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Coulomb blockade of small Pd clusters

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Single-electron tunneling through Au substrate-alkanethiol-Pd cluster-tip junctions is investigated with scanning tunneling spectroscopy. The measured $I(V)$ curves reveal several characteristic features of the Coulomb blockade, namely, the presence of a Coulomb gap and a Coulomb staircase. By using the orthodox theory of single-electron tunneling, the capacitances and resistances of the double junction system as well as the fractional charge are extracted from the experimental data.
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In principle the quantization of the electron charge can be measured by probing the electron transport through a small metallic cluster coupled via two tunnel junctions to an external circuit. Two requirements should be met: (1) the total capacitance of the island to its environment should be so small that the charging energy $e^2/2C$ is larger than the thermal energy kT and (2) the resistances of both tunnel junctions must be larger than the quantum resistance $h/2e^2$. Scanning tunneling microscopy (STM) is a very effective technique to measure single-electron tunneling (SET) of a double junction system (see Fig. 1). The simplest configuration would be a STM tip, a small metal cluster (for instance, Au or Ag), and an ultrathin oxide layer on top of a metal surface.[1] It is also possible to use coated colloidal particles to create a tunneling barrier between the metal cluster and the metal surface.[2] Organic molecules are another option to obtain a tunneling barrier. Self-assembled monolayers (SAMs) of organic molecules as a template for nanoscale circuit device applications have attracted a considerable amount of attention over the last decade. There are several advantages of using SAMs. First of all, SAMs are easy to prepare and they form highly ordered single layers on metal surfaces such as Au, Ag, Pt, etc. Moreover, the possibility to use organic molecules with different properties allows one to control the monolayer in a very precise way. In our experiments we used decanethiol $CH_3(CH_2)_9SH$ molecules. The most important reason for this choice is the high resistance of these relatively long alkanethiol molecules. The molecules are 1.5 nm long, however due to their tilting, the thickness of the SAM is somewhat smaller. A high resistance of the molecule is crucial for our application since it forms one of the junctions in our setup.[3] Both experimental and theoretical studies have shown that the resistance of an alkanethiol molecule exponentially depends on the length of the molecule as expected from the coherent and nonresonant tunneling.[4,5]

In our experiments we used pulsed laser deposition (PLD) to grow small Pd clusters on top of a decanethiol self assembled monolayer.[6] Experiments, using techniques such as evaporation of single metal atoms, have shown that (unless organic molecules with chemically reactive end groups are used) it is virtually impossible to avoid direct contact of the clusters to the substrate due to diffusion of the metal atoms along the molecules.[7–11]

The Au(111) layer (200-nm gold on 5 nm of chromium on glass) consists of large grains which exhibits terraces separated by (mainly) monatomic steps. The substrate was kept overnight in an ethanolic thiol solution and subsequently rinsed with dichloromethane p.a., ethanol p.a., and water. Further details of the sample preparation will be discussed elsewhere.[12] An ultrahigh vacuum (UHV) low-

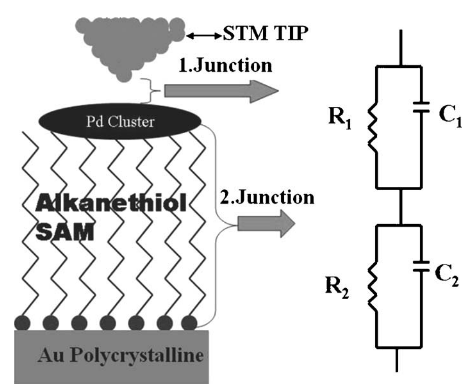

FIG. 1. Schematic model of the double junction system formed by STM tip Pd-cluster SAM Au substrate.

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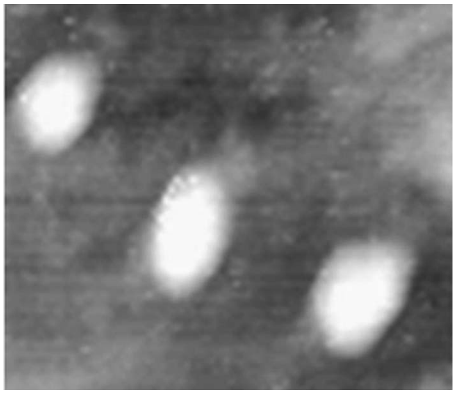

FIG. 2. STM image of Pd clusters on a decanethiol polycrystalline Au substrate. The image (8×10 nm) was taken with a tunneling current of 0.1 nA, and a sample bias voltage of 0.5 V at 300 K. The black\white scale in the image corresponds to a height difference of 2.0 nm.

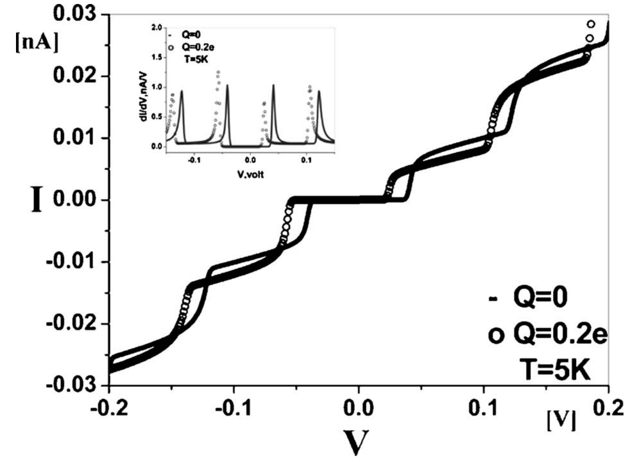

FIG. 4. $I(V)$ curves calculated by using the orthodox theory of single-electron tunneling. $T=5$ K. The resistance and capacitance values are listed in Table I. Inset, dI/dV curve for $Q=0$ and $Q=0.2\ e$.

temperature STM was used to perform measurements with a tungsten tip at 80 K. After preparation, the sample was inserted into the UHV chamber and the sample was directly cooled down to liquid-nitrogen temperature. Since the Pd clusters were physisorbed on the SAM we have used rather low sample biases (0.5 V) and tunneling currents (<0.1 nA).

The STM image reveals that the Pd clusters with a typical radius of a few nanometers are located on top of the decanethiol SAM (see Fig. 2). The Pd clusters look a little asymmetric which might be a signature of a slightly asymmetric tip. In order to check whether the clusters are electrically isolated from the surface or not, we decided to take their $I(V)$ spectra.

In our experiment we have measured the $I(V)$ spectra at each pixel of the STM image. The $I(V)$ curves taken on top of the Pd clusters [see Fig. 3(a)] clearly reveal an equidistant steplike behavior. It should be pointed out here that almost all clusters exhibit this staircaselike behavior in the $I(V)$ curves. On the other hand, the $I(V)$ curves measured on top of the bare SAM [see Fig. 3(b)] do not exhibit these characteristic steps. The $I(V)$ curves taken on the Pd clusters are indicative for single-electron tunneling (Coulomb staircase).

In order to interpret our experimental data we have employed the orthodox model of single-electron tunneling.[13] By using a fitting algorithm we search for the absolute minimum in the mean-square deviation of the experimental $I(V)$ curve from the theoretically obtained $I(V)$ curve. There are five parameters to fit: C_1, C_2, R_1, R_2, and Q_0 (the capacitance and resistance of both junctions and the fractional charge). The fractional charge originates from a difference in the work function of the cluster and the metal substrate.

In order to reduce computation time, it is convenient to start with reasonable estimates for the capacitances and resistances of the double junction system. A comparison of the experimental $I(V)$ with the theoretical $I(V)$ curve reveals that we deal with a strongly asymmetric junction, i.e., $R_2 > R_1$ and $C_2 > C_1$.[14]

The change in energy of both junctions due to tunneling is given by Eqs. (1) and (2). Since the system wants to lower its total energy, the criteria $\Delta E_1^{\pm} < 0$ and $\Delta E_2^{\pm} < 0$ must be fulfilled. Thus by using Eqs. (1) and (2), one can show that if the number of electrons tunneling across the system increases by one, the voltage difference $|\Delta V|$ should exceed the threshold e/C_2. As a consequence of these increments in the bias across the system, sudden jumps in the current will be found. It should be pointed out that the charging energy $e|\Delta V|$ must be larger than the thermal energy kT in order to resolve the Coulomb staircase. Therefore, the $I(V)$ measurements are performed at 80 K with $|\Delta V| \approx 10$ meV steps. Using the relations given above, it can be shown that with a 10-meV resolution, the total capacitance of the system must be less then $2\times 10^{-17} F$. In addition to this, the asymmetry in

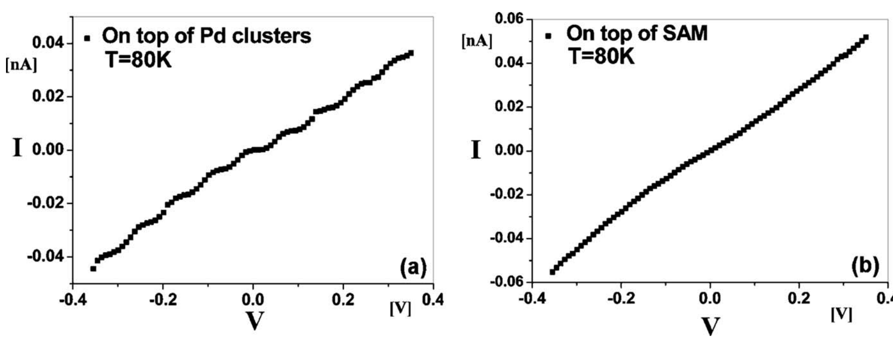

FIG. 3. (a) $I(V)$ curve taken on top of a Pd cluster (b) $I(V)$ curve taken on top of the bare SAM. Sample bias and tunneling current are 0.5 V and 0.07 nA, respectively.

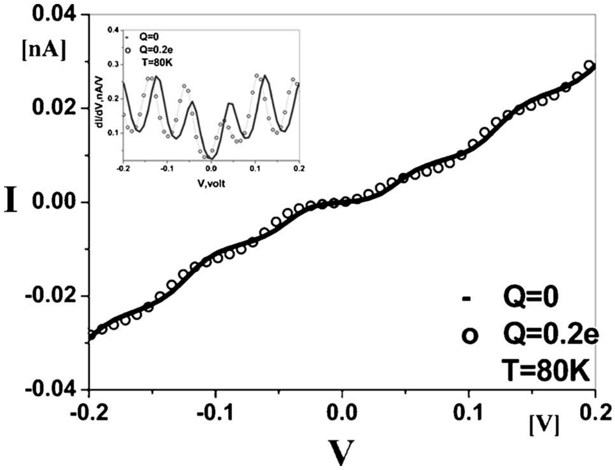

FIG. 5. $I(V)$ curves calculated by using the orthodox theory of single-electron tunneling. $T=80$ K. The resistance and capacitance values are the listed in Table I. Inset, dI/dV curve for $Q=0$ and $Q=0.2\ e$. In the calculations we have used a step size of 10 meV.

the capacitances causes an asymmetry in the tunneling rates as defined in Eq. (3). The asymmetry in the tunneling resistances makes the asymmetry in the tunneling rates even more pronounced. This asymmetry is of key importance, because a symmetric double junction will not exhibit a Coulomb staircase.[15] In order to make a rough estimate of the tunneling resistances, the asymptotic slope of the experimentally obtained $I(V)$ curves were used. The tunneling resistances of both junctions are in the gigaohm range.

$$\Delta E_1^{\pm} = \frac{e}{C_\Sigma}\left(\frac{e}{2} \pm (ne - Q_0) \pm C_2 V\right). \quad (1)$$

$$\Delta E_2^{\pm} = \frac{e}{C_\Sigma}\left(\frac{e}{2} \pm (ne - Q_0) \mp C_1 V\right). \quad (2)$$

$$\Gamma_j^{\pm}(n) = \frac{1}{R_j e^2}\left(\frac{-\Delta E_j^{\pm}}{1 - \exp(\Delta E_j^{\pm}/kT)}\right). \quad (3)$$

Next we want to estimate the fractional charge on the Pd cluster. It can be shown that even at 80 K, it is still possible to trace the effect of the fractional charge on a strongly asymmetric double junction system. As shown in Fig. 4, the effect of a fractional charge (0.2 e) on the $I(V)$ curves is quite pronounced at 5 K. The exact value of the fractional charge can also be extracted from the dI/dV curve (see the inset of Fig. 4). However, at elevated temperatures, it is more cumbersome to extract the fractional charge from the $I(V)$ or dI/dV curve (see Fig. 5).

TABLE I. Calculated fractional charge, resistance, and capacitance values of both junctions.

Q_0	$\sim -0.01\ e$
R_1	~ 0.17 GΩ
R_2	~ 5.5 GΩ
C_1	~ 0.75 aF
C_2	~ 2.0 aF

As shown in Fig. 6(b) the experimental dI/dV curve is almost symmetric around zero bias. Thus our initial estimate for the fractional charge is ~ 0. The results of our calculation are shown in Fig. 6 and Table I.

Because the size of the Pd clusters slightly varies we have only considered a single cluster in Fig. 6 and Table I. A change in the size of the cluster does not only affect the capacitance of the junctions but also the number of molecules connecting the cluster to the substrate. The latter implies that also the resistance of the second junction will depend on the cluster size. From transmission electron microscopy (TEM) images of the sample,[12] however, we know that the size distribution of the Pd clusters is quite narrow (2.3 ± 0.5 nm). This explains why similar experiments on other clusters resulted in quite similar results for the capacitance and resistance values. Finally, the resistance of the second junction, i.e., the resistance of the decanethiol molecule, is of the same order of magnitude as measured previously.[16–18]

In conclusion, we have shown that small Pd clusters deposited on an alkanethiol self-assembled monolayer are electrically isolated from the underlying Au substrate. The substrate-alkanethiol-Pd cluster-tip system exhibits two single electron-tunneling characteristics at 80 K, namely, the presence of a Coulomb gap and Coulomb staircase.

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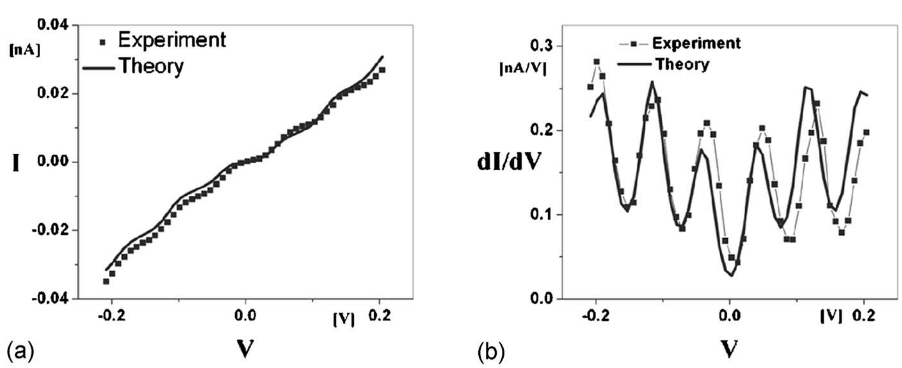

FIG. 6. (a) Experimental and theoretical $I(V)$ curves. The experimental $I(V)$ curve is taken on top of a Pd cluster at 80 K. (b) Experimental and theoretical dI/dV curves.

[1] C. Schonenberger, H. Van Houten, and H. C. Donkersloot, Europhys. Lett. **20**, 249 (1992).
[2] C. Schonenberger, H. Van Houten, H. C. Donkersloot, A. M. T. Van Der Putten, and L. G. J. Fokkink, Phys. Scr. **45**, 289 (1992).
[3] C. C. Kaun and H. Guo, Nano Lett. **3**, 1521 (2003).
[4] J. Zhao and K. Uosaki, Nano Lett. **2**, 137 (2002).
[5] W. Wang, T. Lee, and M. A. Reed, Phys. Rev. B **68**, 035416 (2003).
[6] E. A. Speets, B. J. Ravoo, F. J. G. Roesthuis, F. Vroegindeweij, D. H. A. Blank, and D. N. Reinhoudt, Nano Lett. **4**, 841 (2004).
[7] R. P. Andres, S. Datta, M. Dorogi *et al.*, J. Vac. Sci. Technol. A **14**, 1178 (1996).
[8] D. Anselmetti, T. Richmond, A. Baratoff, G. Borer, M. Dreier, M. Bernasconi, and H. J. Güntherodt, Europhys. Lett. **12**(3), 241 (1990).
[9] M. Dorogi, J. Gomez, R. Osifchin, R. P. Andres, and R. Reinfenberger, Phys. Rev. B **52**, 9071 (1995).
[10] T. Ohgi, H. Y. Sheng, and H. Nejoh, Appl. Surf. Sci. **130–132**, 919 (1998).
[11] T. Ohgi and D. Fujita, Surf. Sci. **532–535**, 294 (2003).
[12] E. A. Speets, B. Dordi, B. J. Ravoo, N. Oncel, A.-S. Hallbaeck, H. J. W. Zandvliet, B. Poelsema, G. Rijnders, D. H. A. Blank, and D. N. Reinhoudt, Small **1**(4), 395 (2005).
[13] D. V. Averin and K. K. Likharev, in *Mesoscopic Phenomena in Solids*, edited by B. L. Altshuler, P. A. Lee, and R. A. Webb (Elsevier, Amsterdam, 1991).
[14] A. E. Hanna and M. Tinkham, Phys. Rev. B **44**, 5919 (1991).
[15] D. K. Ferry and S. M. Goodnick, *Transport in Nanostructures* (Cambridge University Press, Cambridge, 1997).
[16] L. A. Bumm, J. J. Arnold, T. D. Dunbar, D. L. Allara, and P. S. Weiss, J. Phys. Chem. B **103**, 8122 (1999).
[17] D. J. Wold and C. D. Frisbie, J. Am. Chem. Soc. **122**, 2970 (2000).
[18] A.-S. Hallbäck, N. Oncel, J. Huskens, H. J. W. Zandvliet, and B. Poelsema, Nano Lett. **4**, 2393 (2004).