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Single-electron manipulation to and from a SiO_2 surface by electrostatic force microscopy

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Occupation of individual electron states near the surface of a SiO_2 film is controlled by reversible single-electron tunneling to or from a metallic electrostatic force microscope probe. By switching the polarity of an applied dc bias between the probe and the sample to adjust the Fermi energy of the probe with respect to states near the dielectric surface, individual electrons are repeatably manipulated in and out of the sample. The single-electron charging and discharging is detected by frequency detection electrostatic force microscopy. © *2005 American Institute of Physics*.
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Scanning tunneling microscopy[1] (STM) is useful for characterizing electronic states of metals and semiconductors with atomic spatial resolution. However, its application to insulating materials is limited by the requirement that a minimum current (typically 1 pA–1 nA) flow between the STM probe and the sample. To characterize localized, electrically isolated states in insulating samples, an alternative method is required. Recently, single electron tunneling between a metallic electrostatic force microscope[2] (EFM) probe and insulating thin films was demonstrated by *amplitude and phase*,[3] or *frequency*[4] detection. This letter demonstrates that by switching the applied dc bias between the probe and the sample, single electrons can be repeatably manipulated between the probe and electronic states near the sample surface.

Frequency detection EFM measures electrostatic force gradients near a sample surface. Under typical experimental conditions, changes in surface charge on a 10-nm-thick SiO_2 film of less than 1/10 of an electron can be detected in a 1 Hz bandwidth.[4] In frequency detection EFM, a metallic force microscope probe is mechanically oscillated at its resonance frequency by an external oscillator. The oscillation is maintained at resonance frequency, f, and fixed amplitude, a, by a feedback circuit. A force gradient, F', acting on the probe shifts its resonance frequency away from the natural frequency, f_o, according to the equation $\Delta f = -f_o F'/2k$, ($F' \ll k$). A typical probe has $f_o \sim 300$ kHz, quality factor $Q \sim 10^4$ under ultrahigh vacuum conditions, stiffness $k \sim 50$ N/m, and a probe tip radius of 35 nm or less.[5] The probe is oscillated at an amplitude of 10–30 nm. A schematic for the measurement is shown in Fig. 1(a). As the minimum tip-sample gap, z_m, is reduced into the nanometer range, with an applied dc voltage, V, (typically a few volts) between the sample and the probe, the probe tip experiences a smoothly increasing electrostatic force gradient and the resonance frequency shifts down monotonically by a few hundred Hertz before tip-sample contact. The measured data are curves of resonance frequency shift versus probe-sample gap. Any change in surface charge under the probe tip modifies the electrostatic force gradient on the tip causing a shift in the resonance frequency. A single electron tunneling event between the probe tip and the surface produces an abrupt shift in the resonance frequency of the probe of 1–10 Hz under typical experimental conditions.[4]

The tunneling probability depends strongly on the vacuum gap, increasing by almost an order-of-magnitude per 0.1 nm, as the probe approaches the sample.[6] A one-dimensional square barrier model is used to estimate the gap at which the single electron tunneling rate becomes 1 electron/s. An electron in a state 1.5 eV above the center of the SiO_2 band gap at the sample surface sees an ~3.8 eV tunneling barrier. The tunneling rate for such a state becomes 1 electron/s at a vacuum gap of 1.9 nm. With a 10–30 nm amplitude, only a fraction of the cycle is spent in the tunneling range, therefore the gap for a tunneling rate of 1 electron/s is expected to be somewhat less than 1.9 nm.

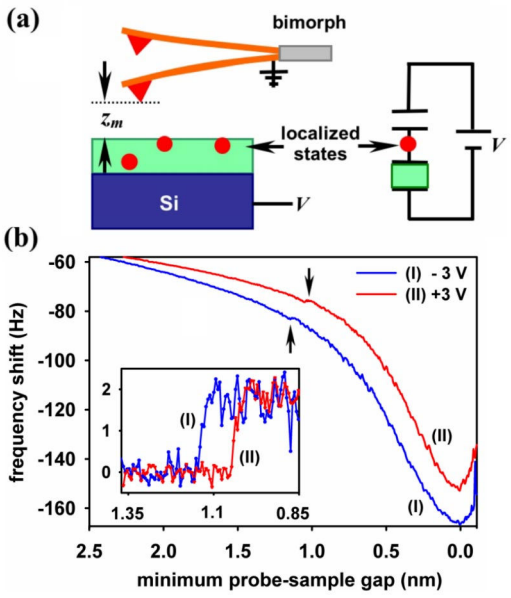

FIG. 1. (Color online) (a) Schematic of the probe-sample system for single electron tunneling measurements; (b) typical curves of resonance frequency shift vs probe-sample minimum gap measured near a sample with a 10 -nm-thick SiO_2 film. The curves have been obtained at opposite dc voltage polarities (±3 V). Arrows indicate the position of single electron tunneling events and the tunneling event frequency steps are shown in the inset with the smooth background subtracted. With +3 V sample bias, an electron tunnels from tip-to-sample, while at −3 V bias, an electron tunnels from sample-to-tip.

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Numerous measurements show that single electron tunneling events between the probe and surface occur only at sub-2 -nm minimum gap.

Figure 1(b) shows two measurements of the resonance frequency shift versus tip-sample minimum gap obtained above a 10-nm-thick SiO_2 film with applied voltages of ±3 V. Starting at the left side of the graph, the probe is scanned downward toward the sample and the resonance frequency shifts smoothly downward. For both bias polarities, abrupt 1.75 Hz discontinuities appear at about 1.2 nm minimum tip-sample gap. The discontinuities are caused by single electron tunneling events between the probe and sample. The inset shows the frequency steps with the smooth background frequency shift subtracted for clarification. At either voltage polarity, the single electron tunneling causes a reduction in the net electrostatic force gradient, leading to the same positive shift of the frequency (While the change in surface charge is opposite for the two polarities, so is the electric field which determines the direction of the force).[7] After the tunneling event occurs, the probe is moved toward the sample until tip-sample contact (gap=0) is reached, where a repulsive force gradient (caused by tip-sample contact) balances the attractive electrostatic force gradient, causing the frequency to shift upward. The surface is touched in this measurement to demonstrate the position of the tunneling events with respect to the surface. In a single electron manipulation experiment the sample is not contacted by the probe.

Measurements are performed by an EFM constructed from a commercially available AFM (Omicron Multiprobe S). In this study, standard Si samples with device quality 10- or 20-nm-thick thermal SiO_2 layers are used. The sample surfaces are prepared by heating to 500–600 °C for 30–45 min in 10^{-8} Torr vacuum. The probes (MikroMasch NSC 15/Ti–Pt) have platinum coated tips with a nominal probe radius of less than 35 nm. The measurements are performed at room temperature (298 K) under 10^{-8} Torr vacuum to maintain clean, water free surfaces.

In a single electron manipulation measurement, the probe is positioned above the sample surface with a minimum gap of 2–5 nm. The probe is moved toward the surface at a rate of ~0.5 nm/s. Provided there exists an electronic state at the surface near the probe apex, tunneling may occur between the probe and the state when the probe comes sufficiently close to the sample for a finite tunneling rate. Since elastic tunneling conserves electron energy, the Fermi energy of the probe must be chosen to permit electrons to tunnel into or out of a state of a given energy on the surface as shown in Fig. 2. In order for tunneling to occur, an electron in an occupied state in the probe/sample must see an unoccupied state in the sample/probe at the same energy.

An energy band diagram for single electron manipulation is shown in Fig. 2. The sample is biased at a positive voltage polarity with respect to the probe as shown in Fig. 2(a). If the tip is scanned into tunneling range, electrons will tunnel into unoccupied states lying at or below the probe Fermi energy, E_f. Electrons tunneling to states lying at higher energies experience a smaller energy barrier and are expected to tunnel first (at a larger vacuum gap). The sample and probe are then separated. If the probe is brought back toward the surface again under the same applied voltage, no tunneling is expected since all accessible states are occupied, due to the tunneling which occurred in the first scan, as shown in Fig. 2(b). When the applied voltage polarity is reversed and the probe and sample are brought into tunneling range, the electrons in the filled states at the surface tunnel back into the unoccupied states in the probe as shown in Fig. 2(c). Again, when the probe is brought back into tunneling range at the same applied bias, no electron tunneling is expected since the states in the sample have emptied in the previous scan.

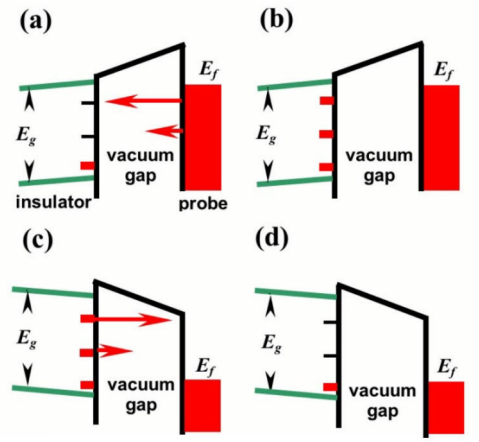

FIG. 2. (Color online) (a) Energy band structure of the probe-sample system for single electron manipulation. States in the band gap, E_g, of the dielectric are denoted by dashes. Thick dashes indicate occupied states. Arrows indicate the single-electron tunneling direction.

The experimental curves of frequency shift versus probe-sample relative displacement demonstrating this single electron manipulation to a 20-nm-thick SiO_2 film are shown in Fig. 3. Figure 3 shows *only* the scans in which single electron tunneling events occur as in Figs. 2(a) and 2(c) and does *not* show the featureless intermediate cases described in Figs. 2(b) and 2(d) in which no tunneling events occur. There are four curves in Fig. 3 because the manipulation experiment was performed twice at the same location above the surface. In curve (I), the sample is biased at +3.85 V with respect to the probe. The probe is moved toward the sample while the resonance frequency shift is recorded. The two abrupt frequency shift steps indicate two individual single electron tunneling events from the probe to the surface as described in Fig. 2(a). The probe is retracted to the starting position and scanned up and down once more at the same applied voltage as described in Fig. 2(b). No tunneling events are observed (curve not shown). The applied voltage

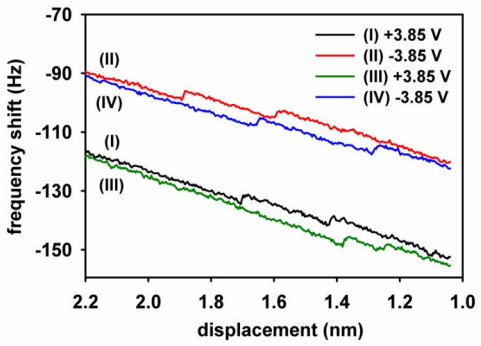

FIG. 3. (Color online) Measured single electron tunneling data corresponding to the experiment described in Fig. 2. Each curve has been shifted vertically by a few Hertz from its partner at the same polarity so that the curves do not overlap.

is then switched to −3.85 V and the probe is moved toward the sample again [curve (II)]. Two electrons tunnel separately from the sample to the probe as described in Fig. 2(c). The probe approaches a second time with −3.85 V applied bias and no tunneling events are observed as described in Fig. 2(d) (curve not shown). Curves (III) and (IV) are a repetition of the measurements (I) and (II) described above to demonstrate single electron manipulation again.

Two tunneling events occur in each approach suggesting that two localized states at different energies and/or spatial locations in the surface are within tunneling range of the probe apex (~ 100 nm^2). One or a few electrons have been deposited and withdrawn from multiple samples under similar conditions with repeatable results. However, such manipulation is not always possible. In some locations no tunneling is observed. In other locations an electron may be deposited to or removed from a localized state at the surface, but upon bias voltage reversal, no additional event is observed. This may be caused by spontaneous tunneling, between the localized state and other electronic states in the vicinity, before the manipulation can be completed.

Electrostatic models[4,7] of the probe-sample system have been used to predict the frequency shift caused by single electron tunneling. A 1D parallel plate model of the system is illustrated by the series capacitance circuit in Fig. 1(a). With a 10-nm-thick SiO_2 film ($\varepsilon = 3.9$) and under the experimental conditions used to obtain the data of Fig. 1(b), the model predicts a resonance frequency shift per electron of 1.6–2.3 Hz with a 1.1 nm tunnel gap. The experimental value is ~ 1.75 Hz. For the data in Fig. 3, acquired near a 20-nm-thick SiO_2 film, the resonance frequency shift per electron produced by the model is 3.1–5.2 Hz while the experimental value is around 3.5 Hz. The range of the model estimates is due to the uncertainty in the exact oscillation amplitude in each measurement [35–45 nm in Fig. 1(b)] and 20–30 nm in Fig. 3. The 1D parallel plate model is expected to overestimate the single electron frequency shift because it does not incorporate the divergent field of the electron. These calculations support the claim that each step observed is due to a single electron tunneling event. Additionally, the uniform magnitude and abruptness of the measured events substantiates this claim. If two electrons were tunneling in each step, it is unlikely that both electrons would tunnel at the same time in all eight of the steps shown in Fig. 3.

In summary, single electron occupation of states at an insulator surface has been controlled by single electron tunneling between a metallic EFM probe under an applied dc voltage when the probe tip and sample are brought within a 2 nm minimum gap. The occupation of states can be controlled repeatably at some points above the surface, while at other locations manipulation is not repeatable, suggesting that electrons may tunnel to nearby states outside the tunneling range before manipulation is completed. The measured frequency shift due to single electron tunneling events agrees with theoretically predicted values.

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[1] G. Binnig, H. Rohrer, Ch. Gerber, and E. Weibel, Phys. Rev. Lett. **49**, 57 (1982).
[2] D. Sarid, *Scanning Force Microscopy with Applications to Electric, Magnetic, and Atomic Forces*, Revised Ed. (Oxford University Press, New York, 1994).
[3] L. J. Klein and C. C. Williams, Appl. Phys. Lett. **81**, 4589 (2002).
[4] E. Bussmann, D. J. Kim, and C. C. Williams, Appl. Phys. Lett. **85**, 2538 (2004).
[5] Specification sheet MikroMasch NSC15/Ti-Pt.
[6] C. J. Chen, *Introduction to Scanning Tunneling Microscopy* (Oxford University Press, New York, 1993).
[7] L. J. Klein and C. C. Williams, J. Appl. Phys. **95**, 2547 (2004).