Nonlinear Alternating-Current Tunneling Microscopy

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(Received 1 September 1988; revised manuscript received 6 March 1989)

A new method of scanning tunneling microscopy is proposed that should allow atomic resolution imaging on insulators. A nonlinear ac technique is used that is shown to allow stable control of a microscope tip above insulating surfaces where dc tunneling is not possible, including aluminum oxide and liquid-crystal layers. Images of copper oxide and WSe_2 have been obtained using this technique. Nanometer features have been observed.

PACS numbers: 68.35.Bs, 72.20.Ht, 73.40.Gk

Scanning tunneling microscopy (STM) is a powerful technique that can obtain atomic resolution on a conducting material. An STM has a metal tip that is held approximately 1 nm from the sample. Because the electron wave functions of the tip and the sample slightly overlap at that distance, some electrons can tunnel from the tip to the sample, and a measurable current can flow.[1] Both this overlap and the current decrease exponentially with the distance between the tip and the sample. The current can be fed back to control the tip height so that the tip traces out contours of constant local density of states.[2]

Tunneling microscopes do not work well on insulating samples; either the surface of the sample rapidly charges up to the tip potential and the tunneling stops, or the tip is pushed through the insulating layer until some current flows. Atomic-force microscopy has been used to study some insulators,[3-5] but it is unable to provide information about surface electronic properties, and may damage some surfaces.[6-10]

Here I demonstrate a new method that should allow atomic-resolution noncontact microscopy of insulating films, or possibly even bulk insulators. This technique involves tunneling a small number of electrons onto and off the surface to be studied during alternate half-cycles of a driving voltage. The position of the microscope tip is controlled by the ac tunneling current. This ac arrangement makes it unnecessary to conduct through the sample, allowing the study of insulators.

The microscope could operate by detecting the tunneling current at the driving frequency, I_1, but I_1 is submerged in a much larger signal from displacement currents in stray capacitances. Instead, the microscope senses I_3, the current at 3ω, where ω is the driving frequency. I_3 is produced nonlinearly as a result of the high electric fields that occur within a small distance of the microscope's tip. The use of I_3, rather than I_1, eliminates the effects of stray capacitances, and eliminates other effects that might not be localized at the tip.

I_2, the current at 2ω, is not used in the present experiments because its sign is dependent on the details of the tip and the sample, and in a symmetrical experiment, $I_2=0$. If $I_2=0$ while it is used to control the tip height in an STM, the tip would push into the sample and destroy the surface under study. Interesting information about the surface might be obtained by using I_3 to control the tip height, and then measuring I_2 as a function of position.

The signal necessary to control the microscope tip, I_3, can be produced by any of three nonlinearities. First is the Coulomb barrier that will limit the tunneling to a single electron per cycle. The charging of the surface (Coulomb blockade)[11-13] that prevents a dc microscope from operating well on insulators can also be significant for an ac microscope. If, for example, an electron which is tunneled onto the surface of an insulator becomes localized within 1 nm of the tip, it can change the potential of the space through which tunneling occurs by ≈ 1 V because of the Coulomb potential. Such a change is enough to drastically reduce the probability of tunneling a second electron, since typical microscope operating voltages are on the order of 1 V.

To illustrate this mechanism, consider the case where $R \gg 1/\omega$, where R is the average tunneling rate. The probability for finding the electron on the sample then snaps from near zero to nearly unity in synchronization to the driving voltage. The current is then a series of δ functions, and all odd harmonics receive equal amounts of power. If one models the microscope as a two-state Markov process (electron on either tip or sample), the amount of harmonic signal can be calculated by numerically solving the rate equation for transfer of probability back and forth. So long as $R > 1/\omega$, charging effects alone will force $I_3 > 0.1\ e^-$/cycle. A signal of that magnitude can be detected by commercial microwave amplifiers when the microscope tip is coupled to a $Q=1000$ resonant cavity. If the sample has a clean surface or is a surface metal, then electrons can travel more than a few nanometers in π/ω, and more charge can be transferred before tunneling stops. However, I_3 from this source may not be any larger.

The second type of nonlinearity that the microscope uses is caused by changes of the density of states near the Fermi level. According to the usual STM theory,[1]

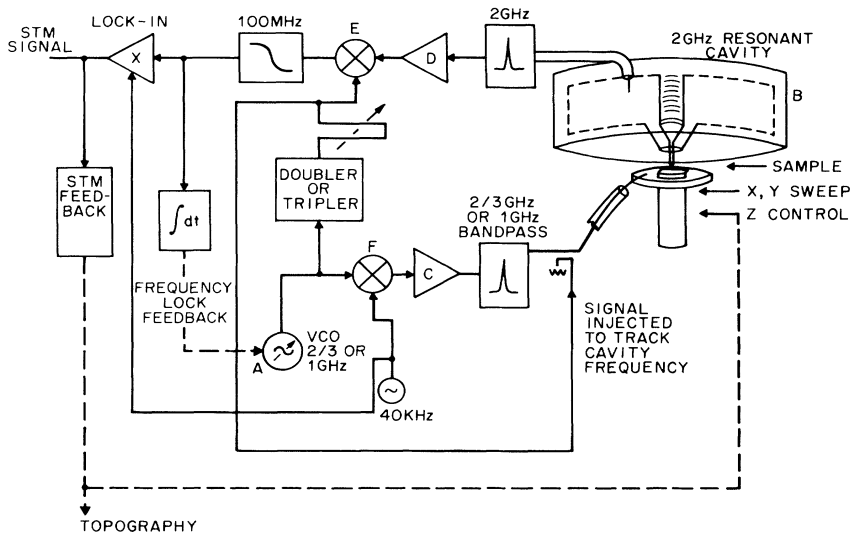

FIG. 1. Schematic diagram of the apparatus. A is the master voltage controlled oscillator (VCO) ($\omega \approx \frac{2}{3}$ or 1 GHz). The output of A is fed through amplifier C (1 W), and drives the sample voltage. D is the receiver amplifier, and mixer E is the homodyne detector. The VCO frequency is locked to that of B by injecting a small signal at 2 GHz, and measuring the phase shift through B.

the tunneling rate is proportional to the integral of the local density of states over energy. If the local density of states is not constant, the tunneling rate will have a nonlinear dependence on the tip-sample voltage. I_3 is proportional to the second derivative of the local density of states, which is always positive if the microscope is operated in the band gap of an insulator.

The third type of nonlinearity can be modeled as a set of classical two-level systems with a dipole moment, d, distributed on the surface of the tip and sample. These dipoles correspond to polar molecules (H_2O and OH^-) adsorbed on the surfaces. In analogy with a typical model of a glass,[14] the hopping between the two states is controlled by a broad, uniform distribution of barrier heights, B_j, from 0 to kT_g. $T_g \gg 300$ K, and might correspond to a structural glass transition temperature in the layer of adsorbed contaminants which contain the two-level systems. Such a system will have a saturable nonlinearity $P_j(n\omega) \approx d\min[(E/E_j^*)^n, 1]$, where P_j is the polarization of system j, d is the dipole moment, and E_j^* is the critical field that will rapidly drive and hold the system in one of its two states. $E_j^* d$ is on the order of the barrier height or kT, whichever is less. There are no systems with $E_j^* < kT/d$ because their coupling to phonons is equivalent to white noise of amplitude kT/d per mode. A field smaller than this cannot saturate the system because it would be only a small perturbation on the thermal noise. Provided that the density of these systems is sufficiently low so that a dipolar glass is not formed, I_n will be the sum of this polarization over space, weighted by the coupling of each system to the tip.

The ac STM will work on thin-film (< 50 nm) samples. Two effects combine to make operation on thicker films difficult. First, more drive voltage must be applied to develop the required voltage V_1 between the tip and the sample, and the larger voltage implies larger power dissipations in the microscope. In my microscopes, up to 11 V at 0.66 GHz can be applied and still hold thermal drift to a manageable level. Second, the coupling between the electron hopping from the tip to the sample and the receiver becomes weaker as the sample gets thicker, so the available signal decreases. It may be possible to operate the ac microscope on bulk insulators by using a very sharp tip so that the tip radius, rather than the thickness of the insulating film, controls the electric field and the coupling.

I have constructed such a microscope, and used it in air to observe a variety of surfaces. The mechanical design of the microscope is loosely based on a design by Sonnenfeld *et al.*,[15] but the sample is scanned, rather than the tip. Scanning techniques are standard. The microscope tip is a Pt-Ir point that is produced either by clipping a wire or by breaking a spot weld between two wires.

The microwave circuitry is displayed in Fig. 1. It is based on a homodyne receiver that has a noise figure of 3.2(5) dB at the output of the microscope's resonant cavity. To make the apparatus less sensitive to drifts in mixer E, the drive signal is phase inverted at 40 kHz, so the microscope signal appears at the output of E at 40 kHz and is then detected by a lock-in amplifier. The bandwidth of the system is determined by the lock-in amplifier, and is typically 300 Hz. Since the resonance of cavity B is narrow (1–2 MHz), the capacitance change of a 1-μm tip during the last micron of the ap-

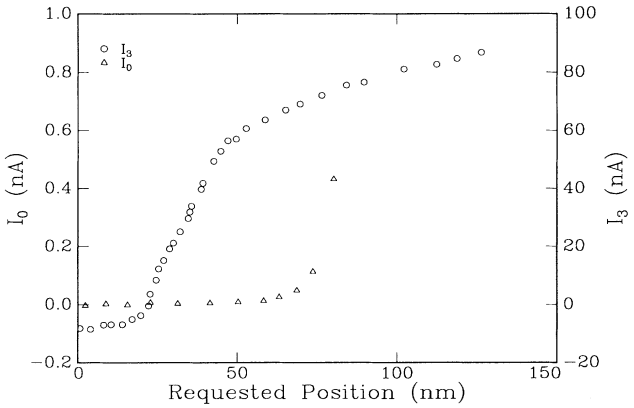

FIG. 2. Tunneling current as the tip is pushed into an Al_2O_3 surface. The tip touches the surface near 15 nm, and breaks through the oxide near 70 nm. The oxide film is 2–3 nm thick; most of the motion between the rise of I_3 and I_0 is taken up by deformation of the tip and the microscope.

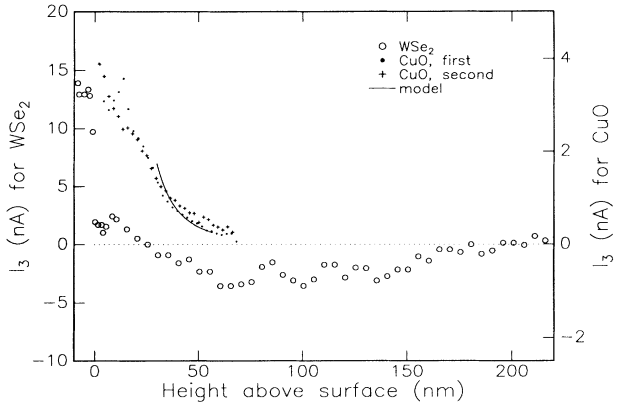

FIG. 3. Current at 3ω as the tip encounters a WSe_2 and a copper oxide surface as a function of tip height. The origin is the point at which the I_0 becomes nonzero. The WSe_2 data shows a sharp step corresponding to the tunneling from the tip to the surface at $z=0$, and a long-range tail. The copper oxide data consist of two successive approaches to the surface. They match well above 25 nm, but show irreproducibility below that height, perhaps indicating the amount of dirt that adheres to the surface. The solid line is a one-parameter fit of the two-level-system model to the copper oxide data.

proach to the surface can shift the cavity frequency by more than its linewidth. Oscillator A, then, must be controlled to track cavity B. This device can also be used as a scanning capacitance microscope and get 100-nm resolution on insulators. A dc bias (V_0) could be applied to the sample, and the dc current measured simultaneously with ac currents.

Nonlinear signals can be observed from AOT[16] on Au, WSe_2, and native oxides of Cu and Al in air, without dc tunneling current. Figure 2 shows I_0 and I_3 as functions of tip height for an aluminum oxide film. The signal due to ac nonlinearities becomes significant long before any dc current begins to flow.

Data were also collected on the variation of I_3 and I_0 as a function of V_0 for aluminum oxide and the AOT on gold. With I_3 controlled at 50 nA from a 30-μm tip, I_0 remained less than 10 pA until the insulator broke down. The lack of dc current shows that the tip is stabilized substantially more than 1 nm above the metal substrate. Al_2O_3 films broke down catastrophically near 6 V, and the microscope tip immediately welded itself to the underlying aluminum. The AOT layer broke down between 2.3 and 3.2 V, but I_0 remained finite, and the film would recover its insulating properties in less than 1 ms after the voltage was reduced. Layers of adsorbed atmospheric contaminants on gold or copper oxide also tend to break down much like the AOT.

Copper oxide and tungsten selenide are more convenient samples for these experiments. They are both semiconductors, and so at low dc voltages they can be treated as insulators, but comparisons can be made to dc tunneling at higher voltages. Figure 3 displays measurements of I_3 versus tip height. For the WSe_2, a weak signal slowly appears at a height near 200 nm. This is presumably due to charge rearrangement (classical two-level systems) in whatever insulating dirt is on the tip and the sample. It can vary in magnitude by a factor of 10 from one sample to another. Next, I_3 jumps sharply upward when the tip is within tunneling range of the surface. The slope of this jump varies somewhat, but can be associated with a characteristic length of 0.5 to 1.0 nm. I_0 typically becomes nonzero at the same time. Finally, the tip touches the surface, and the increase in signal is due to increasing contact area.

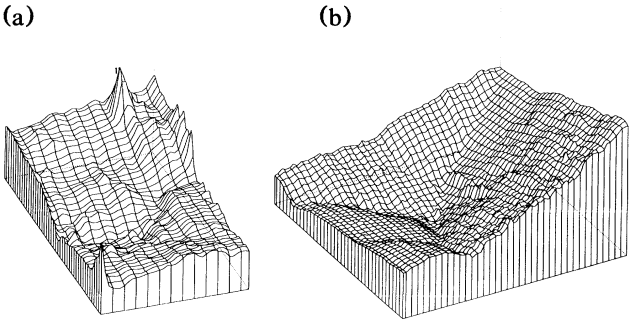

FIG. 4. (a) Mesh plot of a 40.5-nm by 12-nm section of copper oxide surface. This scan was taken at $I_3=2$ nA, $V_1\approx 0.4$ V, and no dc current ($|I_0|<10$ pA with $V_0=-0.2$ V), then lightly smoothed with a 0.6-nm FWHM Gaussian. The vertical relief (neglecting "1") is 5 nm. The peak marked "1" is believed to be associated with a brief spike of I_0 and I_3, but there is no evidence that the surface was modified by the spike. (b) An 81-nm square region of WSe_2 surface taken at $I_3=10$ nA, $V_1\approx 4.4$ V, and V_0 floating, so I_0 is exactly zero. The terrain ranges over 12.5 nm vertically.

The other curves in Fig. 3 show data for a copper oxide film and a one-parameter fit of the two-level-system model to the data. We will assume that each system has a characteristic dipole moment $d=1.87D$, equal to a water molecule. The free parameter in the fit of the model to the data is the density of systems per unit area and energy, ρ. The best fit was with $\rho=4\times10^{-12}$ cm^{-2}K^{-1} with a 1-μm tip radius scaling as the inverse square of the tip radius. If $T_g=600$ K, this corresponds to a 0.4-nm layer of water on the surface, similar to contamination levels observed on other oxides.[17,18]

Figure 4(a) displays an image of copper oxide obtained with this technique and zero dc tunneling current. The scan-line to scan-line matching is generally good, and 1-nm features are visible. Spikes in the current occur occasionally, and may be due to some localized dielectric breakdown,[19,20] as the electric fields are high enough (>1 MV cm^{-1}) for hot-electron effects. Figure 4(b) is an image of a crash site on a WSe_2 surface. In both cases, it is believed that the microscope is scanning the layer of contaminants which have been adsorbed by both tip and the sample, as it is possible to tunnel so that V_0+V_1 exceeds the sample gap, and still observe no dc current.

These images show the potential usefulness of the nonlinear ac tunneling microscope for observations of surfaces that conventional tunneling microscopes cannot image. Obtaining useful images from the microscope will require clean surfaces, as the ac STM detects contaminants adsorbed onto a surface as well as it detects the surface of interest.

I thank Harald F. Hess for useful discussions.

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