needed to support this effort. This may require cooperation between university researchers, industrial research and development laboratories and national laboratories. The development of standard interfaces and operating environments would facilitate the application of new computational approaches across the broader modeling community.

## Electronic Properties and Electronic Transport

As discussed in the executive summary, the Chemical and Semiconductor industries share interest for establishing research programs to enable understanding and design of the electronic structure and electronic transport properties of nanostructured materials. These programs should couple strongly with experiments that provide critical insight. Specific research of interest includes:



- *Development and improvement of methods for electronic structure and electronic transport calculations*

Currently, most ab initio approaches for calculating the electronic structure of materials are largely based on Density Functional Theory (for e.g. implemented in the Local Density Approximation). While the DFT approach is very successful at predicting ground state properties, it is still limited on the system size that it can handle, and is unable to quantitatively predict excited state properties. Fundamental research is needed to address both of these issues, such as linear scaling methods (including algorithms) and many-body approaches for excited states (e.g. GW). Furthermore, many of the systems of interest to the Chemical and Semiconductor industries will integrate nanostructures in higher-level heterogeneous structures, requiring integrated multiscale approaches.

The left panel shows a light emitting diode with nanoparticles as the optically active layer (V. Bulovic, MIT). The right panel shows a GaN nanowire making contact to electrodes (A. Talin, Sandia).

While the basic electronic properties by themselves require attention, an extra level of complexity arises when one asks about electronic transport through nanomaterials, particularly under non-equilibrium conditions. In this area, research is needed to develop ab initio and semi-empirical approaches for electronic transport. An example of a current issue is that ab initio approaches for molecular electronics have not yet agreed on the conductance of benzenedithiol, the simplest model system. Research is needed to converge modeling results by assessing the importance of different approximations and either validating or eliminating them. The themes of linear scaling methods, many-body methods and integrated multiscale approaches are also important for electronic transport.

- *Development of experimental techniques*

The development of accurate modeling approaches requires benchmarking with experimental measurements. Thus, the success of the modeling initiative will depend on our ability to compare in detail modeling and experiment. For nanometer scale materials, characterization of the physical structure, interfaces, material intermixing, and defects is crucial to developing models. Characterization of the transport mechanisms may require application of multiple diagnostic techniques to correlate the transport to the physical structure and materials. This will require high throughput, statistically meaningful measurements; characterization of defects (including dopants) in nanostructures and characterization of the structure of interfaces (e.g. nanostructure-dielectric, organic-inorganic). Detailed, atomistic and structural information are needed, which may require the development of new experimental tools.

- *Specific problems of interest (theory, modeling, experiment)*

In addition to the method development work described above, the workshop participants also identified several specific problems of interest:

### Understanding the properties of electrical contacts between metals and nanostructures

Electrical contacts play a key role in electronic devices, and intensive efforts are invested in understanding and controlling their properties in bulk systems. At the nanoscale, entirely new issues come into play, and the properties of contacts need to be re-visited. More development is needed to model and characterize the atomic structure at the contacts, to predict and measure tunnel barriers,

discover the conditions that lead to ohmic or Schottky contacts and to decouple the transport in the material from effects of the contacts.

#### Role of defects (including dopants) or surface species for stability or sensing

Because of their small size, nanostructures can be strongly affected by the presence of defects, impurities or surface analytes. This is even more critical at smaller dimensions since the number of defects required to affect device performance is very small. For device reproducibility and stability, it is important to quantify the role of defects, dopants and of their fluctuations. Research is needed to develop models and characterize the role of defects or surface analytes on the electronic structure, and in turn the impact on electronic transport.

#### Understanding the origin and the control of noise

Regardless of the type of signal on which a device operates, noise is a critical factor that determines limits of operation. At the nanoscale, the proximity of the whole nanostructure to interfaces or/and the environment raises some fundamental questions on the importance of noise. Modeling and experimental tools are needed to calculate and measure the time-dependent fluctuations in the signal and to explain their physical origin. Approaches for noise control and reduction as well as ways to use noise itself in novel systems are areas of interest as well.

#### Photoconductivity and light emission in nanosystems

As shown in the figure, nanostructures may provide new approaches to improve optoelectronic devices. To harness this potential, a detailed understanding of optoelectronics at reduced dimensions is needed. This includes the role of electron-hole interactions (excitons), radiative versus non-radiative transitions, plasmons, etc. Research in this area should not only address the basic optical properties, but also the non-equilibrium situation of electron transport in the presence of electron-photon interactions. Characterizing the structure, electronic states, optical properties and interfacial interactions in these nanometer scale structures may require use of multiple techniques.

#### Nanoscale and novel devices

While the properties of nanostructures themselves are of interest, there is much interest in exploring the properties of devices using nanostructures as the active elements. This includes nanostructures in conventional devices (e.g. transistors) but also entirely new concepts (e.g. spin-based). Hybrid organic/bio/inorganic devices are also of interest, including novel ways to assemble them.

#### Developing standards and identifying systems for model validation.

An important area that emerged from the workshop is the need to assemble multidisciplinary teams to develop modeling and experimental standards. One of the goals of this effort would be to identify systems that are simultaneously accessible to both the modeling and experimental communities, providing a path for model validation. This will require the design of structures and experiments that can be well characterized and validated.

## Self-Assembled Nanomaterials

**Status of modeling self-assembling materials and processes:** There is a pressing need to develop a general analytic theoretical framework for classifying types of self-assembly and thermodynamic transitions involved. These theories must be validated with a range of simulation and experimental methods. Many of the greatest current theoretical difficulties revolve around the prediction of non-equilibrium growth structures and the kinetics of their growth. These structures and growth processes reflect the forces that drive ordering under far from equilibrium conditions and the local environment. However, it currently is not computationally feasible to theoretically define and predict the properties of self-assembling systems from first principle quantum calculations. The effective utilization of *directional interaction self-assembly* (DISA) to fabricate useful materials will remain a dream until this process is better understood theoretically and adequate experimental methods are developed to characterize the thermodynamic states and kinetic transitions that underlie this type of self-organization process. This problem points to the necessity of rigorous experimental and nano-characterization methodologies sufficient to support appropriate models. If modeling methods are developed that predict and enable the design of thin film materials with orientational control, the lateral ordering of the microdomains, and methods to bias the lattices of the arrays of microdomains, then self assembling materials have the potential to become a standard tool in the fabrication of nanostructured devices.

### **Summary of strategic modeling research needs that warrant support:**

- Fundamental understanding of the correlation between atomic structure, molecular configuration and conformation, symmetry, and variability with macroscopic properties;
  - Predictive models that facilitate the discovery of new material systems and useful nanoscopic properties.
- Concerted experimental, theoretical work, and faster and more powerful simulation techniques that enable predictive molecular simulations.
  - Such simulation techniques will provide useful and essential insights into the fundamental principles that govern directed self-assembly by copolymer-based materials, and the development of sub-lithographic processes that will permit large-scale fabrication of complex sub-30 nm devices
- The coupling of phase separation and self-assembly warrants a sound theoretical foundation;
  - The basic problem of understanding the dynamics of these assembly processes and the transport properties of self-assembling solutions needs significant fundamental research.
- The modeling and control of defects is difficult in utilizing these 'meso-crystalline' materials in applications and needs significant improvement.
- Model validation requires the creation of new methods that enable the integrated characterization of relevant atomic and nanoscale structure, composition, and properties.

### **I. Directed Self-Assembly of Materials at the Nano scale**

Summary of a brief provided by Juan DePablo, University of Wisconsin at Madison

Directed self assembly using diblock copolymers is emerging as a viable alternative for lithography nanofabrication. However, progress in this area requires that a more concerted experimental and theoretical work be pursued. Full blown molecular simulations are highly computationally demanding and can only be pursued for a limited set of systems. Faster and more powerful simulation techniques must be developed for study of directed self assembly with polymeric materials. Molecular simulations must currently be supplemented by approximate, but less demanding self-consistent, theories. Given that much of our current interest is aimed at nanofabrication, it is necessary that we develop self-consistent field approaches that capture some of the molecular-level fluctuations of the system, which we know are important at the nano scale. The development of such simulation techniques and theories will in turn require that careful, controlled experiments on well-defined nano-patterned surfaces be carried out, and the resolution of such experiments will have to be molecular, i.e. phenomena arising at the length of a few nanometers will have to be extracted from the measurements (e.g. the concentration of all components of

a copolymer blend in a thin film as a function of distance from all interfaces, including that with a patterned substrate). It is important to emphasize that while such experiments would have been nearly impossible a decade ago, the emergence of modern nanopatterning techniques (e.g. e-beam, x-ray, EUV lithography) has itself enabled some of the experiments that are envisaged. Recent work in which nano-channels or nano-patterns are drawn on a surface, and on which various block copolymer systems are allowed to assemble, provide unprecedented testing grounds on which to develop theory and simulations further. Once fully validated, such simulation techniques will provide useful and essential insights into the fundamental principles that govern directed self-assembly by copolymer-based materials, and the development of sub-lithographic processes that will permit large-scale fabrication of complex sub-30 nm devices.

## **II. Block Copolymer Lithography: Merging of “Bottom Up” With “Top Down” Processes**

Summary of a brief provided by C.J.Hawker and T.P.Russell,  
(Excerpts from Materials Research Society Bulletin, **30(12)**, 952-966 (2005))

Can self-assembly processes be seamlessly integrated into existing fabrication processes? Is it possible to bias the three dimensional self-assembly of nanostructured elements into fabrication processes where the assemblies are rapid, robust, and inexpensive with a large processing window? Block copolymers represent one versatile class of materials that may provide an avenue for overcoming the challenges of sub-50 nm feature sizes and producing devices that can outpace Moore’s Law. While much is known about the bulk behavior of block copolymers, the number of applications that have emerged that fully exploit their self-assembled morphologies have been limited. However, models are needed that predict and enable the design of microdomain orientation, lateral ordering, and macroscopic properties. The benefits of such models would be the discovery of self assembling material systems with the potential to become a standard tool in the fabrication of nanostructured devices.

The parameters that underpin the morphology in thin films of block copolymers include the segmental interactions between the components, the rigidity of each block, the surface energies of the components, and the interactions of the blocks with the underlying substrate. In general, preferential interactions of one block with the substrate or a lower surface energy of one component will force a segregation of one block to either the surface or the substrate. Due to the connectivity of the blocks, this forces an orientation of the microdomains parallel to the substrate. While this is desirable for some applications, other applications require that the microdomains be oriented normal to the surface. In the absence of any surface modification, an external field will normally be required to overcome these preferential interactions. Alternatively, as will be discussed later, surfaces can be chemically modified to control the interfacial interactions of the blocks with the interfaces, removing any preferential affinity of the blocks. Balanced interfacial interactions, while necessary, are not sufficient, since both orientations satisfy this boundary constraint. However, by slightly modifying one of the blocks by the random placement of a second unit along the chain, small changes in the surface energies, segmental interactions and rigidity can be made without sacrificing the overall microphase separated characteristic of the block copolymer. This underscores the synthetic versatility in designing and tailoring block copolymers to control the morphology in thin films.

For essentially all synthetic polymer systems, one inevitably faces the issue of polydispersity, i.e. the distribution of molecular weight obtained in the synthesis. In the case of a block copolymer, the polydispersities of the two blocks can, also, lead to a distribution in the volume fraction of the components from one chain to the next. This may have deleterious consequences in the definition of the microphase separated morphology, since the volume fraction of the components will influence the curvature required to pack chains at the interface between the microdomains.

## **III. Various types of self-assembly processes arise in practice**

Summary of a brief provided by Jack Douglas, NIST Polymers Division

This section summarizes challenges in modeling self-assembly and validating these models for the effective control of synthetic self-assembly. On the one hand, there are *packing dominated* self-assembly

processes that arise in the crystallization of atomic and molecular (organic, metallic and mineralogical) fluids and the formation of larger scale periodic structures from colloidal particles and block copolymers, virus particles, etc. Although there are still many difficulties in the apriori prediction of crystal morphology based on particle structure and interaction, there have been numerous computational and theoretical studies of this type of self-organization process. Structural organization in the biological world represents another broad class of self-assembly transitions, in which the ordering does not generally lead to structures describable by periodic space groups and in which packing interactions do not generally dictate the geometry of the resulting organized structures. The diversity and efficiency of structures in the biological world speak to the potential of this approach to 'bottom-up' material assembly. Unfortunately, the effective utilization of *directional interaction self-assembly* (DISA) to fabricate real materials will remain a dream until this process is better understood theoretically and adequate experimental methods are developed to characterize the thermodynamic transitions that underlie this type of self-organization process. To address these challenges, interdependent models are needed that enhance the predictive and design capacity of simulation methods in the field of self-assembly and the modeling of biological processes, which comprehend the impact of solvents and local environments.

As a first step in this process we must identify canonical types ('universality classes' by analogy with critical phenomena) of directional assembly processes that occur in practice and introduce coarse-grained models that abstract the essential physical ingredients and component symmetries of these systems. The assembly of particles with certain symmetries leads to the formation of structures that *preserve the symmetries of the particle interaction potential at a local scale within the organized structure*, thus providing an organizing principle for self-assembly. The introduction into models of seeds energetically compatible with growth or through the formation of 'curved' (i.e., non-tiling) clusters, having a relatively low energy, may provide a tool for generating material systems that exhibit new symmetries. Current coarse grain models of self-assembly suggest many questions relating to how the interplay between short-range and the directional interactions affect the chirality and topological structure (linear or branched chains, genus, knotting, etc.) of the organized structures. The coupling of phase separation and self-assembly is also a basic phenomenon that must be theoretically attacked and the basic problem of understanding the dynamics of these assembly processes and the transport properties of self-assembling solutions is virtually an unknown scientific territory. There are clearly a range of problems that will require a sustained theoretical effort by numerous researchers over many years.

## **Summary (Cross Cutting Modeling Needs)**

For models to be capable of predicting structure and properties of existing nanomaterials and enable design of new nanomaterials, innovative algorithms and techniques must be developed and their accuracy improved through validation on well characterized experiments.

As was mentioned in the executive summary, cross-cutting needs for improved modeling of nanomaterials synthesis and properties are:

1. Innovative algorithms to model accurately over multiple length and timescales for realistic system sizes
2. Close collaboration between modelers and experimentalists to validate models and to design experiments
3. Systematic experiments that develop fundamental understanding
4. Modelers need increased access to high speed computing capabilities
5. Guidelines for models to be more accessible and portable in different computing environments

**Algorithm Development:** Current ab initio calculations require significant computation to model events for even several nanoseconds and are limited to 100s of atoms, while current models capable of modeling larger size systems for longer times require extensive characterization of parameters from simulation or experiments. For synthesis and critical properties, effects that occur at the nanometer scale interact with longer range fields and phenomenon, and models of different spatial regimes cannot currently seamlessly couple these long range and nanometer scale phenomenon. Similarly, physical phenomenon occurring at sub nm scales, such as bond breaking, often occur in femtoseconds, but the models of longer range phenomenon that occur over longer time scales, such as diffusion that may occur over days or weeks do not currently include the atomistic processes well. Thus, new computational techniques are needed to model synthesis or properties and seamlessly bridge physical phenomenon from atomic scale to macro scale and from femtoseconds to days. The development of these new algorithms and improvement of models will require increased access to high performance computing capabilities and may require increased interaction between mathematical researchers, modelers, computer scientists, and experimentalists.

**Model Validation:** For improved models to be capable of predicting structure and properties of yet to be designed materials, close collaboration will be needed between modelers and experimentalists to design experiments that can effectively validate models. Current ab initio modeling is limited to ~100s of atoms and can only be done at timescales many orders of magnitude smaller than can be experimentally captured, so experiments must be designed to validate and improve models. On the other hand, experiments are not able to characterize phenomenon that occur at femtoseconds and different metrology capabilities are used to characterize phenomenon at atomic dimensions vs. at macroscopic dimensions. Thus, close collaboration will be needed between modelers and experimentalist to design experiments that can develop the fundamental understanding of all interactions and use this to validate models and improve predictive capability.

Since electronic properties determine many of the other physical properties and the models (DFT, and beyond) require significant computational resources for physically realistic systems, it is important to determine and validate the level of model complexity required for different nanomaterials. Thus, developing a validated hierarchical “map” of which models are “good enough” for different nanomaterials electronic property modeling would be very valuable. Again, this would need to be validated with well characterized experiments.

**Systematic Experiments:** The development of more sophisticated modeling will require the development of a reliable set of statistically valid observables on which to validate these models. As experiments are jointly designed, they need to include variations of the critical input variables that correlate nanostructure

and longer range structure to macro properties. Since many of these effects may be coupled, experiments will need to be designed to separate factors. This may require application of a broad range of metrology capabilities to correlate structure and interactions at the atomic scale with conditions and fields applied at the macro-scale. This characterization may require a combination of spectroscopy, microscopy, and nanometer scale metrology capabilities be used to understand the physical interactions that occur in these complex systems and materials. Critical experiments will need to be repeated multiple times by different research groups to develop statistically significant correlations between nanostructure and properties.

**Nanometrology:** While new probes of nanometer scale structure and properties are emerging, the interactions between the probe and sample make quantitative extraction of nanostructure and properties difficult. In some cases, calibration standards would enable improved correlations between experiments, but in other cases new models of the sample-probe interaction need to be developed to enable extraction of structure and properties. As more complex probes are developed to apply multiple stimuli to nanomaterials in 3D, it will be important to develop analysis capabilities to decouple the probe-sample interactions and quantify properties at the nanometer scale.

**Access to High Speed Computing:** Development of innovative algorithms and validating the accuracy of models will take significant computing resources. Improved models of atomic bonding, electron exchange and potentials will require increased computation time and this will require access to supercomputers. Further, as modelers work with experimentalist to validate the accuracy of models, this will require many simulations. Thus, there will be a critical need for modelers to have access to supercomputers or large clusters of computers including increased frequency of access to these facilities.

**Accessibility and Portability of Models:** The recommendations made in this report may lead to models that more realistically predict nanomaterial structure, synthesis and properties. Developing software that is readily adapted to existing operating systems and hardware platforms reduces the barrier for rapid exploitation by industrial and academic modeling groups that will utilize these advanced tools to accelerate nanomaterial research and development.

## Appendix

**Nanomaterials Modeling Workshop Agenda**  
NIST

100 Bureau Drive  
Bld. 227, Rm. A202

**May 24, 2006**

**Time EDT**

- |             |   |
|-------------|---|
| 8:00        | Introductions   |
| 8:15        | Meeting Goals   |
| 8:45        | <u>Synthesis of Nano-structured Materials</u> (Chair: Sadasivan Shankar, Scribe: Dave Roberts)<br><i>Modeling of carbon nanotube growth and resulting nanostructure</i> |
| 8:50        | <i>Modeling:</i> Jack Wells, Giulia Galli   |
| 9:50        | <i>Experimental:</i> Ageeth Bol, Renu Sharma  |
| 10:50       | Discussions   |
| 11:15       | Lunch   |
| 11:45       | <u>Nanomaterial Surface Chemical Reactivity</u> (Chair: Anne Chaka, Scribe: Susan Fitzwater)<br><i>(Catalyst, nanoparticles, surface reactivity)</i>                    |
| 11:50       | <i>Modeling:</i> Emily Carter   |
| 12:20       | <i>Experimental:</i> Greg Blackman, Renu Sharma   |
| 1:20        | Discussions   |
| 2:15        | Break   |
| 2:30        | Nanomechanical & Interface Properties (Chair: Steve Lustig, Scribe: Ravi Prasad)  |
| 2:35        | <i>Modeling:</i> Lyle Levine  |
| 3:05        | <i>Experimental:</i> Chris Li, Matthew Begley   |
| 4:05        | Discussions   |
| 5:00        | Summarize Results   |
| 5:30        | Review & Day 2 Agenda   |
| 6:00-9:00PM | Chem-Semi Work Group Meeting: Develop Draft of Key Research Needs<br>Location: Courtyard Marriott   |

## Nanomaterials Modeling Workshop Agenda

NIST  
100 Bureau Drive  
Bld. 227, Rm. A202

### May 25, 2006 (Thursday)

#### Time EDT

- |           |   |
|-----------|---|
| 8:00      | Introduction  |
| 8:15      | Day 1 Summary & Meeting Goals   |
| 8:45      | Electronic & Transport Properties (Chair: Francois Leonard) Scribe: Susan Fitzwater                                 |
| 8:50      | Modeling: Jerry Bernholc  |
| 9:20      | Experimental: Michael Fuhrer, Mark Reed   |
| 10:20     | Discussions   |
| 11:15     | Lunch   |
| 11:45     | Self Assembled Material Properties (Mechanical, Electronic & Chemical) (Chair: Dan Herr, Scribe: Sadasivan Shankar) |
| 11:50     | Modeling: Juan De Pablo   |
| 12:50     | Experimental: Tom Russell   |
| 1:20      | Discussion  |
| 2:15      | Review Meeting and Next Steps   |
| 2:45      | Meeting Feedback  |
| 3:00      | Close   |
| 3:00-4:00 | Chem-Semi Work Group Meeting: Develop Draft of Key Research Needs (Location NIST)                                   |

## **Nanoparticle Synthesis Abstracts**

### **Toward multiscale modeling of carbon nanotube growth**

Jack C. Wells  
Center for Nanophase Materials Science & Computer Science and Mathematics Division  
Oak Ridge National Laboratory

#### Abstract

It is difficult to exaggerate the potential importance of carbon nanoscience and, particularly, carbon nanotubes and nanofibers to the future of advanced materials development. By recent popular accounts, carbon nanotubes are the "hottest" research topic in the physics community today.<sup>2</sup> These nanotubes are the best known of a broad class of sp<sup>2</sup>-bonded carbon nanostructures making significant impacts in science and technology. Although *in situ* techniques for directly observing the growth are developing<sup>3</sup>, it is widely agreed that a much better understanding of the nucleation and growth of carbon nanotubes is needed. This is a challenging problem, as the time and space scales cover many orders of magnitude and the mathematical and computational aspects of such problems are formidable. In particular, improved fundamental understanding of the growth mechanisms, innovation in the area of multi-scale modeling and simulation, coupled with the application of high-performance computing are necessary to establish predictive computational capabilities. To date in the area of modeling and simulation, most studies have focused on single scales with homogeneous descriptions of the phenomena. The published literature contains studies of reaction mechanisms employing density-functional theory, classical and quantum molecular dynamics studies of nanotube nucleation, and studies of nanotube growth employing statistical, kinetic Monte-Carlo methods and also growth studies utilizing continuum conservation (heat- and mass-transport) equations. In addition to better controlled, more systematic, *in-situ* observations of growth phenomena, a more systematic application of existing multiscale concepts<sup>4</sup> and the development of new ideas for coupling across length and time scales is necessary to progress toward predictive models of carbon nanotube growth.

### **Modeling Synthesis of Nanotubes and other Carbon Nanoparticles**

Guilia Galli  
University of California, Davis

Using ab-initio molecular dynamics, we have investigated the early stages of SWCNT growth on metal catalysts. Motivated to understand the microscopic mechanism involved in this growth process, we carried out a series of simulations of C deposition on a Fe nanoparticle. Our results show that a sp<sup>2</sup> bonded cap is formed on an iron catalyst, following the diffusion of C atoms from hydrocarbon precursors on the nanoparticle surface. The weak adhesion between the cap and iron enables the graphene sheet to "float" on the curved surface, as additional C atoms covalently bonded to the catalyst "hold" the tube walls. Hence the SWCNT grows capped. At the nanoscale, we did not observe any tendency of C atoms to penetrate inside the catalyst, consistent with total energy calculations showing that alloying of Fe and C is very unlikely for 1 nm

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<sup>2</sup> Nature, **441**, 18 May (2006).

<sup>3</sup> S. Helveg, et al., Nature **427**, 426 (2004); A. A. Puzos, et al., Appl. Phys. A **81**, 223 (2005); M. Lin, et al., Nano Lett. **6**, 449 (2006).

<sup>4</sup> D. Vvedensky, J. Phys.: Condens. Matter **16**, R1537 (2004).

particles. Root growth was observed on Fe but not on Au, consistent with experiment. Our results imply that the presence of a supersaturated solution is not necessary for root growth of SWCNT on metal catalyst and thus this type of growth does not necessarily requires a very high T to occur.

### **Understanding Carbon Nanotube Growth**

Ageeth Bol  
Nanomaterials & Devices Group  
IBM TJ Watson Research Center

The carbon nanotube (CNT) literature is full of CNT growth recipes and growth results. A lot of these results are however not well understood. In this presentation I will first give an overview of the different CNT growth techniques and present the general accepted view on the mechanism behind CNT growth. After that I will show some results that can not be explained by this mechanism. Particularly, I will discuss the chemical state of the catalyst during growth, the role of intermediates, the influence of addition of hydrogen, water or oxygen on the growth process and the difference between tip and base growth. Then I will turn to carbon nanotube alignment during growth which is important for applications. Several techniques will be presented and the mechanisms will be discussed.

### **Growth mechanisms of Carbon Nanotubes**

Renu Sharma  
Center for Solid State Science, Arizona State University, Tempe, AZ 85287-1704

Carbon nanotubes have attracted much attention since their discovery because of their remarkable properties. However, the selective synthesis of nanotubes with a desired structure and property is still a challenge. In order to determine the best synthesis conditions for a certain type of CNT, it is important to understand the relationship between the synthesis conditions (temperature and pressure) and their structure and properties. Recent *in situ* TEM observations of the nucleation and growth of CNT have provided some insight about the relationship between growth mechanism, structure and synthesis conditions. But a systematic study is required in order to draw definite conclusions and use this information to scale-up their synthesis. Moreover, there are still some fundamental issues, such as role of catalyst surface, growth limiting factors, reactions rate, state of catalyst particle during growth, etc., that need to be resolved. Moreover, our current time resolution (0.033 s) is insufficient to record all the events that might be happening. For example, we observe continuous growth rate with measurements made with 0.3 s time resolution, while 0.03 s time resolution reveals the discontinuous nature of the growth process. Modeling and thermodynamic calculations can provide the time resolution that is experimentally not available. These calculations can also assist us in understanding some of the experimental observations such as diffusion of carbon atoms, heat flow etc.

## **Surface Chemical Reactivity Modeling Abstracts**

### **Status & Challenges in Modeling Nanomaterials and Surface Chemistry**

*Emily A. Carter*

*Department of Mechanical and Aerospace Engineering and Program in Applied and Computational  
Mathematics  
Princeton University*

One of the technical requests put forth by the semiconductor and chemical industries is to develop modeling techniques for accurate characterization and control of surface chemistry over multiple time and length scales. An honest appraisal is given of the status and limitations of various methods spanning both length (electrons to continuum) and time (fs to hours) scales. In particular, while periodic density functional theory (DFT) has been anointed as the method of choice for a first principles description of surface and interfacial chemistry, it is best used as a qualitative indicator because its quantitative accuracy is still limited by its approximate description of electron exchange and correlation (XC). Photochemistry (which involves excited states and charge transfer), amorphous materials, strongly correlated systems (such as high  $T_c$  superconductors and Kondo materials), and molecular materials such as polymers (plastics, rubbers) are all poorly described within periodic DFT. These challenges are being worked on by a number of researchers, as outlined in the talk. One particular approach due to the author is presented, namely an embedded configuration interaction theory, which has been developed to enable an improved description of XC in a local region of condensed matter. This method has been used to accurately treat ground and excited states of adsorbates on metal surfaces and more recently to address the strongly correlated electronic effects arising in Kondo systems (magnetic impurities in non-magnetic host metals). Beyond electrons, one must examine ways to couple information from the atomic scale up the length scale ladder. Results will be presented that: (i) couple atomic scale surface chemistry to millimeter scale mechanical stresses in order to realistically model stress corrosion cracking of steel via an informed continuum approach, or (ii) simultaneously couples a very fast linear scaling DFT method (orbital-free DFT) to a finite element description of material deformation, in order to describe nano-indentation experiments. Lastly, open issues in multiscale modeling are laid out, with the ultimate goal of providing a seamless multiscale, multiphysics, adaptive description of nanomaterials.

## **Limitations in Characterization of Surfaces on a Nanoscale**

by Greg Blackman  
DuPont

Despite decades of development and research the tools that we have available to characterize surfaces on a nanoscale are not sufficient. In some cases we can obtain structure, but details about the chemistry and properties on a nanoscale remain elusive. Difficult problems such as the bonding of molecular coatings to nanoparticles, dispersion of nanoparticles in polymeric matrices, or the affects of nanoparticles on the micro, macro and end use properties are still “grand challenges”. Obtaining statistically relevant results when individual agglomerates or defects can cause catastrophic failure within a part or device remains difficult. The state of the art in several surface characterization techniques will be described using real world industrial examples. There is unlikely to be a single technique that provides a complete solution to such difficult problems, so an integrated, multi-technique approach is emphasized.

## **Redox Process in Ceria-Zirconia**

Renu Sharma

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Catalytic processes are most intriguing chemical processes as they are employed by more than 90% of the chemical industries but their exact function is difficult to discern. For example, the ability of cerium oxides to reversibly form mixed +3 and +4 valence oxides ( $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$ ) leads to excellent oxygen storage capacity (OSC). But the oxygen vacancy ordering can inhibit the reversible nature of the redox process. It has been reported that addition of zirconia not only improves the life of redox property but also lowers the reduction temperature. In situ observations, using an environmental scanning transmission electron microscope (ESTEM), have recently been employed to obtain an atomic level understanding of redox process in ceria-zirconia catalyst system. The ability to observe structural and chemical heterogeneity and relate it to the catalytic activity provides the much needed information to improve the redox property. The effect of the addition of Zr on the chemical activity of ceria, such as vacancy formation, can be modeled in terms of its effect on lattice energy and strain. In situ observation can also be used to determine the exact role of intergranular and intragranular heterogeneity. Although such in situ observations provide some fundamental understanding of the catalytic process, the ‘real life’ reaction conditions can not be achieved using current instrumentation. Therefore it is important to improve the instrumentation design to be able to observe chemical reactions at higher gas pressures, an atmosphere instead of a few Torr, and higher temperature (above 1000C). Modeling the properties of ceria poses another challenge as current calculation methods can not be used for highly correlated f-orbital electrons of ceria. Further development of new algorithms combining DFT, molecular dynamics and empirical methods may be able to provide a solution for this problem.

## **Nanomechanical and Interface Modeling Abstracts**

### **Nanomechanical Properties of Nanostructures and Interfaces**

(Hard-Hard Interfaces)

Lyle Levine

National Institute of Standards and Technology

Quantitative modeling of nanoscale mechanical properties requires modeling over many length scales. Required modeling approaches include continuum methods for long-range elastic effects, classical potentials when atomistic behavior becomes important, and quantum methods such as density functional theory to handle chemistry, large bond distortions and bond breaking. Validation testing with corresponding experiments is critical, but non-linear sensitivity to small experimental details can greatly complicate this approach. For example, we have shown that including the presence of atomic corrugations on the surface of a modeled nanoindenter can change the predicted dislocation nucleation process from the bulk to the sample-indenter interface. Modelers and experimentalists must work together to develop experiments that both groups can work with successfully. The resulting experimentally-validated multiscale models could then be used as “standard reference simulations” that other modelers could use to test their own modeling approaches. This would be a valuable first step in providing quantitative uncertainties for nanomechanical modeling predictions.

### **Nanomechanical and Interface Properties - Challenges and Opportunities**

Xiaodong Li

University of South Carolina

Although many nanomaterials such as nanoparticles, nanotubes, and nanowires of different materials have been synthesized/fabricated by various techniques, their mechanical and interface properties have not been well explored. A precise measurement of the mechanical and interface properties of these nanomaterials is required for accurate modeling predictions as well as to use them as structural/functional elements in devices. Reliability study is the key for practical applications of such small structures and devices. Mechanical properties of materials are size-dependent. The extremely small dimensions of nanomaterials impose a tremendous challenge to many existing testing and measuring techniques for experimental studies of their mechanical and interface properties. In particular, instruments (hardware) for measuring the mechanical and interface properties are still lacking. Calibration procedures have been largely ignored. Reliable experimental data for verifying the modeling results are still lacking.

### **Nanomechanical Characterization of Materials using External Probes**

Matthew R. Begley

University of Virginia

This talk describes the challenges that arise in extracting nanoscale mechanical properties via nanoindentation, and several experimental approaches designed to overcome these challenges and identify elastic modulus, hardness, residual stress and yield or fracture strength. Nanoindentation of thin films (less than a micron) comprised of porous metals/ceramics or polymers requires special attention, as the reduced modulus of such materials increases the required precision of tip calibration and contact surface definition. This is highlighted by considering the consequence of errors in contact definition with regards to property extraction. A key implication is that penetration depths on the order of tens of nanometers are required to eliminate testing artifacts, which usually manifest as an up-turn in modulus with decreasing depth. A new approach to surface definition is described, which relies on changes in harmonic displacement as contact is initiated. The approach greatly reduces the ambiguity of depth-dependent properties for compliant materials. Alternatively, one can avoid many of the problems associated with nanoindentation through the use of freestanding microfabricated thin film structures: tip calibration is not relevant, and contact definition is less critical. Moreover, substrate effects are avoided, and it is possible to extract residual stress, CTE and fracture strength. This talk outlines the theoretical

and experimental framework needed to extract properties by point-loading of freestanding structures. This framework is illustrated using results obtained for sub-micron polymeric films, micron-scale nanoporous ceramics (i.e. low-k materials), and nano-porous metals. The talk concludes with a brief overview of novel approaches to nanoscale characterization, including chemo-mechanical coupling induced by adsorption, as well as cracking of nanoscale metallic films.

## **Electronic and Transport Property Modeling Abstracts**

### **Modeling of Electronic and Transport Properties**

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Nanoscale and molecular electronics promises to revolutionize computing, sensing, and electronic warfare. However, molecular-scale control and manufacturing are difficult tasks, which require major advances to become practical in large-scale applications. The development of molecular scale devices and circuits can be greatly enhanced by predictive simulation of their components, development of new materials and processes and by formulating design principles that will make molecular circuitry smaller, more efficient and more reliable. We discuss several recent applications: (i) Nanotube-cluster systems, which behave as effective chemical sensors whose electrical response changes dramatically upon adsorption of small molecules onto the metal clusters, enabling detection of minute quantities of adsorbants. (ii) We show that the celebrated Negative Differential Resistance (NDR) effects can be expected for a wide range of small organic molecules attached to semiconductor leads. This enables the design of molecule-based NDR devices based mainly on processing considerations, rather than the choice of specific molecules. (iii) Multiscale modeling of copolymer mixtures and the "design" of new ferroelectric polymers; and (iv) Calculations of optical signatures of complex surface structures for feedback controlled layer-by-layer growth with nearly monolayer resolution.

In collaboration with W. Lu, M. Buongiorno Nardelli, V. Meunier, S. Nakhmanson, F. Ribeiro, W. G. Schmidt, S. Wang, and Q. Zhao.

### **Electronic Transport in Molecules and Nanowires**

Mark A. Reed

Departments of Electrical Engineering and Applied Physics

Yale University

This talk will review two of the outstanding theoretical modeling challenges in nanostructure transport:

1. Electron devices containing molecules as the active region have now become achievable. The basic transport mechanisms in the most simple systems have been elucidated, specifically in self-assembled monolayers (SAMs) using nanometer scale devices. Detailed kinetic studies are necessary to distinguish between different conduction mechanisms; for example, in alkanes temperature-independent electron transport is observed, proving tunneling as the dominant conduction mechanism when defects are eliminated from the device structure. Inelastic electron tunneling spectroscopy of the molecules in the junction has turned out to be a valuable tool in identifying the molecular structure.
2. Single-crystal, semiconducting nanowires (NWs) are a subject of intense contemporary interest because they represent the limit of crystalline semiconducting solids and have been successfully synthesized from a vast array of traditional semiconducting materials. We will review the synthesis and transport properties of a number of nanowire systems, and contrast their advantages and limitations.

## Bulk Transport, Interfaces, and Defects in Carbon Nanotubes

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Department of Physics and Center for Superconductivity Research,  
University of Maryland  
College Park, MD 20742-4111  
USA

The properties of a carbon nanotube (CNT) device depend sensitively not only on the “bulk” properties of the CNT itself, but also the interfaces between CNT and electrodes, and various defects (charges, dopants, vacancies, adatoms) which may be present in the CNT or surrounding media. As illustrative examples, I will discuss several recent experiments from my group on individual semiconducting carbon nanotubes (CNTs) in field-effect transistor (FET) configurations, which attempt to address the properties of bulk, interface, and defects, and discuss efforts to connect experiments to modeling in each regime.

Experiments to determine the bulk electron transport properties of CNTs have been significantly advanced by the ability to grow of long ( $> 1$  mm), high-quality CNTs by chemical vapor deposition. Our group has fabricated long-channel CNT-FETs (tens or hundreds of microns) in order to determine the electric-field-dependent carrier velocity. At low electric field, the mobility may exceed  $100,000$   $\text{cm}^2/\text{Vs}$  at room temperature in large-diameter CNTs, exceeding that of the best known semiconductors. Analysis of the FET behavior at higher drain bias indicates that semiconducting CNTs do not experience current saturation due to optical phonon emission (as observed in metallic CNTs) but rather show saturation of the carrier velocity at  $\sim 2 \times 10^7$   $\text{cm/s}$ , approximately three times higher than the value for Si FETs. Modeling of the unipolar transport by other groups using single-particle Monte Carlo and multi-particle Boltzmann transport methods taking into account the electron-phonon coupling of the full spectrum of phonon modes is in good qualitative agreement with the experimental results at low and high field. However, a significant question remains as to whether interaction effects can be ignored in these models. In this light it is not surprising that model/experiment agreement is particularly poor in the ambipolar regime, where strong exciton binding is likely important.

The importance of the CNT/metal interface, and in particular the Schottky barrier (SB) at that interface, has been pointed out by the group of Avouris et al. The SB-CNT-FET model is extremely successful in the limit of large SB height, thin dielectric, and short (ballistic) channel. Other groups have reported negative SB height contacts to CNTs with certain metals (Pd, Au), though the experimental evidence is more qualitative. Our group has found poor agreement with the SB-CNT-FET model for positive or negative SB height for many devices on thick dielectric. However, we find that upon high current treatment, a low-conductance state emerges which is in excellent agreement with the SB-CNT-FET model with a mid-gap alignment of the Fermi level. Upon exposure to ambient, the high conductance state is recovered. The high-conductance state in the air-exposed nanotube is not due to work-function change of the electrodes, but rather to p-type doping, which reduces the SB *width* and produces an Ohmic tunnel contact.

CNTs are composed entirely of surface atoms, and defects in the CNT and in the surrounding environment are expected to have a large effect on their conductance. We have examined the anomalous ( $1/f$ ) noise in semiconducting CNT-FETs and found that the noise power is inversely proportional to the number of carriers, following Hooge's law with a Hooge parameter comparable to conventional FETs, indicating that CNTs are not (as might be expected) unusually noisy due to their high surface-to-volume ratio. Interestingly, the temperature, pressure, and gate-voltage dependence of the noise indicates that (1) adsorbates probably do not play a large role in the noise, and (2) Hooge's law (traditionally assumed to imply non-interacting charge carriers) is obeyed even in a one-dimensional conductor in the degenerate regime.

Nanomaterial Modeling Workshop Attendees  
May 24-25, 2006

1.	Donald Anthony	Council for Chemical Research (CCR)
2.	Lyn Beary	NIST
3.	Matthew Begley	University of Virginia
4.	Jerzy Bernholc	North Carolina State Univ.
5.	Gregory Blackman	DuPont
6.	Ageeth Bol	IBM
7.	Brian Bridgewater	Rohm and Haas
8.	Altaf (Tof) Carim	DoE
9.	Emily Carter	Princeton University
10.	Richard Cavanagh	NIST
11.	Anne Chaka	NIST
12.	Clark Cooper	NSF
13.	Kerwin Dobbs	DuPont
14.	Juan De Pablo	University of Wisconsin
15.	David Depaoli	ORNL
16.	Jack Douglas	NIST
17.	George Fitzgerald	Accelrys
18.	Susan Fitzwater	Rohm and Haas
19.	Emory Ford	MTI
20.	Michael Fuhrer	University of Maryland
21.	Michael Gaitan	NIST
22.	Giulia Galli	UC Davis
23.	C. Michael Garner	Intel Corp.
24.	Carlos Gonzalez	NIST
25.	Daniel Herr	Semiconductor Research. Corporation
26.	Terrence Jach	NIST
27.	Ji Ung Lee	GE Global Research
28.	Francois Leonard	SNL
29.	Lyle Levine	NIST
30.	Xiaodong Li	University of South Carolina
31.	Steve Lustig	Dupont
32.	Kevin Lyons	NSF
33.	Theresa Mayer	Pennsylvania State University
34.	James Murday	NRL
35.	Brian Peterson	Air Products and Chemicals, Inc.
36.	Ravi Prasad	Praxair
37.	Mark Reed	Yale University
38.	Nicholas Ritchie	NIST
39.	David Roberts	Air Products & Chemicals, Inc.
40.	Thomas Russell	University of Massachusetts
41.	Sadasivan Shankar	Intel Corp.
42.	Renu Sharma	Arizona State Univ.
43.	Mark Stiles	NIST
44.	Jack Wells	ORNL