Single electron tunneling detected by electrostatic force

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Single electron tunneling events between a specially fabricated scanning probe and a conducting surface are demonstrated. The probe is an oxidized silicon atomic force microscope tip with an electrically isolated metallic dot at its apex. A voltage applied to the silicon tip produces an electrostatic force on the probe, which depends upon the charge on the metallic dot. Single electron tunneling events are observed in both the electrostatic force amplitude and phase signal. Electrostatic modeling of the probe response to single tunneling events is in good agreement with measured results. [DOI: 10.1063/1.1403256]

The scanning tunneling microscope (STM) has been used extensively to image the surfaces of many materials with atomic scale resolution.[1] This exquisite spatial resolution is due to the strong (exponential) gap dependence of the electron tunneling rate. The STM has primarily been applied to conducting and semiconducting samples, because an average current of 1 nA–1 pA is generally required. Under special circumstances, the STM has been used to measure the effects of single electron charging. Coulomb blockade has been observed as step-like variations in the current–voltage spectrum on small metallic dots.[2] Telegraph noise has also been observed in STM measurements on thin insulator films.[3] In both these cases, many electrons (>pA currents) are used to observe the single electron charging phenomena. In this letter, a force based method is described for direct observation of single electron tunneling events between a scanning probe and a conducting surface.

It has previously been shown that the electrostatic force microscope has adequate sensitivity to detect a change in surface charge corresponding to a single elementary charge.[4] More recently, direct tunneling of a few electrons between a scanning probe microscope (SPM) probe and sample has been demonstrated.[5] However, detection of a single electron tunneling event between probe and sample has not been achieved. The ability to measure single electron tunneling events between a SPM probe and sample has many potential applications. One of these is the imaging of electrically isolated electronic states (filled or unfilled) with atomic spatial resolution. The energy and location of such states cannot be characterized by STM due to the minimum current required by the STM. Atomic force microscopy (AFM) cannot identify the energy of such an isolated state, because no electron transfer occurs. Examples of such states might include surface states or defects at the surface of insulating materials, and metallic clusters or molecules on insulating surfaces. A great interest in the physical properties of these types of nanometer scale systems currently exists. Second, detection of single electron tunneling events also makes possible the detection of ultrasmall currents (i.e., tens or hundreds of electrons per second). Many material systems which are difficult to image with typical STM currents, such as weakly adsorbed molecules, might be imaged at currents which are orders of magnitude smaller (atto-amperes).

The single electron tunneling measurements reported here are based upon electrostatic force detection of the charge on a small, electrically isolated metallic dot fabricated at the apex of an oxidized silicon AFM tip. See Fig. 1(a). All measurements described here are performed at room temperature, and are not based upon Coulomb blockade. The method for probe fabrication has been described previously.[5] For tunneling measurements, the probe is positioned near a conducting sample surface and a voltage $V = V_{dc}$

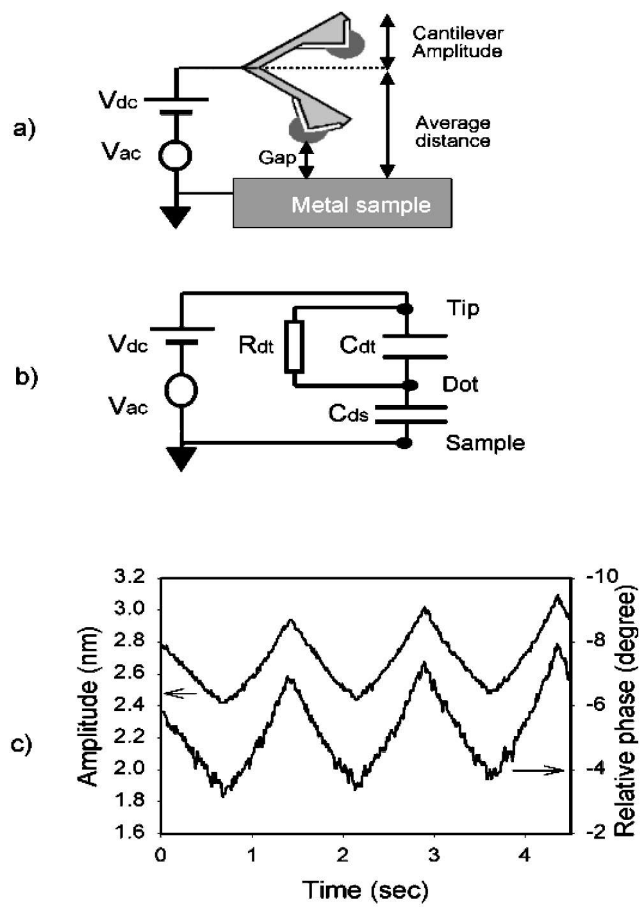

FIG. 1. (a) Experimental setup for single electron tunneling measurements, (b) equivalent electrical circuit for the probe, (c) amplitude and phase response of the cantilever as the sample is moved toward and away from the probe.

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$+V_{\mathrm{ac}}\cos(\omega t)$ is applied between the silicon tip (through the monolithic silicon cantilever) and the conducting sample. The electrostatic forces produced by this applied voltage cause the cantilever to bend (both static and dynamic deflections occur). An optical beam deflection method is used to convert this motion to an electrical signal. A lock-in amplifier is used to detect the amplitude and phase of the oscillation of the cantilever at the frequency (ω) of the applied voltage. The force on the probe can be divided into two parts. One acts on the silicon cantilever with its monolithic tip at the applied frequency. It will be called the background force amplitude, F_b, as it weakly depends upon the charge on the dot. It is given by the usual equation for electrostatic force[6]

$$F_b(\omega)=\frac{\partial C}{\partial z}V_{\mathrm{dc}}V_{\mathrm{ac}}, \tag{1}$$

where C is the capacitance between the silicon cantilever (and tip) and the sample. The derivative is with respect to a change in gap z between the probe and surface. There is an additional force on the probe, which depends upon the net charge q_d on the metallic dot. This force (at the detection frequency ω) can be approximated by the following expression: $F_d(\omega)=q_{\mathrm{ds}}E_{\mathrm{ds}}(\omega)$, where q_{ds} is the charge at the surface of the dot nearest the sample and $E_{\mathrm{ds}}(\omega)$ is the electric field present between dot and sample at the applied frequency. A consideration of the equivalent circuit shown in Fig. 1(b) shows that the magnitude of this sinusoidal force is given by

$$\begin{aligned} F_d(\omega)\approx q_{\mathrm{ds}}E_{\mathrm{ds}}(\omega)&=\frac{q_d}{\left(1+\dfrac{C_{\mathrm{dt}}}{C_{\mathrm{ds}}}\right)}\frac{V_{\mathrm{acd}}}{z}\\ &=\frac{q_d}{\left(1+\dfrac{C_{\mathrm{dt}}}{C_{\mathrm{ds}}}\right)}\frac{V_{\mathrm{ac}}}{\left(1+\dfrac{C_{\mathrm{ds}}}{C_{\mathrm{dt}}}\right)z}. \end{aligned} \tag{2}$$

Here C_{dt} is the capacitance between the dot and the silicon tip, C_{ds} is the capacitance between the dot and sample, z is the distance between the metal dot and sample and V_{acd} is the magnitude of the capacitively coupled voltage on the dot at the drive frequency. The forces F_b and F_d cause the cantilever to oscillate with an amplitude given by[6]

$$A(\omega)=\frac{|F_t|}{k'}\frac{1}{\sqrt{\left(1-\dfrac{\omega^2}{\omega_0'^2}\right)^2+\dfrac{\omega^2}{Q^2\omega_0'^2}}}, \tag{3}$$

where F_t is the sum of F_b and F_d, k' is the effective spring constant, ω_0' is the cantilever resonant frequency, Q is the quality factor of the cantilever, and ω is the frequency of the applied voltage (drive frequency). Both k' and ω_0' depend upon the force gradient, $\partial F/\partial z$, felt by the probe, i.e., $k'=k_0-\partial F/\partial z$ and $\omega_0'^2=(k'/m)$, and k_0 is the spring constant of the cantilever when the probe is far from the sample surface (no force gradient).

The finite stiffness of AFM cantilevers, the typical applied voltages and the small gaps required for electron tunneling measurements cause force gradient effects to be large. Resonant frequency shifts can dominate the observations, and snap in of the cantilever to the surface can occur. Both experiment and simulation have shown that it is advantageous to choose the frequency of the applied voltage to be somewhat below resonance, when the probe is far from the sample surface. Under this condition, the cantilever resonance is shifted near the drive frequency as the probe approaches tunneling range. This produces a higher sensitivity to charge transfer (near resonance) and helps to avoid snap in of the cantilever before tunneling occurs.

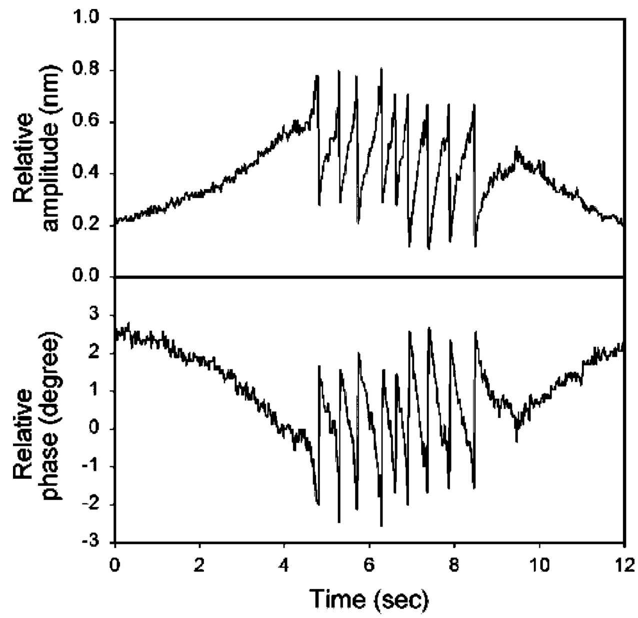

FIG. 2. Relative amplitude and phase response of the cantilever as the probe comes into tunneling range of the surface. Each electron tunneling event corresponds to an abrupt decrease in amplitude and increase in phase.

To illustrate the amplitude and phase effects observed outside of tunneling range, a periodic 2.5 nm triangular gap modulation is applied to the sample. The cantilever amplitude and phase response to three cycles of this modulation are shown in Fig. 1(c). As expected, the cantilever amplitude increases as the gap decreases. The change in the phase is caused by the gap dependent force gradient, consistent with theoretical predictions. In this data set, the probe never comes within tunneling range (<2.5 nm gap). A small thermal drift in the system (gradual decrease in the probe to sample gap distance) can be observed as a slight increase (decrease) in the cantilever peak amplitude (phase) with each cycle in Fig. 1(c).

When the probe is moved into tunneling range, a very different response is observed. Figure 2 shows the amplitude and phase of the cantilever deflection when the probe is brought very close to a freshly cleaved graphite surface. As can be seen, multiple abrupt changes in amplitude and phase of the cantilever oscillation are observed. This response can be understood by considering the effect of a single tunneling event.

If the gap modulation were to bring the average cantilever position within 2.5 nm of the surface and the peak oscillation amplitude was 1 nm, the minimum gap (between dot and surface) would be 1.5 nm. If a single electron tunneling event were to occur at this gap, then the cantilever oscillation amplitude would immediately drop, due to the loss of an electron from the dot and the concomitant reduction in force

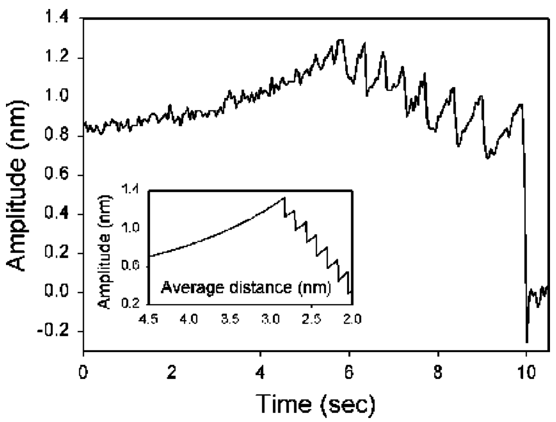

FIG. 3. Seven single electron tunneling events observed in the cantilever amplitude, before the cantilever snaps into the surface. Inset: simulated cantilever amplitude as a function of gap, for single electron tunneling at 1.5 nm from the surface.

$F_d(\omega)$. This reduction in amplitude (0.5 nm in Fig. 2) would take the dot out of tunneling range (minimum gap would be 2.0 nm), and no further tunneling would occur. If the sample were to continue to move toward the probe by the triangular gap modulation, the minimum gap distance would eventually reach 1.5 nm again. At this point in time, another tunneling event would become likely. As this event occurs, the amplitude would again drop and the minimum dot to sample gap would increase out of tunneling range. Thus a series of tunneling events would be observed, all of which would occur at approximately the same minimum dot to sample gap.

In the data shown in Fig. 2, the probe is withdrawn by the gap modulation before it snaps into the surface. The experimental parameters for the data include a 44.950 kHz cantilever resonance frequency (far from surface), a drive frequency 500 Hz below the cantilever resonance, a Q of 65, a nominal spring constant of 3 N/m, an applied voltage $V_{ac}=1$ V, an average voltage $V_{dc}=0.5$ V, a lock-in amplifier time constant of 30 ms, and a total gap modulation movement of 1.2 nm.

Due to the high charge sensitivity near resonance, a 0.5 nm amplitude drop occurs with each tunneling event. A phase change of the cantilever oscillation is also observed with each electron tunneling event (4°). See Fig. 2. This is caused by a change in force gradient, with each electron lost. The rate at which the probe approaches the surface (rate of the gap modulation) can be chosen, thus determining the time interval between the tunneling events. Many data sets similar to that shown in Fig. 2 have been observed under varying conditions.

Figure 3 shows a similar data set containing seven electron tunneling events with a different probe on a freshly cleaved graphite sample. In this case, the force gradient was such that the probe snapped into the surface after the seventh tunneling event (seen as the large reduction in amplitude at 10 s). The experimental conditions for this data set include a 39.420 kHz cantilever resonance frequency, drive voltage at 300 Hz below cantilever resonance, Q value of 30, spring constant of 3 N/m, $V_{ac}=2$ V, and $V_{dc}=-0.2$ V.

The data shown in Fig. 3 are conclusive evidence for single electron tunneling. The justification for this claim is the following. When the minimum gap is larger than 2.5 nm, the probability of tunneling on the time scale of the measurement is negligible. As the minimum gap between probe and sample is decreased, the tunneling probability increases to a small but finite value. Eventually, a tunneling event does occur. While infrequently one might observe two tunneling events occurring simultaneously (with twice the amplitude change), the probability of observing two simultaneous events seven times in a row is negligibly small. Each of the seven abrupt steps seen in Fig. 3 therefore corresponds to a single electron tunneling event.

Further evidence for single electron tunneling can be found in the modeling of the electrostatic force response to a tunneling event. Using the experimental parameters described above for the data in Fig. 3, and assuming the silicon tip radius is 60 nm and the dot radius is 35 nm, a simulation of this measurement was performed using an approximate model of the silicon tip and dot. The model includes the electrostatic forces and force gradients on the silicon tip and metallic dot, and the mechanical response of the cantilever. The simulation is based upon a simple parallel plate model. The model calculations assume that tunneling will take place when the minimum dot to sample gap becomes less than 1.5 nm. The simulated response is shown in the inset in Fig. 3. The loss of charge at a minimum gap of 1.5 nm on the dot causes a discrete amplitude change of 0.2 nm, in good agreement with the measured data ($\approx$0.2 nm amplitude change per electron). Note that in Fig. 3, there is a slight and gradual increase in the magnitude of the step size seen in the amplitude, as the tip approaches the sample. This is caused by the fact that the average probe to sample spacing is gradually decreasing as the dot loses each electron. This reduction in average gap increases the force gradient and the magnitude of the electrostatic forces, and increases the sensitivity to a charge change. While the measurements shown here were performed in an air ambient, the same measurements have been repeated in high vacuum (10^{-8} Torr) with equivalent results.

In summary, a scanning probe technique is reported which is capable of detecting single electron tunneling events by electrostatic force. This technique provides a means for measuring ultrasmall currents (sub atto-ampere) and for directly measuring the properties of electrically isolated states with atomic spatial resolution. Finally, it is worthy of note that when tunneling to an electrically isolated state at a surface, the state itself may act as the "dot" in this method.

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