Electron tunneling detected by electrostatic force

L. J. Klein and C. C. Williams[a)]
Department of Physics, University of Utah, Salt Lake City, Utah 84112

J. Kim
Center for Nanospinics of Spintronic Materials and Department of Physics, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

(Received 19 June 2000; accepted for publication 13 October 2000)

A method is introduced for measuring the tunneling of electrons between a specially fabricated scanning probe microscope tip and a surface. The technique is based upon electrostatic force detection of charge as it is transferred to and from a small (10^{-17} F) electrically isolated metallic dot on the scanning probe tip. The methods for dot fabrication, charging, and discharging are described and electron tunneling to a sample surface is demonstrated. © *2000 American Institute of Physics.*
[S0003-6951(00)05149-4]

The electrostatic force microscope (EFM),[1–4] derived from the noncontact atomic force microscope (AFM),[5] measures the electrostatic force acting on an AFM tip due to the Coulomb interaction with nearby charge distributed on a sample surface. Imaging of charge deposited on insulator surfaces by corona discharge[2,4] and contact charging[3] has been demonstrated. Nanoclusters have also been electrostatically characterized by EFM.[6] Single electron sensitivity[4] in charge decay has been achieved. However, in all of these studies, the total charge transferred to the sample is difficult to control and quantify due to the complex nature of the charging process and uncertainty about the electrostatic properties of the tip and sample.

In this letter, we describe a method for detection of an ultrasmall amount of charge transferred between a specially fabricated scanning probe microscope (SPM) probe and a surface. The method is based on electrostatic force detection of the charge on a small isolated metallic dot at the end of an oxidized AFM tip. The small metallic dots are fabricated at the end of AFM tips using a field evaporation process shown by Lin *et al.*[7] In that work, 3.9 V are applied between a metallic STM tip and a Pt sample (positive), which causes field evaporation to occur. Since in our work the metallic dots must be electrically isolated, conductive silicon AFM tips are first thermally oxidized (50 nm oxide thickness) to provide an insulating layer. The oxidized silicon tips are then coated with a thin film of Ni (10 nm) so that large electric fields can be applied during field evaporation. The Ni film is chosen for its chemical properties and because the critical evaporation field for negative ions from Ni is higher than that for positive ions of Pt.[7] The Ni coated, oxidized AFM tips are brought close to the Pt sample by AFM, and several voltage pulses of 30 ms width and 4 V amplitude are applied to the sample in air. This causes some Pt to be transferred to the tip. The tip is then dipped in a nickel etch (3:3:1:1, H_3PO_4:HNO_3:CH_3COOH:H_2O), leaving an isolated metal dot (platinum on nickel, 200 nm diameter) at the end of the oxidized silicon tip. A typical probe, imaged with a scanning electron microscope, is shown in Fig. 1.

The electrical properties of the fabricated probes have been characterized by EFM. The equivalent circuit of the probe/dot/sample is shown in Fig. 2(a) when the probe is far from the sample. The metallic dot has a capacitance and a resistance to both the sample surface and the oxidized silicon tip. When the tip is more than 5 nm from the sample, the tunneling resistance to the sample may be considered infinite. The dot capacitance to the silicon tip can be estimated using the known oxide thickness and size of the dot. This capacitance is on the order of 10^{-17} F. The resistance between the dot and the silicon tip can be determined by charging the dot and measuring the charge decay time constant. For the equivalent circuit shown in Fig. 2(a), the time constant is $\tau = R_{dt}(C_{dt} + C_{ds})$, where R_{dt} and C_{dt} is the resistance and capacitance between the dot and the silicon tip, respectively, and C_{ds} is the capacitance between the dot and the sample.

The time constant of the probe is measured by positioning it at a distance of order 100 nm to the sample surface. The metallic dot is charged by applying a direct current (dc) voltage (1–3 V) to the sample with respect to the silicon tip for a few seconds. After removal of the dc voltage, the charge on the dot decays back to the silicon tip with a time constant τ. An alternating current (ac) voltage (typically 1 V

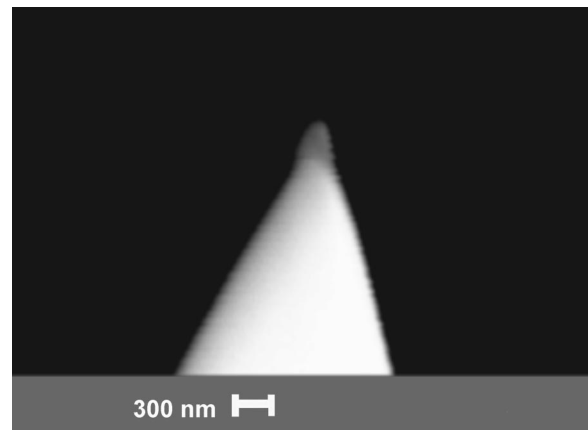

FIG. 1. Scanning electron microscope image of a metallic dot at the end of an oxidized AFM tip. The dot diameter is ~200 nm.

a)Electronic mail: clayton@physics.utah.edu

 © 2000 American Institute of Physics

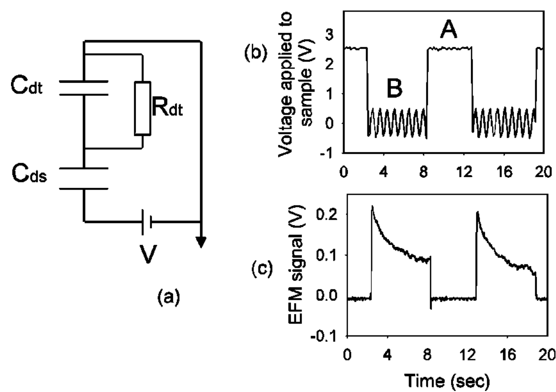

FIG. 2. (a) Equivalent electric circuit of the oxidized tip with metallic dot far from the surface, (b) the charging voltage applied to sample, and (c) the probe response. The gap between tip and sample was held constant at 35 nm during this measurement.

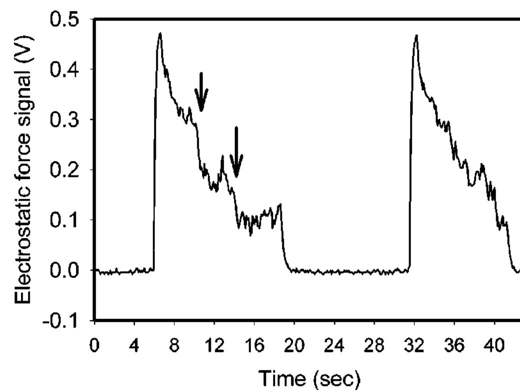

FIG. 3. Fluctuations and discrete steps seen in the EFM charge decay signal.

peak) is applied to the sample at the resonance frequency of the cantilever to produce the electrostatic forces which enable the decay of the charge to be measured by the standard EFM method.[4] The charge decay measurements are performed at room temperature in a ultrahigh vacuum AFM system (base pressure of 10^{-8} Torr). A freshly cleaved graphite sample is used. The cantilevers have a resonance frequency of 156 kHz, a force constant of ~50 N/m and a Q of 25 000 in vacuum. No height feedback is used in these measurements.

Figure 2(b) shows a schematic diagram representing the charging and measuring voltage applied to the sample for two charge/discharge cycles. In interval A, a dc voltage is applied to the sample with no ac voltage applied. The dot is charged during this interval. In interval B, the dc voltage is turned off and an ac voltage is applied to measure the charge decay by EFM. In Fig. 2(c), two examples of charge decay are seen in the measured EFM signal. The charge decay time constant is a few seconds. It is observed that this measured time constant varies from tip to tip, ranging between 1 and 100 s. The corresponding resistance R_{dt} for these tips can be calculated. Since for ~100 nm gaps, C_{ds} is much smaller than C_{dt}, the time constant τ is approximately $R_{dt}C_{dt}$. With a measured time constant of 1–100 s and a C_{dt} of 10^{-17} F, the resistance R_{dt} for these probes ranges between 10^{17} and $10^{19}\,\Omega$. Under these conditions, the probes are measuring decay currents which are in some cases below 0.1 attoamp (10^{-19} amps). Note that tips without dots show no charge decay, as expected.

Since the thermally grown oxide is too thick for tunneling to occur, it is believed that the charge conduction between dot and silicon tip is dominated by thermal hopping of electrons through traps in the oxide. This is consistent with the observation that each fabricated probe shows a different amount of fluctuation in the charge decay. Because of the small dot size, a very small number of paths exist for an electron to hop back to the silicon tip. The number and spatial distribution of these traps, as well as dot size, varies from probe to probe. As few electrons are involved, there are large statistical fluctuations in this thermal driven hopping process. These fluctuations can be seen in the two charge decay traces shown in Fig. 3. Note that the probe providing the data in Fig. 3 is different from that used in Fig. 2(c).

Occasionally, discrete steps are seen in the charge decay traces of some of the probes. Two discrete steps in the decay data are shown in Fig. 3 (indicated by arrows). These steps may correspond to a single electron which has made a single thermal hop from the metallic dot back to the silicon tip. These single steps are superimposed upon a background decay caused by other electrons which make several smaller hops through the oxide. EFM calculations based upon a 50 nm gap, a 1 V ac EFM voltage and the model used by Schonenberger *et al.*[4] show that the discrete steps visible in Fig. 3 are comparable to the EFM signal predicted for the removal of a single electron from the dot.

The probes have been used to transfer electrons to a sample surface by tunneling. In this experiment, the probe is first charged using the method described above at a height of 50 nm from the surface. As the charge begins to decay (during interval B), the ac EFM voltage is turned off and the sample is quickly moved close to the probe dot (within tunneling range). After a short interval (50 ms), the sample is pulled back to its original position and the ac EFM voltage is turned on again. The EFM signal before and after this short interval is recorded. If tunneling to the surface has occurred while the probe is close to the surface, a discrete change in the amplitude of the EFM decay signal is observed. If no transfer to the surface has taken place, the EFM signal will simply have continuously decayed. In order to assure that no physical contact is made while the tip is close to the surface, measurement of the AFM optical deflection signal is performed (with the EFM cantilever oscillation signal filtered out by a low pass filter).

In Fig. 4(a), a sequence of charging/decay traces is shown with the corresponding optical deflection signal 4(b) recorded simultaneously. In these data sets, the EFM signal is adjusted (by dc voltage) so that at the beginning of the charge decay, the EFM signal is close to zero. The transient spikes seen in the charge decay trace 4(a) are caused by the 50 ms in/out movement of the sample. If tunneling occurs, it will occur during this short interval. The periodic square wave (0.4 nm deflection) seen in the optical deflection signal 4(b) is caused by the attractive force produced by the charging voltage. The applied voltage in this case is similar to that shown in Fig. 2(b). Four charge/discharge cycles are shown. Any contact between tip and sample would results in an optical deflection signal spike which is more positive than the top of the square wave during interval B.

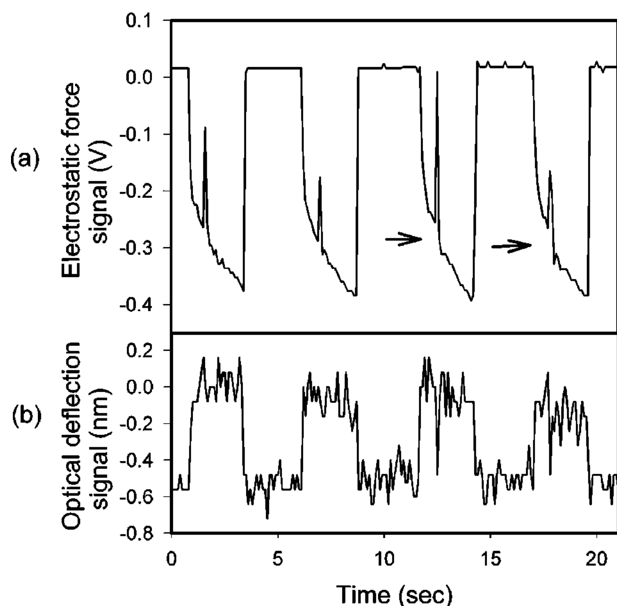

FIG. 4. (a) Abrupt change in the EFM decay signal when the tip is moved to tunneling distance (seen in third and fourth decays). (b) The optical deflection signal shows the force interaction between the tip and sample.

In these measurements, no contact is made. Note that a small negative spike is observed in the optical deflection signal during the third and fourth decay. This spike corresponds to an additional attractive tip/sample force as the sample is brought very close to the tip during the 50 ms in/out movement. A small discrete change is seen to have occurred in the EFM signal during this 50 ms movement in the two corresponding charge decay traces (see arrows in Fig. 4). In contrast, the EFM signal decays continuously in the first two decay traces. This data set demonstrates that charge transfer has occurred, but no physical contact has been made. Tunneling and thermionic emission are the only physical mechanisms to explain this non-contact charge transfer. Thermionic emission can be eliminated because charge transfer is observed only when the tip is in near contact (<3 nm) of the sample. Additionally, charge transfer to freshly cleaved graphite surfaces is very repeatable, as compared with older graphite samples. An estimation of the charge transferred to the surface in this data set is on the order of a couple of electrons. This estimation is based upon the model used by Schonenberger *et al.*[4] with a 50 nm gap and a 1 V ac EFM voltage.

In summary, a scanning probe method has been described, based upon electrostatic force detection. A method of probe fabrication has been described and a simple circuit model for the charge decay has been proposed and verified. Detection of the tunneling of a few electrons from the probe to a sample surface has been demonstrated. Due to the exponential dependence of the tunneling probability on tip-sample distance, exquisite control of both the tunneling rate and atomic scale placement of the charge should be achievable. When fully developed, the method may provide the means by which single electrons can be injected by tunneling to a surface with atomic spatial resolution.

The authors would like to thank W. Wingert and M. Delong for help in the fabrication of the probes. This work has been funded by the National Science Foundation, DMR-9626286.

[1] Y. Martin, D. W. Abraham, and H. K. Wickramasinghe, Appl. Phys. Lett. **52**, 1103 (1988).
[2] J. E. Stern, B. D. Terris, H. J. Mamin, and D. Rugar, Appl. Phys. Lett. **53**, 2717 (1988).
[3] B. D. Terris, J. E. Stern, D. Rugar, and H. J. Mamin, Phys. Rev. Lett. **63**, 2669 (1989).
[4] C. Schonenberger and S. F. Alvarado, Phys. Rev. Lett. **65**, 3162 (1990).
[5] Y. Martin, C. C. Williams, and H. K. Wickramasinghe, J. Appl. Phys. **61**, 4723 (1987).
[6] D. M. Schaadt, E. T. Yu, S. Sankar, and A. E. Berkowitz, Appl. Phys. Lett. **74**, 472 (1999).
[7] H.-N. Lin, C. S. Chang, and T. T. Tsong, J. Appl. Phys. **77**, 2825 (1995).