Scanning-Tunneling-Microscope Observations of Coulomb Blockade and Oxide Polarization in Small Metal Droplets

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The *I-V* characteristics of two serially coupled small tunnel junctions (about 10^{-18}–10^{-19} F capacitances) are measured at 4 K. The junctions are formed using a scanning tunneling microscope to probe a metal droplet deposited on an oxidized metal substrate. Sharply defined Coulomb steps due to single-electron dynamics, oxide polarization, and nonlinear (voltage dependent) tunneling rates are observed. The results show very good quantitative agreement with theoretical calculations based on the semiclassical picture.

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Twenty years ago Zeller and Giaver[1] and Lambe and Jaklevic[2] studied charging-energy effects on single-electron tunneling using a system of small metal droplets sandwiched between two oxidized metal electrodes. In Ref. 1 a conductance dip centered at zero bias was observed in the *I-V* characteristic resulting from the charging energy of a single electron on a droplet. An electron can tunnel into a droplet only when the bias voltage is greater than $e/2C$ (where C is the droplet capacitance). In Ref. 2 the capacitive part of the tunneling conductance was measured by an ac technique. The charging energy of the droplets produced oscillations in the capacitance. Memory effects related to variation of the bias potential of individual droplets resulting from random polarization in the oxide layer were observed. Additional experiments[3] on a similar system further elucidated these memory effects. With the advance of submicron fabrication, interest in charging effects has been renewed. New effects[4-6] are predicted when the dimensions of a tunnel junction are reduced so that the electrostatic energy, $e^2/2C$, becomes larger than the thermal energy k_BT.

Motivated by Refs. 1 and 2, Mullen *et al.*[7] studied theoretically two serially coupled junctions driven by a voltage source. Pronounced steps are predicted when the two time constants (RC) of the two junctions are very different. Details of these structures (discussed below) allow a critical test of the theory. Using a system similar to that of Refs. 1 and 2, Barner and Ruggiero[8] and Kuz'min and Likharev[9] have observed steps in the *I-V* characteristic in good qualitative agreement with the theory.[7,9] Quantitative comparison is not possible because of the averaging over droplet sizes. A more direct experiment on a single set of two serially coupled junctions with about 10^{-15} F capacitance fabricated by a lithographic technique was performed by Fulton and Dolan.[10]

Two serially coupled junctions may be realized[7] by using a scanning tunneling microscope (STM) to probe a small metal droplet deposited on an oxidized metal substrate as shown in Fig. 1. The advantages of such an experiment are that (1) extremely small capacitances (about 10^{-18} F) can be obtained, and (2) it is easy to vary the junction parameters either by moving the tip of the STM with respect to a specific droplet or by probing different size droplets. A similar experiment (in which the tip was embedded in the Al droplet oxide and the feedback system switched off) was performed by van Bentum, Smokers, and van Kempen.[11] Clear steps were observed in the *I-V* characteristic in agreement with their theoretical calculations which are similar to that of Ref. 7. Recently,[12] an experiment using superconducting droplets also showed good agreement with theory.

Here we report results of experiments which provide for a critical test of the theory of Mullen *et al.*[7] The *I-V* characteristics show, with excellent resolution, sharp steps and other details with limited background effects. For the experiment we have built a low-temperature STM similar to that described by LeDuc, Kaiser, and Stern.[13] A detailed description will be presented elsewhere.[14] Gold tips are used and the current-voltage data are taken with a constant-amplitude ac sweep voltage of about 20 Hz frequency. The tunneling tip is positioned at constant altitude by a piezoelectric element controlled

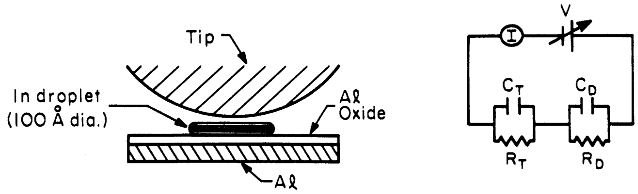

FIG. 1. Schematic showing an In droplet separated from an Al ground plane by a tunneling oxide layer ($\simeq 10$ Å thickness) with an Au STM tip positioned about 10 Å above it. The equivalent circuit is shown with a voltage source and capacitor C_T for tip to droplet and C_D for droplet to ground plane. The resistors characterize the tunneling probability for each junction and are strictly shot-noise devices.

by a feedback signal derived from the ac current amplitude. The whole unit fits at the end of an immersion rod which is inserted into the neck of a 2.54-cm-diam liquid-helium storage Dewar.

The metal droplets are prepared by evaporation in a high-vacuum chamber (approximately 10^{-8} Torr ultimate pressure). Aluminum films are deposited onto clean glass substrates and oxidized by exposure to pure oxygen at about 0.2 Torr for several minutes. An indium film is then evaporated atop this oxide. Under these conditions, indium metal films spontaneously form small droplets in the form of platelets well separated from one another. Previous work[2] indicates that the average droplet diameter is about equal to the thickness of the film as measured by a quartz-crystal microbalance. The samples are stored in dry air or installed immediately in the STM and inserted into the Dewar. The above technique can produce metal droplets with diameters ranging from about ten to a thousand angstroms.

Typical I-V characteristics are shown in Figs. 2 and 3. The two I-V characteristics shown in Fig. 2 were obtained from the same droplet in subsequent averaging cycles; the inset has a larger voltage range. We present both of them to demonstrate the stability and reproducibility of the experiment. The curves (Fig. 2) are produced by averaging over about 20 sweeps during a time in which the STM I-V characteristic is stable as viewed on an oscilloscope. The curves show clear staircase structure and a number of distinctive features such as rounding of the steps, slopes of the individual step plateaus, asymmetry of the step positions, behavior near zero bias, and nonlinear envelope, all of which are present in the individual I-V characteristic viewed in real time (Fig. 3 was taken from an oscilloscope photograph). We emphasize that the primary effect of the averaging is to remove high-frequency noise. The pronounced asymmetric features are very common and occur in a majority of runs. A number of examples are obtained in which steps as sharp and well defined as those in Figs. 2 and 3 are observed. The particular examples are chosen because the data were obtained during especially stable operation.

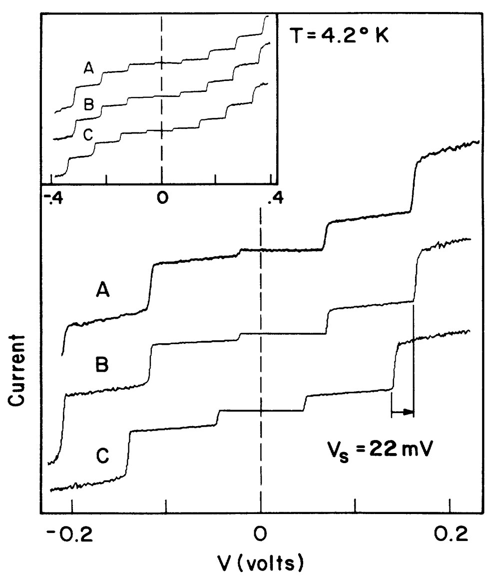

FIG. 2. Curve A is an experimental I-V characteristic from an In droplet in a sample with average droplet size of 300 Å. The peak-peak current is 1.8 nA. Curve B is a theoretical fit to the data for $C_D = 3.5\times10^{-19}$ F, $C_T = 1.8\times10^{-18}$ F, $R_D = 7.2\times10^6$ Ω, and $R_T = 4.4\times10^9$ Ω. The obvious asymmetric features in curve A require a voltage shift $V_s = 22$ mV ($V_p = 18$ mV). Curve C, calculated for $V_s = 0$, shows the (seldom observed) symmetric case. As explained in the text, a small quadratic term was added to the computed tunneling rate for each junction. Inset: A wider voltage scan for this same droplet; again, the topmost curve is experimental data.

Following Ref. 7 we use the semiclassical approach[4,5] (assuming an ideal voltage source) to analyze the experimental observations. The basic assumption is that the state of each junction is described by a single classical variable, the voltage across the junction. For fixed external applied voltage V, oxide polarization V_p,[15] and N surplus electrons on the droplet, the tip-drop and drop-substrate voltages (V_T and V_D, respectively) are given by

$$V_T = V - V_D\,,$$
$$V_D = \frac{VC_T}{C_D + C_T} + \frac{Ne}{C_D + C_T} + V_p\,. \tag{1}$$

The time evolution of the system is then described by a stochastic process composed of a series of single-electron

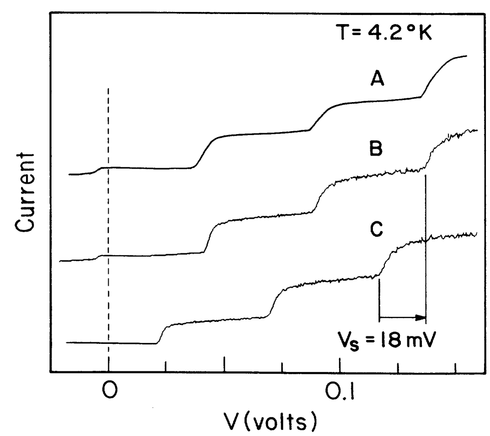

FIG. 3. Curve A is an experimental I-V characteristic from an In droplet in a sample with average size of 100 Å. The peak-peak current is 1.4 nA. Curve B is a theoretical fit to the data for $C_D = 6\times10^{-19}$ F, $C_T = 3.4\times10^{-18}$ F, $R_D = 2.4\times10^6$ Ω, and $R_T = 1.2\times10^8$ Ω. The fit requires a voltage shift of 18 mV ($V_p = 15$ mV) and curve C is calculated for $V_s = 0$. Compared with the example of Fig. 2, the extra rounding of the top edges of the steps is caused by the lower value for R_T/R_D for this case.

tunneling events that alter N. That is

$$N(t+\delta t)=\begin{cases} N(t)-1, \text{ with probability } [r_T(V_T)+l_D(V_D)]\delta t, \\ N(t)+1, \text{ with probability } [r_D(V_D)+l_T(V_T)]\delta t, \\ N(t), \text{ with probability } 1-[r_T(V_T)+l_T(V_T)+r_D(V_D)+l_D(V_D)]\delta t, \end{cases} \quad (2)$$

where $r(V)$ and $l(V)$ are the instantaneous rates of an electron tunneling from the right and left, respectively, calculated using the classical model. The capacitive charging energy affects the tunneling rates through the change in the electrochemical potential, μ; for example, for tunneling across the tip-droplet junction (assuming the charge relaxation in the droplet is faster than the tunneling process),

$$\Delta\mu_T=eV_T-e^2/2(C_D+C_T). \quad (3)$$

At low temperatures, the tunneling rate is exponentially small for $V_T<e/2(C_D+C_T)$ (the Coulomb blockade), and then proportional to $\Delta\mu_T$ above this value.

The values of the four junction parameters (R_T, C_T, R_D, and C_D) are required to provide a fit to the data, but it is not a fitting to four independent parameters. We know that the experiment operates in the limit $R_T>R_D$ and $C_T>C_D$, the case where well defined steps are predicted. We identify the tip-droplet junction as the high-resistance junction because the observed current amplitude varies with the tip altitude. The width of the steps measures e/C_T, and the slope of the individual plateaus determines the ratio of C_D/C_T. The typical value of 10^{-18} F for the measured capacitances is reasonable. For example, the geometric capacitance of a 100-Å diameter droplet with a 10-Å barrier and $\kappa=10$ is 7×10^{-18} F. This indicates that the droplet size determines the value of both C_D and C_T. The estimate of the droplet diameter agrees with the typical size measured by scanning the substrate.[14] However, we do not understand at this time why C_T is greater than C_D. At $T=4$ K, the thermal energy is well below the charging energy of this system. Looking along positive bias, the bottom edge of the steps are very sharp (with increasing T these edges become rounder). The rounding of the top edge of the steps (prominent in Fig. 3) has to do with the time constants of the two junctions, and is determined by the ratio R_T/R_D. Finally, to determine the value of each of the resistances we use the fact that the step height is approximately e/C_TR_T in the experimental limit.

As we mentioned above, the typical experimental I-V curves are not symmetric about zero bias. We believe the origin of the asymmetry to be oxide polarization. The polarization voltage, V_p, is simply determined by the voltage shift, V_s, shown in Fig. 2, where $V_s=V_p(C_T+C_D)/C_T$. The asymmetry can persists for long times; the curves of Fig. 2 were stable for over a period of 1 h. The offset voltage is less than half of the step width (corresponding to the equivalent charge of $e/2$); otherwise, an additional electron could tunnel into the droplet. When the offset is close to the half step width, the step closest to zero voltage has a very small height and the Coulomb blockade region appears to have twice the expected width.

To further study the oxide polarization, we have started an experiment in which we shine light on the droplet using an optical fiber. The preliminary results show that, starting with a shifted I-V characteristic (polarized droplet), the curve becomes symmetric within seconds of applying the light.

If only a constant density of states and an energy-independent tunneling matrix element are assumed, the envelope of the staircase should be linear with slope $R=R_T+R_D$, giving steps of equal height. This is clearly not the case in the experimental I-V characteristics whose envelope rises faster than linear, indicating nonlinearity in the individual tunneling rates as a function of voltage. Many effects[16] (barrier effects,[17] inelastic tunneling,[18] structure in the density of states, and many-body excitations) can produce nonlinear behavior in the I-V characteristics of tunnel junctions. We believe that for low temperatures, intermediate size droplets, and applied voltages above 0.1 V, the main effect is the increase in the tunneling matrix element resulting from a deformation of the barrier shape and reduction of the effective barrier height at high voltages. As a first step, we have accounted for the nonlinearity by adding (phenomenologically) the same quadratic ($\alpha V^2/R$) term to the tunneling rates for each of the junction. We determine the prefactor of this term from the observed variation in the step heights ($\alpha=9$ V^{-1} in Fig. 2, $\alpha=1$ V^{-1} in Fig. 3). Using typical values of the work functions, α is calculated to be of the order of 1. The accuracy of the experiment enables a future detailed study of the various effects leading to nonlinearity. Specifically, in some cases where the droplet size was ≤ 50 Å, stronger nonlinearities are observed. These are likely to be a signature of the modifications in the density of states resulting from quantum size effects. Simple considerations[19] indicate that such effects should be very pronounced in droplets smaller than 50 Å, which are well within experimental reach.

From the comparison of the experimental observations with the theory, we conclude that the external circuit acts as an ideal voltage source (unlike what was previously assumed[11]). This is also consistent with an estimate of the time of tunneling, τ_T. Using the Büttiker-Landauer[20] definition for the time of tunneling and assuming a work function of a volt, we obtain τ_T of the order of 10^{-15} sec. At 10^{15} Hz, the impedance of the external circuit is smaller than that of the junctions.

Moreover, our estimate of τ_T is translated (using the Fermi velocity) to an effective tunneling area of 10 Å diam which is consistent with the STM scanning resolution. Another important time is the dwell time (the time between tunneling events) which is related to the spectroscopic resolution of the STM.

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[1]H. R. Zeller and I. Giaever, Phys. Rev. **181**, 789 (1969).

[2]John Lambe and R. C. Jaklevic, Phys. Rev. Lett. **22**, 1371 (1969).

[3]R. E. Cavicchi and R. H. Silsbee, Phys. Rev. B **37**, 707 (1988); Phys. Rev. B **38**, 6407 (1988).

[4]E. Ben-Jacob, Y. Gefen, K. Mullen, and Z. Schuss, Phys. Rev. B **37**, 7400 (1988), and references therein.

[5]K. K. Likharev, IBM J. Res. Develop. **32**, 144 (1988), and references therein.

[6]For a current-biased junction, voltage oscillations at frequency I_{dc}/e and amplitude $e/2C$ are predicted as long as the external current I_{dc} is smaller than e/RC. In addition, the *I-V* characteristic is expected to display an $e/2C$ shift from Ohmic behavior and parabolic current-voltage dependence at low currents (Refs. 4 and 5). Experiments using single junctions are nontrivial because it is difficult to realize a suitable current source [M. Iansiti, A. T. Johnson, C. J. Lobb, and M. Tinkham, Phys. Rev. Lett. **60**, 2414 (1988). In this experiment the external source has features of a current source. P. J. M. van Bentum, H. van Kempen, L. E. C. van de Leemput, and P. A. A. Teunissen, Phys. Rev. Lett. **60**, 369 (1988). Although a voltage source was used, the interpretation given is that it acts effectively as a current source.] and the oscillations are high frequency. An additional difficulty arises from the fact that the predicted *I-V* characteristic does not have enough distinctive features for critical comparison. Similar *I-V* curves may result from other effects [R. Wilkins *et al.* (to be published)]. The simple shift is observed in the present experiment when the junctions have similar parameters.

[7]K. Mullen, E. Ben-Jacob, R. C. Jaklevic, and Z. Schuss, Phys. Rev. B **37**, 98 (1988); I. O. Kulik and R. I. Shekhter, Zh. Eksp. Teor. Fiz. **68**, 623 (1975) [Sov. Phys. JETP **41**, 308 (1975)].

[8]J. B. Barner and S. T. Ruggiero, Phys. Rev. Lett. **59**, 807 (1987).

[9]L. S. Kuz'min and K. K. Likharev, Pis'ma Zh. Eksp. Teor. Fiz. **45**, 389 (1987) [JETP Lett. **45**, 495 (1987)].

[10]T. A. Fulton and G. J. Dolan, Phys. Rev. Lett. **59**, 109 (1987).

[11]P. J. M. van Bentum, R. T. M. Smokers, and H. van Kempen, Phys. Rev. Lett. **60**, 2543 (1988).

[12]K. A. McGreer, J-C. Wan, N. Anand, and A. M. Goldman (to be published); results are in qualitative agreement with the calculations of K. Mullen, E. Ben-Jacob, and S. T. Ruggiero, Phys. Rev. B **38**, 5150 (1988).

[13]H. G. LeDuc, W. J. Kaiser, and J. A. Stern, Appl. Phys. Lett. **50**, 1921 (1987).

[14]Wilkins *et al.*, Ref. 6.

[15]We adopt Ref. 2's picture of the oxide polarization, assuming it can be expressed in terms of applied voltage that corresponds to an induced fractional charge. The effect is similar to capacitively biasing the drop (Fulton and Dolan, Ref. 10).

[16]E. L. Wolf, *Principles of Electron Tunneling Spectroscopy* (Oxford Univ. Press, New York, 1985).

[17]W. F. Brinkman, R. C. Dynes, and J. M. Rowell, J. Appl. Phys. **41**, 1915 (1970).

[18]J. Lambe and R. C. Jaklevic, Phys. Rev. **165**, 821 (1968).

[19]R. C. Jaklevic and John Lambe, Phys. Rev. B **12**, 4146 (1975).

[20]M. Büttiker and R. Landauer, Phys. Rev. Lett. **49**, 1739 (1982).