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Title: **Scanning Probe Microscopy Competency Development**

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Scanning Probe Microscopy Competency Development

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at Los Alamos National Laboratory (LANL). The project collaborators developed an ultra-high vacuum scanning tunneling microscope (UHV-STM) capability, integrated it with existing scanning probe microscopes, and developed new, advanced air-based scanning force techniques (SPMs). Programmatic, basic, and industrially related laboratory research requires the existence of SPMs, as well as expertise capable of providing local nano-scale information. The UHV-STM capability, equipped with load-lock system and several surface science techniques, will allow introduction, examination, and reaction of surfaces prepared under well-controlled vacuum conditions, including the examination of morphology and local bonding associated with the initial stages of film growth under controlled growth conditions. The resulting capabilities will enable us to respond to a variety of problems requiring local characterization of conducting and nonconducting surfaces in liquids, air, and UHV.

Background and Research Objectives

One objective of this project was to bring an ultra-high vacuum scanning tunneling microscope (UHV-STM) on-line in a timely fashion and integrate this instrument with the existing network of scanning probe and surface technologies. Programmatic, basic, and industrially related efforts require the existence of a range of scanning probe instruments and the concomitant expertise to respond to a variety of laboratory needs for the information obtainable by these advanced, high-resolution surface techniques. As pressure increases for the development of new materials and new ideas for exploiting the properties

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of both old and new materials and structures, so does there exist a need to evaluate them at the same scale at which the structure-property relationships are important. In many cases, these properties need to be examined at resolutions that have not previously been possible and/or deemed important heretofore. With the demand for higher density data storage, micro- to nano-mechanical chip-mountable devices, molecular-based flat-panel displays, and nano-granular structural materials, there is a need to develop characterization methods suitable for probing structure and related properties at these smaller dimensions.

Scanning proximity probes, such as the scanning tunneling and atomic force microscopes, are already utilized routinely to examine a variety of properties at the atomic to nano-scale; they were developed and are particularly well-suited for this scale regime. In addition, the rapid and ever-expanding development of new characterization proximity probe techniques and expertise is in progress using "cousin" scanning proximity probes. Examples include the repulsive force, frictional force (FFM), magnetic force (MFM), and electric force (EFM) microscopes made possible by the development of tapping-mode microscopes combined with phase/frequency sensitive techniques. The Laboratory's present capabilities for examining surfaces in air must be expanded to include these new air-based force techniques, as well as the examination of surfaces prepared under clean, well-controlled conditions.

The present Los Alamos UHV-STM system was designed to combine a commercially proven state-of-the-art tunneling microscope with several surface science techniques to provide comprehensive surface characterization of reacting or growing surfaces at the atomic/molecular- and nano-scale. The vacuum environment allows for the *in situ* preparation of surfaces, including cleaving, ion milling, and thermal annealing; the resulting surface morphology, local bonding arrangement, and local density-of-states then can be mapped in the as-prepared form. To facilitate transfer of samples from ambient or other fabrication/reaction systems without degradation of the UHV-STM environment, we determined the need for an entry load-lock system.

The resulting combined air- and vacuum-based capabilities will enable us to respond to a variety of important problems requiring localized imaging of conducting and nonconducting surfaces in liquids, air, and vacuum. Additional temperature-dependent characterization and UHV-AFM capabilities need to be developed in the future to enable *in situ* studies of kinetic/thermodynamic processes and understanding of properties at the appropriate energy regime for the development of new materials with new properties. Although more development is needed, this project has made it possible for Los Alamos to close the gap between our capabilities and those existing at other Department of Energy laboratories, as well as internationally.

Importance to LANL's Science and Technology Base and National R&D Needs

This project enhances a variety of materials capabilities that fall under the Laboratory's Nuclear and Advanced Materials core competency. Development of new materials, both electronic and structural, requires knowledge of properties at the nano-scale. Expertise in the area of scanning probe microscopy, implementation of a UHV-STM capability, and the development of new scanning probe techniques capable of locally measuring properties at this scale are vital to the development of these new materials.

The existing air instruments at the Laboratory's Center for Materials Studies (CMS) were initially set up to provide programmatic support for the Yucca Mountain Project (YMP) and the Superconductor Technology Center (STC) superconductivity work. The YMP site characterization program needed characterization of the surface morphology, roughness, and radionuclide sorption reaction properties of iron oxide natural crystals from YM tuff composites. These oxides were expected to play an important role in the retention of neptunium and americium in the vicinity of the storage facility in the likely event of a water breach of the underground vault. The SPMs are the only characterization tool capable of studying the local structure-controlled sorption process *in situ* at the atomic level.

The MFM not only gives both structural and related magnetic information, it also determines the deposition-controlled microstructure of as-grown films, before and after annealing. Moreover, the MFM can provide important insight into the extrinsic structurally controlled magnetic properties of collosal magnetoresistive (CMR) materials for read heads. One example is strain-induced magnetic domains generated by surface boulders or film-substrate lattice mismatch. The EFM, which maps surface charge/potentiometric distributions, is important for elucidating the growth or conditioning, mixed sp^2-sp^3 determined electrical properties of diamond-like carbon films (DLC) that are being developed for flat-panel displays.

We also recently have identified several projects associated with the Laboratory's core missions that will benefit from the present and future development of SPMs. One such project, well-suited to the UHV-STM, involves understanding hydrogen reactions at the surface of depleted uranium. The capability of preparing and characterizing a pristine depleted uranium surface *in situ*, then reacting that surface with a well-controlled amount of purified hydrogen while following the reaction with the STM, has been determined feasible; plans have begun to implement this work. A second strategic project under exploration is the examination, in air, of the surface of high-explosive materials as received and under the influence of an applied stress. With the acquisition of the appropriate test modules, deformation of the surface can be characterized *in situ* using tapping-mode force microscopy. This setup is suitable for the study of the deformation of a variety of surfaces, including that of uranium oxide. Frictional force microscopy using either lateral force or phase shift techniques is being explored and tested for monitoring superfluid cleaning of Be parts.

In addition to the development of new SPM techniques for specific projects for Los Alamos, industry, and universities, the project has positioned the Laboratory's Center for Materials Science (CMS) to respond to the needs of many Laboratory programs on an as-needed basis. Prior to the initiation of this project, Los Alamos had no functional UHV-STM capability or centralized dedicated scanning probe facility for both the development of new state-of-the-art techniques and demonstration of utility to Laboratory-wide programs.

Scientific Approach and Accomplishments

The SPMs have also been used to demonstrate the usefulness and flexibility of these techniques to a variety of potential users over the entire lifetime of this proposal period; the approach was to identify specific programmatic needs and to focus attention on the development of the appropriate new capabilities, such as magnetic- and electrical-force microscopies, for determining the structure and related properties of CMR materials and DLC films, respectively.

The SPMs are some of the most powerful and important tools now used to study nucleation and growth processes of metal and metal oxide thin films being developed at Los Alamos and other Department of Energy and industrial laboratories for the new generation of device applications, such as high-temperature superconducting (HTS) materials for SQUID devices and collosal magnetoresistive films for the next generation of read heads for high-density magnetic storage media. Moreover, the SPMs are invaluable tools for monitoring lithographic processes; providing ready information such as step angles, heights, residual photoresist; and surface damage resulting from the ion milling and cleaning procedures. This information is needed to evaluate the film growth and electrical transport measurements.

Major accomplishments during this project include:

- These microscopies have aided in understanding the role of deposition parameters on growth processes that determine the microstructure of high-temperature superconducting and new collosal magneto-resistive films. The former resulted in the publication of two different book chapters, one in print and one appearing next spring.

- Characterization of component layers in the multilayer fabrication of device structures has contributed to the successful development of SNS ramp-edge HTS josephson junctions. AFM characterization of the Ni substrates, used for the YBCO/YSZ depositions, was one of the methods used to determine the nature, cleanliness, and quality of the these substrates before successful fabrication of films on flexible substrates.
- Knowledge of the microstructure of $La_{0.7}Ca,Sr_{0.3}MnO_3$ films has aided in the interpretation of temperature-dependent resistivity and coercivity trends in these materials as a function of growth temperature and post-deposition anneal. A combination of STM and TEM data was used to determine the amorphous character of low-temperature unannealed films that had low conductivity.
- Development of the magnetic force microscope is making it possible to directly image magnetic domain structures in these films, which is expected to yield critical data needed for insight into the origin of the MR phenomena. Magnetic structure was observed to be associated with surface defects, such as boulders, that could detract from the performance of these films as read heads for magnetic storage media. Initial testing of the MFM dual-pass technique on strain-induced magnetic structure on the surface of bent FeBSi magnetic ribbons demonstrated the ability to correlate structure-property relationships.
- Equally exciting is the development of the potentiometric microscope, which is capable of probing local changes in potential associated with structural or chemical features. Because all HTS and CMR films are polygranular, this instrument is expected to reveal insight into intergrain coupling. One HTS film was characterized with this technique, revealing potentiometric variations that were associated with grain boundaries that result from the island growth nature of these films. A DLC film that had been conditioned by application of a high voltage was also characterized by this technique, showing electrical variations in the neighborhood of the resulting craters where enhanced emission was observed.
- Characterization of wear tracks on ion-implanted silicon samples (work done by a Graduate Research Assistant student Padma Kodali) is being used to understand the effect of implantation on tribological properties (e.g. friction and wear) to be correlated with hardness and fracture toughness measurements.

- Environmental work for Yucca Mountain on iron oxide–water interface reactions was featured in the 1994 Laboratory Director's highlights; this work demonstrated the power of the AFM to study reactions *in situ* to determine the responses of mineral surfaces to environmental conditions.
- Reconfiguration of the UHV-STM system has been nearly completed. New, improved operating software and interface have been installed, along with a new vacuum chamber, sample positioning carrousel, metal and semiconductor sample heating stages, and load-lock/sample injection transporter. High-resolution sample manipulation viewing is being added, along with a gas purification input filter and sample preparation antechamber for uranium reaction work. The now completed system is a significant improvement over the original one and is now almost up to par with UHV-STM systems at the other Department of Energy facility.

Introduction of *in situ* magnetic, electrical, and mechanical forces to broaden the structure-property and cause-effect characterization capabilities is in the development stage but will make a significant impact on the quantification of the properties being measured by these techniques. Modular tensile/compressive and 3- or 4-point bending sample holders, available for *in situ* stressing of samples, will be added soon, along with software and ss cantilever/diamond tip for *in situ* nano-indenting-scratch testing/imaging capability. Still to be added is a variable temperature capability for a to-be-developed dual STM/AFM that would allow control of the energies at which measurements are taken. Most significantly, that capability would permit measurement of electrical properties of HTS materials and magnetic properties of CMR films above and below their respective critical temperatures. Other techniques, whose additions would allow chemical determination and hidden crack mapping, are the near-field optical and acoustic scanning probes.

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