Single-electron tunneling to insulator surfaces measured by frequency detection electrostatic force microscopy

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Single-electron tunneling events between a metal probe and an insulator surface are measured by frequency detection electrostatic force microscopy. Single-electron tunneling events typically cause 1–10 Hz shifts in the 300 kHz resonance frequency of the oscillating force probe. The frequency shifts appear only within a sub-2 nm tip–sample gap and their magnitude is roughly uniform under fixed experimental conditions. An electrostatic model of the probe–sample system yields results consistent with the measurements. © *2004 American Institute of Physics*.
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For years the scanning tunneling microscope[1] (STM) has been used to characterize surfaces. Unfortunately, its application to insulator surfaces is limited because it requires a measured current in the picoampere range to operate. To characterize electronically isolated states in insulator surfaces, force detection of single electron tunneling has been demonstrated by Klein and Williams.[2,3] The single electron tunneling events to insulator (SiO_2) surfaces were detected by amplitude/phase electrostatic force microscopy (EFM). Additionally, a model was constructed for the nonlinear dynamics of the force probe and the amplitude/phase response due to the single electron tunneling events.[4]

This letter describes measurement of single electron tunneling events between a metallic probe and an insulator surface by frequency detection EFM.[5] In this technique, changes in the resonance frequency of an oscillating force probe are measured due to electrostatic force gradients near a sample. An electron tunneling between the probe and an insulator changes the electrostatic force gradient and shifts the probe's resonance frequency by changing the net charge on the insulator surface.[3] Frequency detection EFM is advantageous because it is insusceptible[6] to the nonlinear dynamical instability[4] observed in amplitude/phase measurements. In addition, the experimental conditions required to observe single electron tunneling events are simpler than in the amplitude/phase detection case.

Measurements are performed with an atomic force microscope (Omicron, Multiprobe S) modified for EFM in a 10^{-8} Torr vacuum. An amplitude regulating circuit maintains the probe oscillation at the resonance frequency and a fixed amplitude (~ 10 nm). A dc voltage of 1–4 V with respect to the sample flatband potential is applied between the probe and the sample. The force gradient due to the dc voltage monotonically reduces the probe resonance frequency as the tip–sample gap is reduced. For a metallic probe with cantilever stiffness, $k = 50$ N/m, and a 35 nm tip radius, and a silicon sample with a 10-nm-thick SiO_2 film, the resonance frequency typically drops by a few hundred hertz as it approaches the surface. A FM detector (nanoSurf, easyPLL) measures the resonance frequency shift. Figure 1(a) shows the experimental schematic and Fig. 1(b) shows an energy diagram for tunneling with a dc voltage biased probe-sample system.

In frequency detection EFM, the thermal frequency noise in a bandwidth, B, is $\delta f = \sqrt{f_o k_b T B / \pi k Q \langle a^2 \rangle}$, where f_o is the probe resonance frequency, k_b is the Boltzmann constant, T is the temperature, k is the cantilever stiffness, Q is the probe quality factor, and $\langle a^2 \rangle$ is the mean-square oscillation amplitude.[7] For typical experimental conditions, the thermal frequency noise in a 10 Hz bandwidth is expected to be 0.01 Hz, corresponding to a minimum detectable force gradient, $\delta F'_{\min} = 2k\ \delta f / f_0$,[7] of 3×10^{-6} N/m. Far from the sample, the measured noise level is comparable to this theoretical value. When a voltage biased tip is brought near the surface, the frequency noise increases significantly. The increase appears to be caused by force gradient fluctuations due to random charge motion in the sample. A typical measured frequency noise is 0.4 Hz in a 10 Hz bandwidth, leading to a minimum detectable force gradient of 10^{-4} N/m. At this noise limit, the EFM is sensitive to a change in surface charge of less than 1/10 of a single electron in a 10 Hz bandwidth under typical experimental conditions.

To measure single electron tunneling, the probe is positioned above the insulator surface and scanned up and down perpendicular to the surface by a few nanometers. The resonance frequency shift is recorded versus the displacement of the probe. When the minimum gap between the probe and

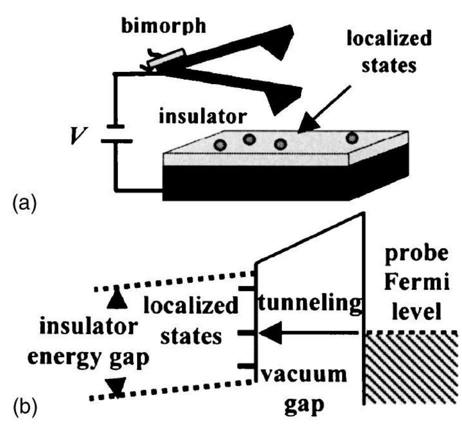

FIG. 1. (a) A schematic of the experimental arrangement. (b) An energy diagram for the dc voltage biased probe-sample system.

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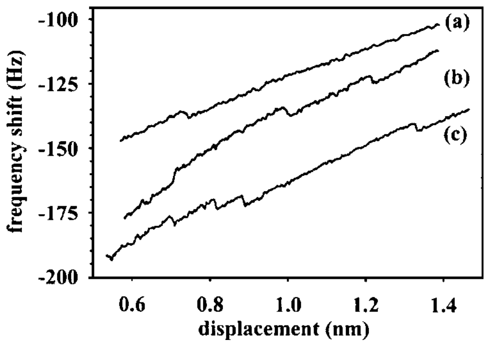

FIG. 2. Frequency shift curves measured within 2 nm of SiO_2 surfaces. Curve (a) was acquired near a 4.6 nm film and (b) and (c) were acquired near a 10 nm film. The abrupt steps are caused by single electron tunneling events.

the sample is less than 2 nm, abrupt steps occasionally appear in the frequency shift versus distance curves as shown in Fig. 2. The frequency steps are caused by single electron tunneling events between the probe and the sample. An electron tunneling "forward" (in the direction of the electrostatic force due to the dc voltage) causes a positive frequency step as in Fig. 2(a), while an electron tunneling in the "reverse" direction causes a negative frequency step. Figure 2(b) shows two forward events, and one reverse event. In numerous measurements, the forward events outnumber the reverse events by about 10:1. The steps in Fig. 2 do not appear absolutely abrupt because the detection bandwidth is 10 Hz and a single scan data acquisition is done in 3 s. Each data point is numerically averaged with its two neighbors to reduce noise. Frequency steps have been observed on 4.6-, 10-, and 20-nm-thick SiO_2 layers and 3.9-nm-thick HfO_2 layers on Si substrates.

In most locations, no events (frequency steps) are detected. However in some locations, a single step is seen, as shown in Fig. 2(a). Even more rarely, a multiple step sequence is observed as shown in Figs. 2(b) and 2(c). The spatial infrequency of events is due to the sparse distribution of states near the insulator surface. The individual frequency steps are due to single electron tunneling to a localized, electronically isolated state. The sequences are due to several electrons separately tunneling to a few states in the vicinity ($\sim$100 nm^2 area) of the tip apex.

To establish the measured frequency steps as tunneling events, many 3 nm range scans have been acquired in which the tip approaches the surface, and the surface location is registered by tip–sample contact (repulsive forces). Figure 3 shows typical results from (a) a 10 nm SiO_2 film and (b) a 20 nm SiO_2 sample with the surface contact point established as the zero of the horizontal axis. A tunneling event appears in each case with sub-1 nm tip–sample gap. Hundreds of such curves have been collected and in all cases the events appear within a 2 nm tip–sample gap.

The strong gap dependence supports the claim that the frequency steps are caused by electrons tunneling between the probe and sample. Thermal or photoemission of electrons from the tip or surface would not depend strongly on tip–sample gap. If these mechanisms were operative, some frequency steps would occur outside of the sub-2 nm range. To determine that the steps are not caused by field ionization, the probe was scanned over the 3 nm range with a 6 V dc bias applied, as opposed to the 1–4 V dc, to increase the

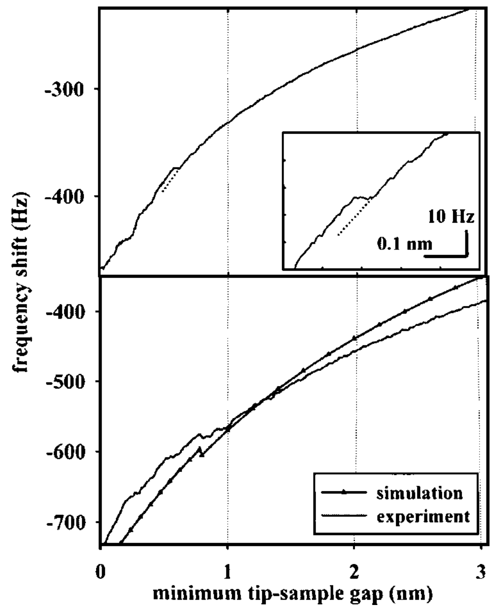

FIG. 3. (a) A frequency shift curve acquired near a 20 nm SiO_2 film. The inset shows the tunneling event in detail. The dotted line has been added to help define the tunneling event. (b) Overlay of a frequency shift curve measured near 10 nm SiO_2 and a simulation using a 3D spherical model of the probe tip.

electric field between the tip and sample. No events were seen outside the 2 nm range under this condition. The relatively uniform magnitude of the frequency steps, as in Figs. 2(b) and 2(c), supports the single electron conclusion, as does the fact that trap states in the insulator are expected to provide a state for only one electron. Further evidence is provided by modeling, which is discussed in the following.

Frequency shift curves have been computed for a one-dimensional parallel plate tip–sample model[4] and an approximate three-dimensional (3D) spherical tip/plane model. The models give similar results; however, the spherical model best fits the frequency shift versus distance curves. In both models, the force on the probe is computed for the neutral oxide and for the oxide charged with one electron. For the uncharged oxide, the force component acting on the probe toward the surface is

$$F(z) = -\frac{1}{2}\frac{\partial C}{\partial z}V^2, \tag{1}$$

where z is the tip–sample gap, C is the net capacitance between the doped Si substrate (treated as a conductor) and the metal probe, and V is the applied dc voltage with respect to the flatband potential.[8] The spherical model uses the exact solution for the capacitance between a conducting sphere of radius r held at a gap g from a conducting plane and incorporates the oxide of thickness t and relative dielectric constant ε_{ox} by taking $g=z+t/\varepsilon_{ox}$. This approximation assumes that the electric field lines fall normal to the oxide surface. When the oxide is charged by a single electron tunneling event, the applied voltage, V, in Eq. (1) is replaced with $V \pm e/C_{ox}$.[4] Here $C_{ox}=\varepsilon_{ox}\varepsilon_0 A_{eff}/t$ is the oxide capacitance over an effective tip area A_{eff}. For $A_{eff}=r^2$, a good correspondence is found between the measured and model frequency shift versus distance curves for reasonable values of the tip radius. The approximation $V \rightarrow V \pm e/C_{ox}$ is valid when the tip radius is much larger than the sum of the oxide thickness and the vacuum gap.

The frequency shift, Δf, is computed from $F(z)$ by a dynamic model of the oscillating probe.[9,10] For oscillation amplitudes comparable to the mean tip–sample gap, the resonance frequency shift, $\Delta f(z_m)$, of the probe is

$$\Delta f(z_m) = \frac{f_0}{2k} F'_{\mathrm{eff}}(z_m)$$

with

$$F'_{\mathrm{eff}}(z_m) = \frac{-2}{\pi a}\int_{-1}^{1} \frac{F(z_m + a(1+u))u}{\sqrt{1-u^2}} du, \quad (2)$$

where a is the fixed amplitude of oscillation, and k is the cantilever stiffness.[10] Here z_m is the minimum tip–sample gap which is related to the gap by $z=z_m+a(1+u)$, with $u=\cos(2\pi f_0 t)$, and $F'_{\mathrm{eff}}(z_m)$ is an effective force gradient since the instantaneous force gradient varies considerably over one cycle.[9] The formulas in Eq. (2) apply for force gradients which are small compared to k. Frequency shift curves for the uncharged oxide are calculated by Eqs. (1) and (2). The curves for the uncharged and charged oxide are combined to generate a complete frequency shift curve incorporating the tunneling event.

Figure 3(b) shows a measured frequency shift curve and a simulation using the 3D spherical model. Measured parameters for the model are the SiO_2 thickness (10 nm), the tunneling gap (0.79 nm), the oscillation amplitude (10 nm), the probe's free resonance frequency (323.3 kHz), and the applied dc bias (4 V). The probe properties are varied to fit the data, however they are constrained by manufacturer specifications. The varied parameters are the probe stiffness (45 N/m, specified as 20–75 N/m) and tip radius (40 nm, specified as less than 35 nm).[11]

The model agrees with the measurement as well as may be expected since the actual geometry of the tip is not known; the gap-dependent voltage drop in the Si substrate is not taken into account, the charge configuration in the insulator is not known, and the field in the oxide is assumed to be normal to the surface. The model predicts a 9 Hz frequency shift associated with single electron tunneling while the measured frequency shift is about 12 Hz. The smooth theoretical and experimental background frequency curves are different by less than 20% over the range, which is reasonable given the approximations of the model.

In summary, single electron tunneling to insulator surfaces has been detected by frequency detection electrostatic force microscopy. The evidence supporting this claim is that the frequency steps interpreted as single electron tunneling occur only within 2 nm of the surface, the states to which tunneling occurs should accept only single electrons and they have a magnitude which is consistent with simple electrostatic modeling.

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