

Monitoring Surface Chemical Reactions and Interactions on Thin Films and Ordered Interfaces

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Proposal summary

I propose to explore the electronic and structural properties of tailored surface interfaces and the surface chemical dynamics and interactions of molecules exposed to these systems. I will investigate how atomic scale surface properties determine the interactions between surface bound molecules and atoms as well as how they associate with the underlying surface or thin film in which they are imbedded. By understanding the ways in which chemical reaction pathways are influenced by the nature of the underlying support, surfaces can then be designed and modified appropriately to either promote or inhibit particular molecular interactions.

My research proposal involves the use of both existing interfaces and the design of other nano-engineered systems. This research necessitates the creation of atomic scale structures and ordered films on surfaces that will serve to control position, alignment, and reactivity of adsorbed atoms and molecules. I will design nanoscale structures that can be created through intermolecular forces, including structural phase separation or the use of energetically tuned molecular beams. This experimental tactic is derived from the observations made when assessing and exploiting the roles of different crystallographic orientations on adsorbate behavior. I will employ this technique as well as take advantage of self-assembly and the growth of other thin films which may or may not communicate the structural and electronic properties of the underlying substrate. Initially, I will investigate three different experimental systems: chiral surfaces, self-assembled thin films, and metal oxide supports. These systems cover a wide range of applications from enantioselective heterogeneous catalysis to molecular electronic device design.

The techniques I will use include ultra-high vacuum (UHV), low and variable temperature scanning tunneling microscopy (STM) and atomic force microscopy (AFM) working in concert with other surface sensitive tools, including electron and photon spectroscopies. Scanning probe instruments are one of the most useful collection of tools for assessing the properties of nanostructured materials. My lab will be part of an emerging field that includes the design of innovative analytical tools for use in nanotechnological applications. My extensive experience in designing, building, and operating ultra-high vacuum, low and variable temperature probe microscopes makes me uniquely qualified to establish a lab of this type.

Introduction

Nanoscale design of electronic devices, catalytic supports, and interfaces relies heavily on a fundamental understanding of the behavior of surface bound atoms and molecules. Model systems, such as clean or sub-monolayer adsorbate coverages on metal and semiconducting surfaces have been used to improve our insight into the ways in which electronic and geometric structure affect thermodynamics and kinetics of surface interactions and dynamics.¹ Over the past two decades, complementary surface sensitive tools have been employed in order to create a comprehensive picture of surface behavior. However, as our ability and desire to understand the behavior of single molecules increases, the need for corresponding atomic scale tools becomes paramount. Remarkable strides have been made in enhancing our understanding of the relative influence of surface compositions, structures, and defects on surface chemical reactions and dynamics. The next step involves probing these issues further by working with more complicated interfaces that closely resemble some of the real systems that motivate the science. This involves heterogeneous catalysis, properties of nanoscale assemblies, electronic device characterization, crystalline phase transformations, and the fundamental physics of adsorbate-substrate interactions.

There have been a number of examples of thin film deposition that allow for the tailoring of surface interfaces and nanoengineered architectures. Using chemical intuition one can control the arrangement and alignment of adsorbed atoms and molecules. Specifically, there are opportunities to maintain control over the orientation of functionalized molecules,² magnetic and electrostatic moments,³ and adsorption geometry.⁴ As the systems become more complex, there is an increased need for an array of surface sensitive tools that will provide a multifaceted approach to solving problems that are intimately related to native structural and electronic features. Scanning probe microscopes have emerged as one of the most powerful families of surface sensitive tools. Their use in ultra-high vacuum in conjunction with variable sample temperature operation further expands the utility of these techniques. Information about surface structure,⁵ single molecule electronic characteristics,² and dynamics,⁶ including phase transitions⁷ and diffusion,⁸ have been successfully probed. Great advances have been made in the application of low and variable temperature scanning tunneling microscopy (STM) but due to the conductivity requirements and the potential for intermixing of surface electronic states, especially in layered materials, there are aspects of some systems that are inaccessible at the local level. Atomic force microscopy (AFM) in both contact and non-contact methods and at low sample temperatures is a rapidly growing technique for atomic level measurements on insulating samples or systems with strong geometric and electronic correlations.

The next step is the combined use of real space tools like STM and AFM to enable the construction of a broader picture of surface phenomena and processes. In addition to real versus reciprocal space tools that extract local electronic characteristics versus surface averaged information, STM and AFM act as complementary techniques in the deconvolution of complicated interfacial structures and behavior. It is with these techniques that it will be possible to improve and further tune the design of selective surfaces by monitoring surface chemical reaction dynamics at the single molecule and atomic level spatially. In this proposal, I will highlight thin film systems that will serve as a starting point for atomic level measurements using low and variable temperature STM and AFM: chiral surfaces, self-assembled monolayers, and thin metal oxide surfaces.

Chiral surfaces

Chemical discrimination is of profound importance in the separation of chiral molecules, ones whose chemical structures do not have superimposable mirror images. One route towards reaction product specificity is the use of modified metal surfaces for enantioselective heterogeneous catalysis. Model systems have been designed and explored recently for the purpose of assessing the role of surface structure on the efficiency and selectivity in chiral molecule separations. Chiral surfaces have been generated through the use of adsorbates⁹⁻¹¹ or kinked vicinal surfaces, which are miscuts from flat planes resulting in a periodic kinked structure along monatomic step edges.¹² A collection of tools has been used to study these systems including STM, reflection absorption infrared spectroscopy (RAIRS), low energy electron diffraction (LEED), and temperature-programmed reaction spectroscopy (TPRS).¹²⁻¹³

An example of adsorbate influence on heterogeneous enantioselectivity, is found in the adsorption of tartaric acid on Cu and Ni surfaces.⁹ This chiral molecule has been shown to impose chirality on an otherwise achiral surface. Figure 1 illustrates the creation of a pair of chiral surfaces generated on Cu(110) as a result of exposing the metal surface to tartaric acid of well defined stereochemistry. This particular molecule is used for the hydrogenation of β -ketoesters such as methylacetoacetate to create enantiospecific products. For the ordered phase illustrated in Figure 1, the adsorbate ordering creates a hydrogen bonded architecture that results in metal channels that do not follow the major crystallographic directions of the underlying lattice. This surface structure has been proposed as a possible route to forcing aligned bonding of a second chiral molecule, like methylacetoacetate, thereby promoting an anisotropic, or selective reaction. In fact, chiral molecules are of particular interest because they allow for a degree of structural control on the intramolecular level. Other chiral systems have been studied recently with STM revealing the ability to discriminate between structural mirror images.¹⁰⁻¹¹

The study of chiral systems are related to previous work on the influence of defects and breaks in symmetry in the intercommunication between surface and adsorbate properties. It has been shown that the adsorption geometry and reactivity of adsorbed species can be influenced by the presence of morphological defects, crystalline deviations, and multiple coordination sites. Examples of the influence of these perturbations manifest themselves in changes in local density of electronic states and available bonding, thereby creating aggregation sites for molecules.¹⁰ One way to systematically study the influence of a particular type of crystalline defect is to work with intentionally stepped surfaces, miscuts from low index Miller planes. These vicinal surfaces have been shown to affect the stability and ordering of species as a result of the periodic changes.^{4,15} It has been well-established that defects, crystalline imperfections such as vacancies, steps, and domain boundaries act as reactive centers where molecules prefer to aggregate and interact. Work that I performed as a graduate student spurred my interest in these types of systems. We observed a modification in the ordering behavior of a monolayer of

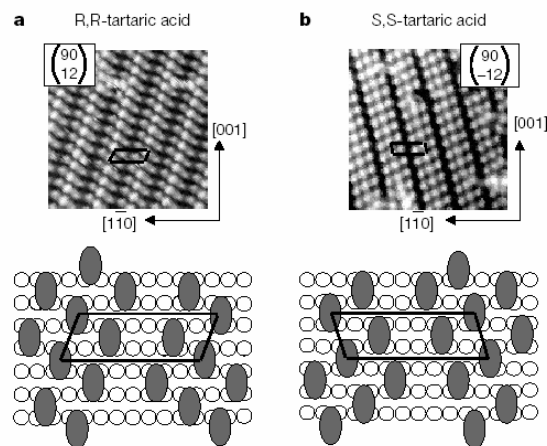


Figure 1. STM images and the corresponding schematic diagrams of mirror chiral surfaces produced by exposing (R,R) and (S, S) tartaric acid to Cu(110).⁹

physisorbed xenon adatoms as a result of adsorption on a stepped metal surface. The degree of manipulation was further increased by using a pre-adsorbed layer of chemisorbed hydrogen whose lattice acted as a template and enhanced the otherwise unobserved lattice ordering of Xe atoms.⁴

With STM and AFM, I will be able to closely examine the adsorption site and geometry of molecules that induce surface chirality, such as tartaric acid, and then observe how a second type of molecule responds to the chiral metal surface. The real time dynamics of interadsorbate interactions may be accessible with low and variable temperature experiments in addition to observing the catalytic reaction at various temperatures as a function of exposure. The steps of reaction like the hydrogenation of methylacetoacetate will be observed, including capturing the behavior of labile intermediates and precursors. Other chiral systems will be studied and the experimental scope will extend to other anisotropic systems like kinked vicinal surfaces. Templated structures will also be investigated where weakly adsorbed molecules may be readily manipulated and directed to predetermined locations and reaction environments.

Self-assembling surfaces

Self-assembled monolayers (SAMs) of alkanethiols have been proposed as model systems for use in corrosion resistance, nanotechnology, and tribology.¹⁶⁻¹⁷ The hydrophobicity and the relatively insulating nature of the film plays a vital role in its various potential uses. Alkanethiolate monolayers on Au have been shown to act as useful matrices for the controlled placement and alignment of long chained molecules.^{2,18-19} In particular, these thin films are being used as a testing host for assessing conductance properties of inserted molecules. The formation of a densely packed SAM using alkanethiol molecules on Au involves the creation of

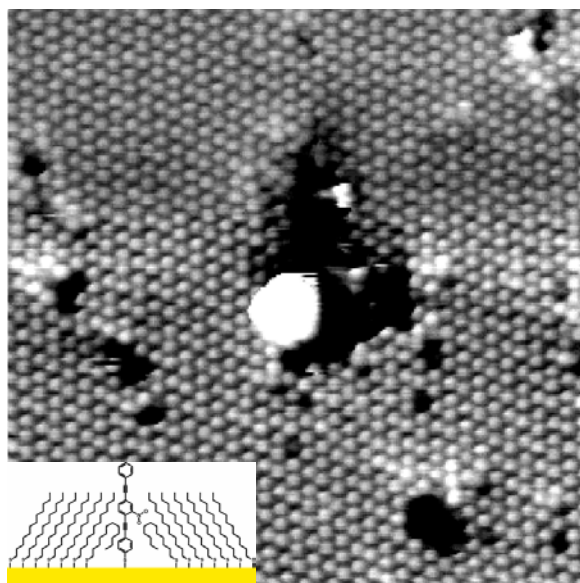


Figure 2. STM image at 4 K showing a NPPBT (4-(2-nitro-4-phenylethynyl-phenylethynyl)-benzenethiol) molecule inserted at a vacancy island in a decanethiol self-assembled monolayer. The inset shows a side view perspective of the relationship between the inserted molecule and the SAM matrix.²⁰

well-ordered, crystalline domains of molecules standing on end. Figure 3 is a STM image of a conjugated molecule, NPPBT (4-(2-nitro-4-phenylethynyl-phenylethynyl)-benzenethiol), inserted in a decanethiol film. The molecule is forced to adsorb such that the backbone of the molecule is oriented close to normal to the surface. This orientation allows for the molecule to be probed along its length with the STM tip acting as one electrode and the Au substrate acting as the second. The exact bonding geometry is dictated by the conformation or tilt, possibility at the S-Au bond. The forced alignment of the inserted molecule is due to two factors: (1) the preference of the sulfur head group of the molecule to bind to the Au surface and (2) the presence of regions in the SAM that are available for molecules to insert into. Alkanethiolate SAM quality can be manipulated depending on specific preparation steps, but defects are always present to act as adsorption

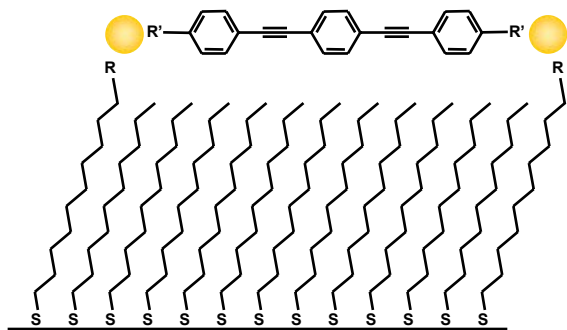


Figure 3. Side view schematic of proposed scheme for orienting conductive molecules for electrical measurements along the conjugated, molecular backbone.

SAM would have substituted ends that would preferentially bind each end of the molecule to be investigated and allow for conductivity measurements to be made along the length of the molecular backbone (Figure 3). The functional groups, R and R' as shown in Figure 3, that are placed on both the test molecule and the inserted molecules in the SAM would dictate the strength of the coupling. This interaction could be chemically tuned to vary from hydrogen bonding to coordination through metal ions to the use of covalent bonds. These measurements enable the assessment of electronic characteristics driven by chemical composition and structure that may be useful in future molecular electronic device design. Further placement of molecules on the SAM template would also allow for the creation of test circuits using conductive molecules linked end to end. The use of STM and AFM as complementary tools would be particularly useful in these experiments considering the convolution of the electronic and geometric properties of the SAM and the inserted molecules. Small changes in molecular conjugation or conformation are capable of strong influences on conduction properties.

In addition to measuring electronic properties of self-assembled monolayers and molecules supported in these films, low temperature measurements would help elucidate some of the issues that govern the passivating or insulating nature of the thin film supports in addition to intercalation pathways. By using self-assembly and single molecule insertion, the chemical functionality and reactivity can be determined on a local level. The reactivity and behavior of these thin films have yet to be studied on a local scale. Oxidation and etching of the SAM could be monitored as a function of exposure of reactive species. I would imagine using the techniques of single molecule insertion into the matrix to intentionally expose reactive ends of molecules that would serve as well defined reactive centers.

Metal oxide and supported metal clusters

In order to closely mimic conventional industrial reaction conditions, catalytic reactions like oxidation of carbon monoxide are now being studied on oxide surfaces, and metal nanocrystallites supported on metal oxides. The complexity of the metal oxide surface manifests itself in both the geometric and electronic structure where contributions from the underlying alloy permeate through the thin film. Figure 4 illustrates the complex unit cell of Al_2O_3 , alumina, epitaxially grown on $\text{NiAl}(110)$.²¹ This surface has only recently been studied with low temperature STM. AFM measurements would serve to help in interpretation of atomic positions in the lattice.

sites. Domain boundaries between ordered regions in the film also serve as adsorption sites.

To further use the SAM as an insulating test matrix for single molecule conductivity measurements, a binary component film would be used to selectively bind molecules parallel to the surface on the methyl terminated SAM. The degree of electronic coupling of a molecule lying flat on the relatively inert SAM would be minimal and relatively non-perturbative. This would be accomplished by exposing the binary SAM to a third molecule, a conductive, conjugated structure like NPPBT, by vapor deposition in vacuum at low sample temperature. The inserted molecules in the

Bias dependent STM imaging of this surface and metal clusters adhered to the oxide have provided insights into the structural nature of this layered system.²²⁻²³ The effect of poorly conducting regions as a result of the oxide formation on the alloy complicates and can often mislead interpretation of STM features. Of particular interest is the role of shape, size, and crystalline order that metal clusters have on catalyzed processes. Recently, groups have reported a very strong bias dependence in STM images of metal oxide features as well as the size of supported metal clusters.²⁴ AFM would help solve many of those issues. Experiments would begin with a model metal oxide system: Al₂O₃, alumina, epitaxially grown on NiAl(110). Metal clusters of Pd, Cu and other catalytically active elements would be studied on this surface using both STM and AFM. The relative effect and importance of cluster size, crystallinity, intercommunication with the oxide support, and the role of cluster edges will be assessed at the atomic level. Close collaboration will be maintained with Dr. Hans-Peter Rust at the Fritz-Haber Institute in Berlin, Germany regarding this work.

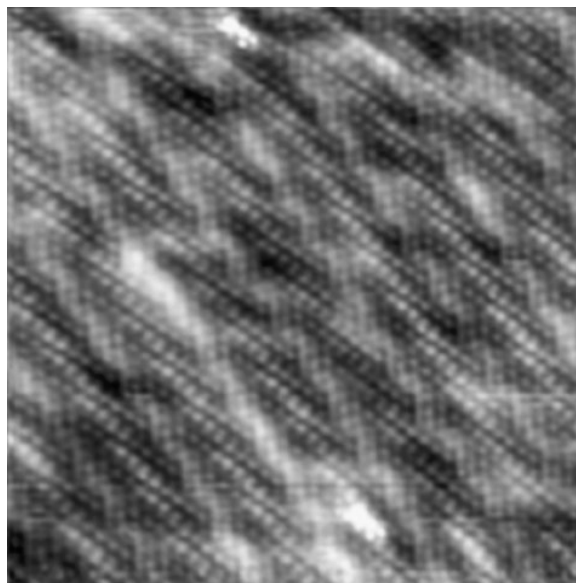


Figure 4. STM image of the complex Al₂O₃ film grown on NiAl(110).²⁵

Instrumentation and Techniques

The complementary use of STM and AFM for the study of atomic-scale properties of metals and metal-thin film systems is a burgeoning field. Only recently has a technique like AFM been used to measure metallic surface features at the atomic scale in addition to semiconductor and insulator systems. The most significant advance recently was made by Giessibl *et al.* where they were able to atomically resolve the exposed surface adatoms associated with the Si(111)-7×7 surface using a novel tuning fork AFM.²⁶ Advances in the design of non-contact or frequency modulated atomic force microscopes (FM-AFM) have enabled the simultaneous use of STM and AFM without the optical alignment requirements present in beam deflection force microscopy. This feature becomes particularly useful when considering a thermally shielded environment like a cryogenic microscope. STM becomes difficult when the conductivity of the surface drops or when the surface electronic structure is complicated by contributions from both the underlying surface and the bound thin film. By acquiring force microscopy data, many of the limitations associated with tunneling microscopy are overcome. Furthermore, the capability to observe the same surface features in series or simultaneously with STM and AFM, in controlled environments like UHV and liquid-He cooled temperatures makes a wealth of surface related phenomena accessible at the local scale.

Figure 4 illustrates the key components of a tuning fork AFM/STM. Briefly, a quartz tuning fork is affixed to a piezoelectric ceramic tube where one prong of the tuning fork is mechanically fixed and the other prong has a metallic tip attached to it. The tuning fork can be excited at its fundamental resonance with an external oscillator and as the tip is brought closer to the sample the resonance frequency will shift as a result of tip-surface forces that will produce

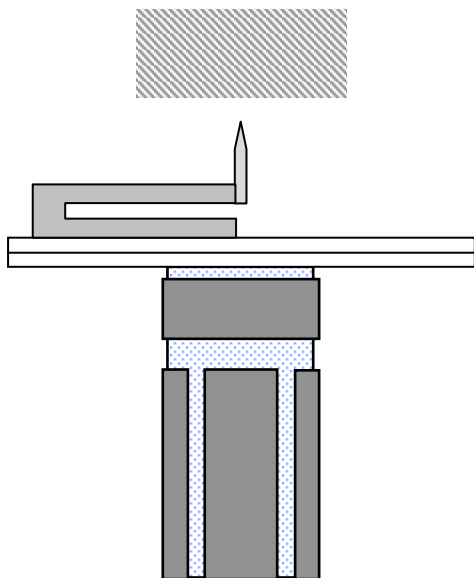


Figure 4. Side view diagram of a tuning fork STM/AFM setup. A quartz tuning fork with a metallic tip attached to one prong is mounted on a piezoelectric ceramic tube. Either tunneling current or the shift in resonance frequency of the tuning fork can be amplified and monitored as a function of sample position.

damping. The amount of frequency shift for the sensor is detected and amplified and its sensitivity to tip-sample distance is used for maintaining feedback. Alternatively, if the tip is brought closer to the surface, then a tunneling current can be measured for performing STM.

Future Directions

I envision my research group expanding its experimental repertoire to include other means of resolving surface reaction dynamics and interactions. Systems would be studied from nanometer to mesoscopic scales where time scales and degree of long interactions can vary substantially. Crystalline, well defined thin films can be grown using liquid immersion, exposure of clean surfaces to gases under vacuum and molecular beam epitaxy. In particular, there are films and structures that can be uniquely grown by beam methods due to the beam energy and composition tunability.

The array of surface sensitive tools will also expand to include electron spectroscopies and photon probes to measure surface structural

order and elemental composition. I imagine enlarging the scope of the research to include not only nanoscale phenomena but chemical dynamics and behavior on the mesoscopic scale as well. Incredible steps have been taken in the past few years in the use of low energy electron microscopy (LEEM) and photoemission electron microscopy (PEEM),²⁷ as well the computational efforts using kinetic Monte Carlo schemes towards the goal of bridging the gap between microscopic observations and macroscopic surface phenomena.²⁸ For example, theoretical modeling of semiconductor growth behavior has been found to be sensitive to lattice exchange processes that occur over long ranges and long time scales. Chaotic behavior in spatiotemporal patterns has been observed in catalytic systems when reaction fronts are monitored over microns.²⁹

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