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FINAL TECHNICAL REPORT
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Electron Tunneling Microscopy

By

John D. Baldeschwieler
Professor of Chemistry
Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, CA 91125

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I. INTRODUCTION



The rapid development of the Scanning Tunneling Microscope (STM) and its derivatives in the past five years has created new techniques not only for examining surfaces and surface processes, but also for surface modification, lithography and performing surface chemistry and spectroscopy at microscopic levels never before attainable. Understanding the mechanisms involved in these processes will enable researchers to utilize fully the tremendous capabilities potentially available with this technology.

STM is based on the phenomenon of quantum mechanical tunneling. A metal tip is brought within a few angstroms of a conducting sample by means of a 3-dimensional piezoelectric ceramic positioner. A tunneling current whose magnitude depends exponentially on the tip-sample separation can be established and maintained by means of a feedback circuit to the positioner. By rastering the tip over the surface (x and y) and monitoring the feedback to the z position, a topographic image of the surface can be formed. A current image can also be obtained by rastering the tip over the surface at a high frequency so that a constant average height over the surface is maintained. The image contrast is produced by

monitoring the fluctuation in current. The exponential dependence of the tunneling current upon the separation of the tip from the surface provides the exquisite resolution of the STM.

II. INSTRUMENTATION

A UHV-STM attached by a long stroke translator for sample transfer to a separate vacuum chamber for sample preparation has been designed and built in our laboratory¹. The sample preparation chamber houses a sample heater, ion sputter gun and XYZ manipulator. Both chambers are equipped with time of flight mass spectrometers. Access ports still remain free for additional surface analytic instrumentation.

The microscope body is based on the IBM (Zurich) "pocket" design² as described in the previous proposal. A few modifications, however, have been implemented. The louse now walks on a SiO₂ plate rather than stainless steel for superior dielectric properties. The eddy current damping of the spring suspension has been supplemented by viton strips threaded through the springs to minimize spring surge. The spring suspension has been optimized to a 1Hz resonance frequency to eliminate effectively most vibrational interference. The STM structure, including its vibration isolation spring suspension, was built by members of the research group and the chemistry department instrument shop. In addition, all associated electronics for STM control were designed and assembled by our group. A glove box equipped for controlled atmospheric sample preparation has also been purchased.

The entire data collection and processing system is PC controlled using software developed in our lab. Both topographical scans and current images are automated and digitally stored for subsequent data processing and display. A Vectrix PEPE graphics card and Mitsubishi 1020x1020 pixel monitor permit real time current grayscale and topographical line scan imaging of data. Our software package and

technique for current imaging will be presented in a manuscript to be submitted to the Review of Scientific Instruments. Unit cell averaged spectroscopy, current vs voltage (I-V) spectra, are also under computer control.

A lock-in amplifier enables us to perform modulation experiments where the average workfunction of a tip and sample can be extracted. Because the current depends exponentially on the tip-sample separation (s) as well as the square root of the average workfunction (ϕ),

$$I \propto \exp(-As\phi^{1/2})$$

where $A=4\pi(2m)^{1/2}/h$, a measure of $d\ln I/ds$ will yield the square root of ϕ . At a given applied bias (V), the tip position is modulated at high frequency over a small s , the current is measured by a lock-in amplifier at the modulation frequency and the resultant average workfunction is calculated.

III. RESULTS

The scanning tips were prepared by grinding tungsten wire. An overall tip radius of about a micron results from this method with much sharper protrusions or "minitips" providing the STM's imaging resolution. We have since implemented two electrochemical methods of preparing both tungsten and gold tips: AC self-termination and DC drop-off. Tips as sharp as 100Å in radius have been etched by these techniques as evaluated by Scanning Electron Microscopy (SEM). No significant differences in STM imaging quality and reproducibility are observed between tungsten and gold tips. However, spectroscopic measurements (I-V curves) are less subject to noise with gold tips. The quieter signal is perhaps due to gold's resistance to oxidation, which is one of the motivations for adopting it as a tip material. A more detailed analysis of tips used in atmospheric conditions has

been reported³ by our group

Many layered compounds such as highly oriented pyrolytic graphite (HOPG) are desirable STM samples because they are easily cleaved and practically inert. Atmospheric contamination of HOPG, however, may provide a nonconducting layer and permit tip-sample contact making the use of HOPG as an imaging standard under atmospheric conditions unreliable⁴. Molybdenum disulfide (MoS_2) is a layered semiconductor which provides an opportunity to examine a compound surface. We have studied MoS_2 by both STM imaging and spectroscopy⁵ in UHV.

The top layer of MoS_2 consists of a hexagonal lattice of S atoms with 3.16 Å spacing. Below this plane is an identical lattice of Mo atoms laterally displaced so as to reduce the 6-fold S planar rotational symmetry to 3-fold symmetry. The surface unit cell is diamond-shaped with 4 atoms at the corners. A single atom of the other type is centered in one triangular half of the cell and a crystal hollow located in the other half.

Our natural mineralogical samples of MoS_2 have variable doping levels and were largely uncharacterized prior to our studies. Sample type and doping were determined by Hall measurements and the type confirmed by the Seebeck coefficient. In both imaging modes, we were able to distinguish the two inequivalent atomic sites in addition to a hollow and observed a 0.3 to >1.5 Å height difference (depending on imaging and tip conditions) between these two atomic sites. This variability in measured corrugation is not surprising because the current measured by STM depends on the spatial extent of the surface wavefunction at a given site and a given energy and not on the position of the atomic cores.

MoS_2 provides an important challenge for theoretically understanding the STM's interaction with two chemically different species of a semiconductor. However, because of the 3-fold lattice symmetry, unambiguously assigning STM spots to sulfur or molybdenum by the STM topological or current data alone is not possible. To address this question, Terry R. Coley, a graduate student working with

both our group and Dr. William Goddard, has undertaken *ab initio* calculations designed to understand the fundamental aspects of the charge transfer process between tip and sample. One goal of these calculations is to predict which position of the tip over the sample gives rise to the greatest current.

We have used *ab initio* quantum chemistry techniques (generalized valence-bond [GVB]) to generate high quality wavefunctions of a large molybdenum disulfide fragment (Mo_7S_6) in the presence of a probe atom. The probe atom provides an acceptor or donor orbital for the electron transfer and is placed at various positions above the MoS_2 fragment. For each geometry, two equivalent energy wavefunctions are possible: one with an odd electron (or hole) on the sample, the other with the charge transferred to the tip. With computer programs developed in the Goddard group, we are able to calculate the Hamiltonian matrix element between these two non-orthogonal wavefunctions. The magnitudes of these matrix elements give information on the ability of the final and initial wavefunctions to couple (exchange) with each other as a function of geometry. This exchange, in turn, relates to the current generated by this charge transfer process.

Results to date for a variety of wavefunctions and tip-sample geometries indicate the following conclusions:

- i) In all cases explored, the electronic coupling between tip and sample is greater for geometries with the tip positioned over the Mo. This results despite the fact that the S nucleus is 1.5\AA closer to the tip than the second layer molybdenums.
- ii) The distance dependence is roughly exponential but with the *relative* rates over S and Mo becoming increasingly disparate at closer approaches. This results in the tip's increasing ability to sense the electronic differences between S and Mo at closer ranges.

These results qualitatively confirm the observed changes in corrugation between experiments (ii) and support an earlier suggestion⁶ that Mo might give rise to the high current spots in STM images due to its surface normal d_{z^2} orbitals.

We have also observed rough patches, hillocks and what appear to be charged defects, similar to those observed by Stroscio *et al.* for oxygen adsorbed on GaAs⁷ where the charge is screened over a characteristic distance around the defect by the carriers in the semiconductor depending on the doping levels and sample properties.

More recently, we have done unit cell averaged spectroscopy on the clean MoS₂ surface, which is inert and "unpinned"⁸. The results of these studies indicate the importance and extent of tip-induced effects that can be quantitatively controlled by doping and tip-sample separation in semiconductors. On an unpinned surface, no surface states or dangling bonds exist to screen the electric field, either applied or existing due to the difference in tip and sample workfunctions in the absence of an applied field. Part of the electric field appearing in the vacuum gap penetrates into the bulk of the unpinned semiconductor resulting in a Schottky barrier, in the limit of metal/semiconductor contact. Even for finite tip-sample separation, this potential drop occurs in the semiconductor and the energy bands "bend". Electrons in the bulk of the sample thus feel a different potential than those at the surface. The screened defect we observed on our sample may be a real-space visualization of band-bending at an unpinned surface.

Band bending is a common phenomenon at metal-semiconductor contacts for unpinned semiconductors. A few STM observations of band bending have been reported, but the theoretical and experimental implications of this effect have not yet been presented. A theoretical model explaining the effects of band bending on STM spectroscopic results for non-degenerately doped, passivated n-type Si(111) has been recently developed in our lab⁹. Since the surface potential decreases with increasing tip-sample separation, STM measurements of the tunneling barrier height at unpinned semiconductor surfaces are affected by band bending and will yield unusually low values. Qualitatively, these results suggest that interpretation of images and spectroscopy on any unpinned semiconductor surface is not

straightforward and requires a close examination of sample characteristics.

In a collaborative effort, Rockwell Corporation provided molecular-beam epitaxially (MBE)-grown GaAs(100) for investigation with the UHV-STM. This semiconductor material was arsenic-passivated by a several hundred angstrom thick arsenic cap which allowed the sample to be handled in air without degradation or oxidation. A pristine GaAs surface is prepared by simply heating the sample in UHV at 450°C for 5 minutes to remove the protective cap. GaAs may be deliberately cut slightly off the [100] direction to expose a highly stepped surface. The structure at MBE-prepared GaAs steps is important from both a scientific and a technological viewpoint, the latter especially in device preparation and quality control. The step height is 2.8Å and should be easily resolvable by STM. N-type samples of both the (100) and 2° off (100)-axis surfaces were provided. Preliminary imaging results show structure that suggests steps. None of the results have yet been published pending further investigation. Spectroscopic studies have shown current-voltage curve rectification consistent with the dopant type and similar to those seen in Kaiser's work on H-terminated silicon¹⁰. No p-type samples have yet been investigated, but could be used in the future for comparison to n-type materials.

We have begun preliminary STM studies on the (110) cleavage plane of GaAs. Techniques for *in situ* cleaving of GaAs in the [100] direction to expose the (110) face have been developed. The GaAs(110) surface has a chainlike structure consisting of alternating Ga and As atoms directed in the [110] direction. Like MoS₂, it is a compound surface with two chemically and electronically distinct sites in the unit cell which offers the possibility to explore the energy dependence of the surface density of states (DOS). Recently, atomically resolved images of this surface have been obtained in both the topographical and current imaging modes. The n-type sample was degenerately doped ($>10^{18}/\text{cm}^3$) and cleaved *in situ* at a pressure of $<10^{-10}$ torr. A 1x1 periodicity is observed, as reported by Feenstra *et al.* with a measured amplitude of $\sim 0.1\text{Å}$ in the topographical image. The surface density of

states is characterized by filled states primarily localized on the As atoms and empty states on Ga atoms. Atomic rows of presumably As atoms are observed in the images taken at a sample bias of -3.0V. At this bias, STM images filled states on the surface. Preliminary studies including I-V spectroscopy of GaAs and voltage-dependent imaging are in progress.

One promising application of the STM also being explored in our lab is site-specific vibrational spectroscopy of individual adsorbed molecules through inelastic tunneling spectroscopy (IETS). While the vibrational spectroscopy techniques currently available can be used to obtain the vibrational spectra of as little as 0.1% of a monolayer, these techniques provide spectra from large numbers of molecules averaged over a large area (usually greater than 1 nm^2). Any means for site-specific vibrational spectroscopy of individual adsorbates would be an important scientific advance and would facilitate the study of chemistry and physics at surfaces.

Vibrational spectroscopy of individual adsorbed molecules together with atomic-scale imaging of their bonding environments should be possible through the use of STM. The STM is essentially the non-planar analogue of the planar metal-insulator-metal (MIM) junctions which are used for inelastic electron tunneling spectroscopy. IETS has been demonstrated to be one of the most sensitive vibrational spectroscopies available, but in the planar MIM junction it is limited by spatial averaging and junction inhomogeneity in the same ways as the other surface vibration probes¹¹. Spectroscopic measurements with the STM similar to those made in the planar MIM junction should be possible, but with atomic-scale localization and on a broader range of systems. In the MIM junction a metal oxide is the insulating barrier and adsorption base. The STM affords more flexibility: the molecule can be adsorbed on any sufficiently conducting surface, and the nonconducting barrier can be vacuum, gas, or even liquid. Combined with the STM's imaging capability, IETS with would be an extremely powerful surface

analysis tool.

As a first step in the development of IETS/STM in our group, we have built and implemented a low temperature STM. Because the most widely accepted proof of vibrational mode detection is measurement of an isotope effect, one of our preliminary goals is to detect the Si-H and Si-D vibrational stretching modes on hydrogenated and deuterated silicon surfaces. After optimizing experimental conditions with this system, additional work will be directed toward vibrational spectroscopy of individual adsorbates such as benzenethiol and t-butyl thiol on gold.

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