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The NIST Workshop on Reliability Issues in Nanomaterials

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Abstract: *The Workshop on Reliability Issues in Nanomaterials was held at the Boulder Laboratories of the National Institute of Standards and Technology (NIST) on August 17-19, 2004. It was designed to promote a particular subset of NIST's responsibilities under the National Nanotechnology Initiative (NNI). The goal was to achieve consensus on two related topics: (a) identification of specific measurement-related barriers to successful incorporation of reliable nanomaterials into widespread engineering practice in the next 5 to 10 years; and (b) identification of measurement methodologies, standards, data, and models that might be appropriate for overcoming these barriers. 34 participants, representing cutting-edge nanomechanics-related research and development in industry, academia, and national laboratories attended and contributed. Adding NIST-Boulder staff who attended brought the total to about 40. The workshop format promoted discussion on the intended topics, and included:*

(i) a pre-workshop questionnaire addressed by plenary and breakout speakers;

(ii) invitation of 10 plenary speakers who gave hour-long presentations, and 23 breakout speakers who gave brief presentations addressing points raised in the questionnaire.

Key conclusions included: Industrial, academic, and national laboratory consensus indicated that there is always a need to understand fundamental causes of failure. Such understanding should then lead to re-design that is more reliable, and to improved manufacturing. The goal of accurate performance and lifetime prediction for nanomaterials depends on the interplay between accurate materials testing and characterization, and reliability models incorporating valid measured data. Attendees agreed that while the synergy among industry, academia, and national laboratories was effective, more fundamental materials research is needed, where the actual division of labor would be determined by market forces and policy.

It was suggested that NIST could serve the unique role of developing metrology, standards, and materials characterization methods for improving reliability of nanomaterials. The most challenging and general metrology recommendation was the development of an "atom imager," a hypothetical instrument capable of measuring the chemical identity and precise 3-dimensional position of every atom within a nanomaterial. Such an instrument was postulated to be the key tool for optimizing fabrication/manufacturing and controlling reliability of nanomaterials. Nearer-term recommendations centered on improving the metrological performance of scanned probe microscopy (SPM) and nanoindentation. A secondary theme in many presentations was the need for modeling to be formally coupled with physical measurement in any study of nanomaterials; however, no novel computational tool or dataset was identified as a priority need.

Keywords: mechanical properties; metrology; nanoindentation; nanomaterials; nanostructures; nanotechnology; reliability; scanned probe microscopy; standards.

Introduction

Nanomaterials lie at the heart of the field known as nanotechnology, which is predicted by the NNI to have tremendous global impact over the next 15 to 20 years. Nanotechnology is estimated to become a $1 trillion industry during this period, with 1/3 of that focused on materials and materials processing [1]. At present, with an estimated $1 billion annual investment in nanotechnology, U.S. government spending has doubled in 4 years and constitutes roughly half of the world governments' annual investment of just over $2 billion. Through the NNI, approximately 22 % of that U.S. investment addresses nanostructured materials "by design," and another 39 % addresses nano-electronics, -photonics, and –magnetics; the rest cover other NNI grand challenges such as health care, environment, energy, instrumentation and metrology, and manufacturing.

The introduction of nanomaterials into current and future technologies opens up an entirely new suite of both materials science and measurement science challenges. Effects of dimensional scaling play a stronger role in the reliability of nanomaterials than in any other materials known to date. Surfaces and interfaces can easily dominate and change behaviors and properties known to develop in bulk materials of the same chemical composition. As such, one cannot simply extrapolate what is known about bulk material behavior to the nanoscale and expect to predict structure or properties accurately.

The full realization of reliable devices at this scale is limited by a host of materials science and engineering barriers centered on nanomechanics. For example, the development of accurate and repeatable metrologies for determining mechanical properties of materials is key to understanding how issues such as plasticity, fracture, adhesion, friction, stress/strain response, micro- and nanostructure, and chemistry determine the mechanical response of materials at the nanoscale. Further, nanomechanical response plays an important yet sometimes indirect role in other types of reliability, such as thermal or electrical reliability. Valid measurements can provide a foundation for building predictive models of nanostructure and behavior that will be based on materials science, as opposed to being purely empirical in nature.

It was the intent of this workshop to identify and discuss specific measurement-related barriers to successful incorporation of reliable nanomaterials into widespread engineering practice in the next 5 to 10 years, as determined by leading researchers in nanomechanics and materials reliability. The workshop was intended to identify measurement methodologies, standards, data, and models that might be appropriate for overcoming these barriers.

We assess current knowledge of nanomaterials fabrication and characterization in the context of reliability, based on questionnaires and discussion during the plenary sessions, and follow with a detailed summary of the issues of concern for making reliable nanomaterials, as articulated by all workshop attendees.

Two definitions of the reliability of nanomaterials are considered, as used in the context of this workshop:

(i) the extent to which nanomaterials exhibit consistent mechanical behavior and associated properties over a long period of time, such as during a device lifetime;

(ii) the extent to which nanomaterial behavior and properties can be predicted over a given period.

The first definition is similar to the conventional use of the term "reliability." However, the second definition must sometimes be used in the design of devices and products, in the event that a material changes or degrades with increasing exposure to design stresses and environments. If the material degrades over time, but that degradation can be well predicted, the material may still be useful. In general, a "reliable" nanomaterial is one that can serve its purpose over the course of an intended device or product lifetime.

Reliability Issues Pertinent to Nanomaterials

Successful incorporation of nanomaterials into widespread engineering use requires us to understand why, how, and when failure will occur. A combination of basic research addressing identification and measurement of failure mechanisms in these novel materials will provide the framework necessary to develop reliability models that are able to accurately predict changes in behavior and properties, and therefore lifetime, a key factor in successful manufacturing.

A number of issues that compromise reliability were identified during the workshop. The detailed lists as articulated by attendees are provided in the Workshop Report [2]. Some selected examples are presented here. We have sorted the reliability issues into three categories:

Nanostructures, behaviors and properties

- Nanomaterials have larger surface-to-volume ratios than bulk materials, which affects friction and wear properties, and stiction in nanomaterials.
- Polycrystalline nanomaterials contain a higher fraction of grain boundary volume, and may be more susceptible to failure mechanisms involving boundaries, including high temperature deformation modes being operative at lower temperatures or failure mechanisms involving diffusion.
- Nanomaterials are almost always used as part of a materials system, and invariably come into contact with other materials, creating interfaces. Failure mechanisms involving delamination or chemical interdiffusion can therefore be exacerbated.
- Defect stability differs from that seen in bulk materials due to stronger influences of surfaces. Strain hardening may not follow the stages seen in bulk materials since dislocations can more easily escape. Internal stresses associated with defects can quickly occupy the entire volume of a nanomaterial. Dislocations may not be energetically favored to exist in extremely small structures, forcing other plasticity mechanisms to operate.
- Grain size is usually smaller in polycrystalline nanomaterials than in bulk materials, causing defect behavior and properties to differ from those seen in bulk materials.
- Localized behavior is much more important in nanomaterials. Even an unusual single grain orientation can compromise the reliability of an electronic interconnect.

Operation under extreme conditions

- Accelerated tests must be developed in manners that suitably reproduce expected operating conditions, but sometimes the expected conditions can even lead to behaviors not yet well understood.
- Normalized external loads can be much more intense than in the case of bulk materials. Nanomaterials are often expected to withstand current densities, electric fields, pressures, stresses, or optical power densities that far exceed the values typically applied to bulk materials. Behaviors under such conditions are largely unknown.

- Time dependence of failure is very different from what is observed in bulk materials, due to vastly different boundary conditions.
- Thermal management in nanomaterials is difficult, due to the high density of interfaces in multi-material systems. This is exacerbated by very high temperatures undergone during thin film or high pressure processing.

Size, shape, and distribution control

- Ordered arrays or patterns of some nanostructures cannot as of yet be sufficiently fabricated. Quantum dots or carbon nanotubes must be made uniformly over large areas in order for many potential devices to be realized. Arrays and patterns must contain well controlled size and structure distributions. Lithographic approaches may not be feasible beyond certain dimensional limits, suggesting the need for self-assembly processes.
- Stresses and strains can become very large in nanomaterials, and their management becomes extremely difficult. Lattice-mismatched quantum dots require high elastic strains (~ 7% for InAs/GaAs) in order to exhibit their unique electronic behaviors, but plastic relaxation must be avoided.

State-of-the-Art in Measurement Technology

Reliability studies of nanomaterials depend on valid measurement of properties and behaviors. Thorough understanding of mechanical properties and behavior of nanomaterials requires accurate knowledge of the external forces and displacements applied to such materials, as well as the corresponding response of those materials.

Many test and characterization methods were discussed during the workshop. Some are now in use, while others are still in development. In general, high-performance tools for measuring bulk materials are commonly used for nanomaterials characterization, with appropriate modifications. For example, high-resolution imaging methods such as atomic force microscopy (AFM), scanning tunneling microscopy (STM), transmission electron microscopy (TEM), and scanning electron microscopy (SEM) are routinely pushed to their limits. X-ray diffraction (XRD) is also used extensively for structural characterization of both aggregates and individual nanostructures. Focused ion beam (FIB) microscopy and manipulation has become a necessity for direct imaging, preparing specimens, and patterning. Advances in mechanical testing and characterization have led to unprecedented resolutions in force and displacement measurement and control. We summarize these state-of-the-art methods here, categorized by application.

MEMS/NEMS

- Nondestructive and/or noninvasive measures for mechanical displacement, both static and dynamic, using electrical or optical methods;
- Automated systems for high-throughput testing;
- Surface analysis and analytical tools for identifying impurities or contaminants, *e.g.*, Auger electron spectroscopy, X-ray photoelectron spectroscopy, secondary ion mass spectroscopy (SIMS);
- Environmental chambers for accelerated testing;
- Shock and vibration testing at the product level;
- Thermal shock and/or cycling tests for delamination and crack growth.

Nanoscale Manufacturing and Assembly

- STM methods for moving and removing atoms, to enable bottom-up fabrication;
- Atomic layer deposition using STM for patterning (idea near realization);
- Surface acoustic waves and accelerometers for mechanical properties;
- Displacements measured by indirect optical methods using lasers, deflection techniques;
- Assembled micro-SEM column to enable novel nanoscale characterization on a chip;
- Assembled linear actuator to enable nanoscale testing on a chip.

Advanced Electronic Interconnect

- Scanning XRD (4-circle goniometer) with area detector for simultaneous measurement and mapping of crystallographic phases, texture, and film thickness on 200 mm wafers; includes 20 μm collimation. Development is underway to make this system apply to films of thickness < 10 nm, where electrical methods are invalid. Such a system can be used in-line during manufacturing.

Semiconductor Nanostructures

- Cleaving *in-situ* within STM ultra-high vacuum for cross-sectional imaging with atomic resolution;
- Spectroscopy within STM for bandgap measurement as a function of position across a wafer;
- Wafer curvature for average stress determination;
- AFM-based patterned nanostructure fabrication using a nano-jet probe;
- FIB nanopatterning for nanostructure position templates.

Mechanical testing

- Young's modulus (E) and hardness (H) by continuous stiffness nanoindentation system and hybrid tribology/ nanoindentation system; Measurements are still not in good agreement, with standard deviations as high as ~ 75 – 125 GPa for E, and ~ 12 – 14 GPa for H for the case of thermal plasma chemical vapor-deposited SiC.
- Calibration of tip shape using fused quartz (not optimal);

- Nanoindentation measurements for H from sub-500 nm grains;
- Modified nanoindentation measurements of sub-40 nm Si nanoparticles;
- Stressed overlayer and edge lift-off tests for adhesion;
- Nanoscale scratch tests for adhesion;
- Acoustic AFM for mapping of elastic properties.

Measurement Needs

We present here an abbreviated listing of the measurement needs discussed at the workshop. A complete listing of all needs is available in the final workshop report [2].

- Tools and/or techniques to measure nanometer motion, addressing 6 degrees of freedom, faster than device resonance frequencies;
- Tools for atomically precise engineering;
- Conversion of inherently two-dimensional measurement methods to three-dimensional methods;
- Metrology for micro- and nanostructure of low-level features, especially early in the process;
- Tools capable of multiple, coupled measurements with a single technique;
- Tools or systems capable of coupled measurements of properties and behaviors, using multiple techniques, *e.g.*, optical, electrical, mechanical;
- High-resolution (in space and energy), fast methods for imaging, morphology, chemistry; this suggests improvements to SEM, AFM, TEM;
- Methods for local measurement of: strain, electrical properties, structures size/shape, spatially-resolved temperature, stress gradients;
- High-throughput adhesion measurement;
- Deconvolution of sample-probe interaction in nanoindentation and SPM;
- Sub-micrometer scaling of mechanical test methods: uniaxial, multiaxial, torsional stressing, deformation mapping, gripping and manipulation;
- Improvements in spatially resolved characterization: SEM, SIMS, *in situ* TEM, diffraction, micro-Raman, FIB (secondary electron imaging), the "atom imager";
- *Nanoindentation needs*: instrument consistency for E, H; nanoindenter tip geometry control; microforce standards; calibration standards for nano-test equipment; direct imaging of contact areas; improvements in position (x, y, z) control and measurement.
- *AFM needs*: simultaneous mechanical testing and imaging; simultaneous nanodeposition and imaging; tip/sample interaction energies need to be understood; contact area effects must be understood; direct imaging of contact areas; more accurate force and displacement knowledge; better characterization of AFM tips; improvements in position control and measurement.
- *Standards*: reflectivity; film thickness; texture; microforce (axial and lateral); AFM spring constant; AFM tip-specimen contact area; calibration specimens for nanoindentation and AFM-based mechanical testing; toughness and strength of thin films.

Action Items for Metrology Development

The list of needs given above seems formidable at first glance. However, it became clear during the course of the workshop that there are three main tools commonly used by materials researchers who are concerned with understanding and improving nanomechanical reliability:

- instrumented nanoindentation;
- scanned probe microscopy;
- modeling.

This short list of tools in no way diminishes the significance of others discussed during the workshop; it simply reflects a larger consensus about commonly used methods for nanomaterials.

Attempts have been made to adapt these tools to most of the measurements listed above, but considerable additional research and development are needed. These "common-denominator" tools lead to the following action items for metrology development for nanomaterials reliability:

- *Near term:* Improved metrological performance of scanned probe microscopy and nanoindentation, for more quantitative measurements of position, displacement, force, temperature, and other relevant quantities;
- *Longer term*: The "atom imager," a hypothetical instrument capable of measuring the chemical identity and precise 3-dimensional position of every atom in a nanomaterial.

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