EUROPHYSICS LETTERS 1 February 1994

Europhys. Lett., 25 (4), pp. 297-302 (1994)

Single-Electron Tunnelling at Room Temperature with Adjustable Double-Barrier Junctions.

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(received 12 July 1993; accepted in final form 2 December 1993)

PACS. 73.40G – Tunnelling: general.
PACS. 61.16D – Electron microscopy determinations (inc. scanning tunnelling microscopy methods).

Abstract. – Ultrasmall double-barrier junctions with capacitance 10^{-19}–10^{-18} F were realized in a system consisting of a metallic substrate, an insulating thin organic film, an isolated metal particle, an adjustable tunnelling gap and the tip of a scanning tunnelling microscope (STM). These structures were characterized by STM topography and local current-voltage (*I-V*) measurements at room temperature. We found clear evidence of Coulomb blockade effects in the *I-V* characteristics which could readily be explained in terms of simulations based on the semi-classical theory of single-electron tunnelling. The charging energies and resistances derived from our experiments clearly exceed the theoretical limits of thermal energy and resistance quantum required for observing single-electron tunnelling. By varying the STM gap we also verified the dependences of the particle capacitance and of the double-barrier series resistance.

In 1969 Giaver and Zeller [1] showed that when studying tunnel junctions containing metallic grains in the limit of small capacitances, the tunnelling process is no longer purely random in nature. The electrical transport through a small metallic island coupled by two tunnel junctions to an external voltage source reflects the quantized nature of the electrical charge stored on the metallic island. When the charging energy $E_C = e^2/2C$ and the resistance of this two-junction circuit exceed the thermal energy $k_B T$ and the resistance quantum h/e^2, respectively, the time-averaged tunnel current through this system is suppressed for voltages $< U_C (= E_C/e)$, a phenomenon referred to as «Coulomb blockade» [2-4]. Moreover, a current-voltage (*I-V*) characteristic with linear asymptotes offset by $\Delta U = \pm U_C$ is predicted if the junction resistance is assumed constant over the relevant voltage range. These simplest manifestations of single-electron tunnelling (SET) effects are clearcut in the case of double junctions because the charge on the intermediate island is an independent variable. On the other hand, for a single ultrasmall junction connected to an external circuit with a typically much lower impedance, charging effects are washed out by quantum fluctuations [3]. Thus we focus our attention on double junctions with individual resistances R_1, R_2 and capacitances C_1, C_2 satisfying the above-mentioned conditions. The resulting Coulomb gap, offset, and in the case of strongly asymmetric junctions «Coulomb staircase», a sequence of equidistant steps at voltages differing by e/C_1 (assuming $R_1 > R_2$), have mostly been studied at low temperatures in metal structures realized using submicrometer fabrication technology [5, 6], and sometimes in conjunction with a scanning tunnelling microscope (STM) [7-9]. First claims of room temperature SET fingerprints were reported by using an STM against a granular metallic film [10] and a metallic substrate in contact with a liquid crystal [11]. Very recently, Schönenberger and coworkers succeeded in convincingly demonstrating SET at room temperature in ultrasmall double-barrier junctions by using small isolated Au particles produced by e-beam evaporation [12] and by colloidal chemistry [13] between an STM tip and an Au surface.

In this letter we report on further evidence of SET effects at room temperature in a double-barrier junction system consisting of an organic monolayer and the tunnelling gap of an STM. Insight into the physics of such small systems may also have a significant impact on ongoing research in the field of molecular electronics. The STM allows us to locate and characterize individual particles and to adjust their charging energy at room temperature.

Our junction consisted of a 1000 Å thick Au(111) film epitaxially grown on mica, and covered by a self-assembled monolayer (SAM) of alkane thiolate molecules ($S(CH_2)_{11}OH$) [1]. These ~ 15 Å thick insulating organic films on Au(111) have previously been investigated by STM [14] and found to be very stable and homogeneous. We found that an average 3–5 Å of additional gold evaporated at room temperature onto such a film nucleates into more or less isolated Au clusters with a diameter of 50–100 Å. Positioning the STM tip over such an Au

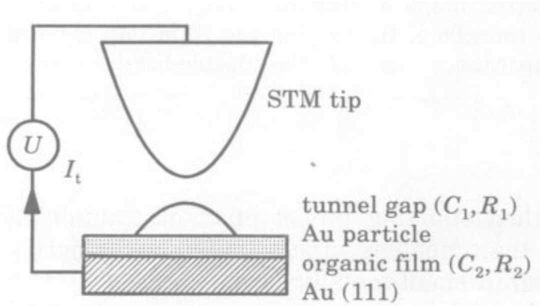

Fig. 1.

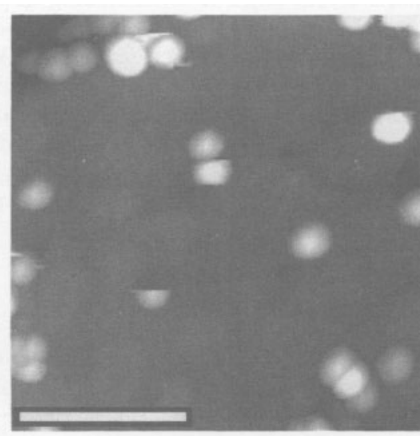

Fig. 2.

Fig. 1. – Schematic arrangement of double-barrier junctions realized with two outer electrodes (Au substrate and STM tip) and a small metallic particle separated by a thin organic film and the STM gap.

Fig. 2. – STM constant-current image (20 pA, 550 mV) of the self-assembled monolayer (SAM) on which isolated Au clusters with a diameter of 50–100 Å can be recognized. The scale bar corresponds to 400 Å.

[1] To prepare a self-assembled monolayer (SAM), the Au substrate is immersed in a dilute (~ 1 mM) solution of $(HS(CH_2)_nX)$ at room temperature for an interval from several hours to days.

particle forms a double-barrier junction where the STM gap and the organic thin film act as the first and second junction, respectively (fig. 1).

The present experiments were performed under ambient conditions at room temperature using mechanically cut $Pt_{80}Ir_{20}$ tips. The compact STM used [15] is equipped with an I/V converter of 10^9 V/A allowing reliable current detection down to very small tunnel currents ($\sim$ 1 pA) with a high bandwidth [16].

Since I-V measurements under ambient conditions at room temperature generally suffer from thermal drift and an increased noise level, we applied STM gap stabilization and noise reduction techniques (2).

In the following, when referring to a preset current in an I-V measurement we mean the tunnelling current which is established before the STM feedback is switched off and before the sample bias voltage is ramped. The separation of the two outer electrodes (the STM gap width) is fixed by this tunnel current and thus can directly be adjusted prior to each I-V measurement.

In fig. 2 we present a typical STM constant-current image showing the topography of the SAM-covered gold substrate where well-isolated, stable clusters with a diameter of 50–100 Å and a height of 20–30 Å can be recognized. They are therefore rather flat and to a first approximation act as ultrasmall parallel-plate capacitors with respect to the substrate and to the end of the STM tip when it is positioned over such a cluster. Assuming an effective plate capacitor area of $A = \pi$ (40 Å)^2, tunnelling distances $d_1 \approx d_2 = 10$ Å and similar dielectric constants of $\varepsilon \approx 1$, we estimate the individual junction capacitances to be $C_1 \approx C_2 \approx$ $\approx 4.4 \cdot 10^{-19}$ F, using $C_i \cong \varepsilon\varepsilon_0 A/d_i$. The charging energy of the particle in this double-barrier junction geometry is therefore $E_C = e^2/2C \approx 180$ meV, where $C = C_1 + C_2$ is the capacitance «seen» by the excess charge on the particle. This energy is large compared to $k_B T$ at room temperature (26 meV) and also to the spacing of energy levels expected from size quantization in an isolated particle with the above-mentioned dimensions ($\Delta E \simeq 1$ meV). The semi-classical description of SET [2, 3, 9] is therefore justified. On the other hand, E_C is still small compared to the characteristic scales of ΔE_1, ΔE_2 determining the energy dependence of the tunnelling probabilities, which result in parabolic background conductances [17].

In fig. 3 we present I-V characteristics all taken with the following parameters: preset current $I_t = 40$ pA and sample bias voltage $U_s = 550$ mV. Curve *a*) is an I-V curve taken over a freshly prepared Au film whereas curve *b*) was taken with the tip positioned directly over the SAM-covered gold film. Both curves exhibit a more or less linear dependence with no low-voltage anomalies like a gap, indicating ideal metal-insulator-metal tunnel junctions. Finally, the I-V curve *c*) was taken with the tip positioned directly over a metallic particle where SET was expected. The characteristic, showing an overlay of the experimental curve (solid line) and the calculated values (circles), clearly exhibits the suppressed conductance at low $|U|$ and the asymptotic offset resulting from the Coulomb blockade. We could fit all experimental I-V characteristics to the semi-classical theory of SET using the analytic solution presented by Hanna and Tinkham [9]. The shape of each I-V curve is in principle determined by six parameters: the individual junction capacitances C_1, C_2, and resistances R_1, R_2, the temperature T and the zero-voltage island charge Q_0 [18], which accounts for the dependence of the electrostatic energy on contact potentials and uncontrolled external charges in the vicinity of the particle. All our I-V curves could be adequately fitted assuming a symmetric double-barrier junction with $C_1/C_2 \cong R_1/R_2 \cong 1$. The calculated points in fig. 3*c*)

(2) This has been achieved by averaging several I-V curves taken successively after switching on the STM feedback control to allow readjustment of the STM gap. The corresponding vertical drift did not exceed 0.1 Å.

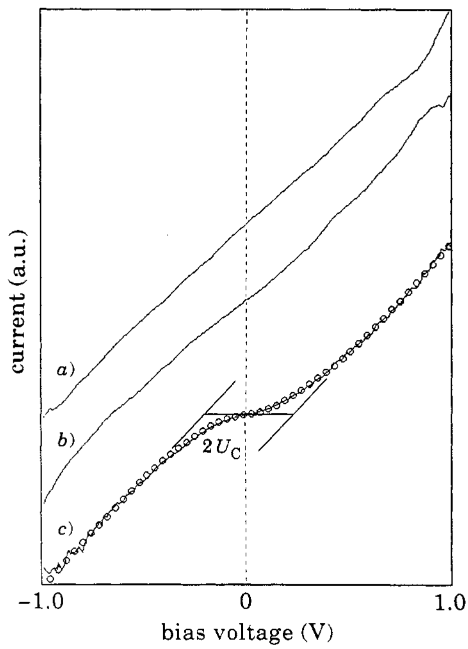

Fig. 3.

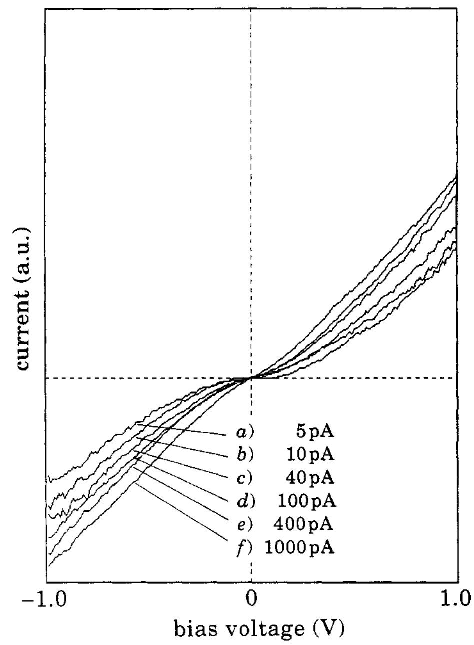

Fig. 4.

Fig. 3. – *I-V* characteristics where the tip-sample separation was adjusted so that $U_s = 550\,\mathrm{mV}$ and $I_t = 40\,\mathrm{pA}$. Curve *a*) was taken over the bare Au substrate. Curve *b*) was measured after the substrate was covered by a self-assembled monolayer of $S(CH_2)_{11}OH$ molecules. Curve *c*) is taken above a metallic particle. In this case the calculated values (circles) obtained from the analytical semi-classical theory of ref. [9] are superimposed on the experimental curve (solid line) and clearly show the non-linearity and the offset $2U_C$ resulting from Coulomb blockade.

Fig. 4. – Successive *I-V* curves taken at different tip-sample separations on top of a metallic particle. The STM gap is adjusted by changing the STM tunnel current prior to switching off the STM feedback. The dependence of the Coulomb offset on the preset current is clearly visible.

were obtained assuming a particle capacitance of $C = C_1 + C_2 = 5.1 \cdot 10^{-19}\,\mathrm{F}$, a total resistance of $R = R_1 + R_2 = 4.5 \cdot 10^9\,\Omega$ and an induced charge of $Q_0/e = 0.27$. This corresponds to a Coulomb energy of $E_C = 157\,\mathrm{meV}$ which is well above the thermal energy at room temperature and a total resistance which clearly exceeds the resistance quantum of $h/e^2 (\sim 25.8\,\mathrm{k}\Omega)$.

To further confirm that the observed gap is indeed due to Coulomb blockade and SET, we varied the particle capacitance between successive *I-V* measurements. Upon increasing the present current, the STM tip-to-sample separation decreases, resulting in an increase in particle capacitance. Since $U_C = e/2C$, a decrease of the Coulomb gap is expected. In fig. 4 *I-V* curves are shown taken at successively increased preset currents between 5 pA and 1 nA. The systematic dependence of the Coulomb gap on the preset current is clearly visible. All *I-V* curves were fitted using the above-mentioned theory and the extracted values for the total resistance and particle capacitance are indicated in fig. 5. Both parameters are plotted against the logarithm of the preset current which can be assumed to be linearly related to the STM gap width. The total resistance is logarithmically plotted in fig. 5*a*), showing nicely the exponential dependence on the STM gap width according to tunnelling theory. The inversely

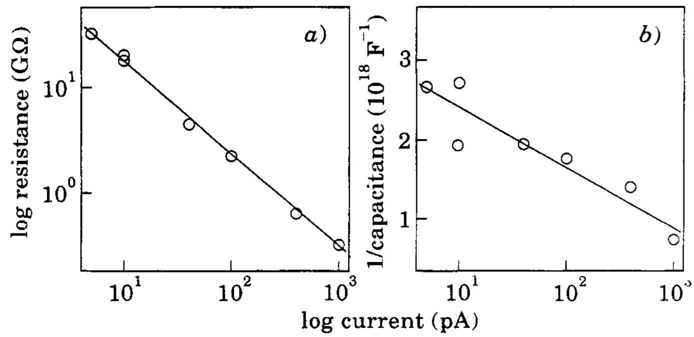

Fig. 5. – Total resistance and particle capacitance from fits of the *I-V* data of fig. 4 fitted to the semi-classical theory of ref. [9]. Both quantities are plotted against the logarithm of the preset current which is linearly related to the STM gap width.

plotted total capacitance in fig. 5*b*) shows a linear behaviour indicating a simple inverse law such as $C = \varepsilon\varepsilon_0 A/d$ as already mentioned above. Assuming a typical tunnelling distance of $d = 10$ Å and $\varepsilon \approx 1$, we calculated (50–80 Å)^2 for the effective capacitor area which is in good agreement with the size of the metallic particles measured in the STM images.

In all *I-V* measurements at room temperature we found no evidence of a «Coulomb staircase» as expected for strongly asymmetric double-barrier junctions where R_2/R_1 and C_2/C_1 are $\gg 1$ or $\ll 1$. This can be explained with enhanced charge fluctuations in the junction vicinity at room temperature which smear out the «Coulomb staircase» or by the essentially symmetric character of our double-barrier junctions. In contrast to a previous study [12] where hard ZrO_2 films with a dielectric constant of $\varepsilon \approx 10$ were used, we work with a soft thin organic film with a much lower dielectric constant of $\varepsilon \approx 1$. The result is a rather symmetric double-barrier junction which prevents us from observing the Coulomb staircase in the *I-V* data at room temperature but on the other hand allows us to adjust the particle capacitance in a wide range and hence the Coulomb gap U_C. The observation of the distance dependence of the Coulomb gap is rather difficult when the dominant capacitance (*e.g.* due to a hard film with a large dielectric constant) can practically not be changed.

A further important point concerns the softness of our organic film and the strong tip-sample interaction forces apparent in STM experiments under ambient conditions on these organic overlayers (^{3}). Upon changing the particle capacitance by approaching the tip towards the metallic particle (by adjusting the preset current) both tunnel junctions, treated as two elastic media in series, are simultaneously deformed, preserving the symmetric character of the double-barrier junction. This was verified by our calculations where all measured *I-V* curves could be fitted best with $C_1/C_2 \cong R_1/R_2 \cong 1$. Lowering the temperatures to stiffen the organic film and performing the experiments in high vacuum to reduce the interaction forces might make the system more asymmetric, allowing the observation of the Coulomb staircase.

In conclusion, we observed single-electron tunnelling at room temperature with ultrasmall double-barrier tunnel junctions consisting of a metallic particle between an organic

(^{3}) From combined STM/AFM experiments at ambient conditions on Au(111) and SAM/Au(111) films, we have evidence of tunnelling gap deformation due to adhesion and/or capillary forces from adsorbed water or other soft surface contaminants which mediate the STM tunnelling gap. See [19].

self-assembled monolayer film and the tunnel gap of a scanning tunnelling microscope. The preparation technique for such thin organic films is reliable and versatile and might be of technological interest for the development of future electronic-device applications. Our experimental data can be interpreted in terms of the semi-classical theory of single-electron tunnelling. By changing the STM gap width we observed the expected dependence of tunnelling resistance and of the Coulomb gap allowing an adjustment of the particle capacity.

Additional Remark..

During the final stages of manuscript preparation the Coulomb staircase has been observed in this system at 77 K and at 4.5 K [20]. As mentioned above, this suggests either a decrease in charge fluctuations in the double-barrier junction vicinity or a more asymmetric double-barrier junction at low temperatures.

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We would like to thank M. BÜTTIKER, T. SCHAUB and especially CH. SCHÖNENBERGER for helpful discussions. We also thank CH. GERBER, B. MICHEL and E. DELAMARCHE for support and preparation of some of the SAM-covered Au(111) films. We acknowledge support from H.-R. HIDBER, A. TONIN, M. MONFREDA and S. RÜEGG in designing electronics. Furthermore we acknowledge help and support from the IBM Zurich Research Laboratory. This work was financially supported by the Swiss National Science Foundation and the «Kommission zur Förderung der wissenschaftlichen Forschung».

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