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Room temperature molecular single-electron transistor

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Considerable interest has been shown in the effects of correlated single-electron tunneling [1] during the past decade. Most of the experiments with lithographically fabricated structures were carried out at temperatures below 1 K. To increase the operating temperature T it is necessary to reduce the typical size d of the structure in order to decrease the typical capacitance C (operation at $T = 300$ K requires $C \lesssim 10^{-18}$ F corresponding to $d \lesssim 3$ nm), which is quite a difficult problem. Several different fabrication techniques were studied to obtain single-electron effects at relatively high temperatures (for a recent review see, e.g., Ref. [2]). Let us mention, for example, room temperature memory effects [3] and single-electron transistors with visible operation up to 300 K [4] using silicon-based structures, the gated system of metal grains [5] operating at 77 K, and room-temperature single-electron transistors made by the nano-oxidation process [6].

Another technique in which small capacitances are easily obtained and which was actually first applied to study single-electron tunneling at high temperatures is based on the use of the scanning tunneling microscope (STM). The simplest single-electron circuit consisting of two tunnel junctions in series is made up of an STM tip, a small conducting particle, and a substrate. The single-electron charging survives up to room temperature for sufficiently small metal particles [7, 8] and can be even stronger when tunneling via single molecules is studied [9 – 12].

The drawback of this technique is the absence of a gate electrode to control the transport. In the present letter we report for the first time the demonstration of a room temperature molecular single-electron transistor with a metal gate controlling the tunneling of single electrons from the STM tip to the substrate via a carboran cluster molecule (see also Ref. [13]).

Langmuir – Blodgett (LB) monolayers of stearic acid with incorporated metallorganic clusters were deposited on the pyrolytic graphite (HOPG) substrate with a pre-formed gate electrode. This electrode was fabricated by the conventional electron lithography technique and consisted of a system of thin (50 nm) and narrow (400 nm) gold strips separated by 400 nm from each other (Fig. 1). All the strips were connected in series and separated from the substrate by a 50 nm thick insulator (Al_2O_3) – see Fig. 2.

The LB monolayer was deposited using a computerized conventional teflon trough by the technique described in more detail in Refs [11] and [14] (see also Refs [15, 16]). A small amount of a mixture of the carboran clusters 1,7-$(CH_3)_2$-1,2-$C_2B_{10}H_9Tl(OCOCF_3)_2$ and stearic acid dissolved in tetrahydrofuran (total molecular concentration 0.001 M) was put on the surface of MilliQ-purified water. After complete solvent evaporation the monolayer was compressed at a speed of about 5 A^2/mol/min. The LB monolayer was transferred from the trough onto the substrate with the gate electrode by Schaefer's method [17].

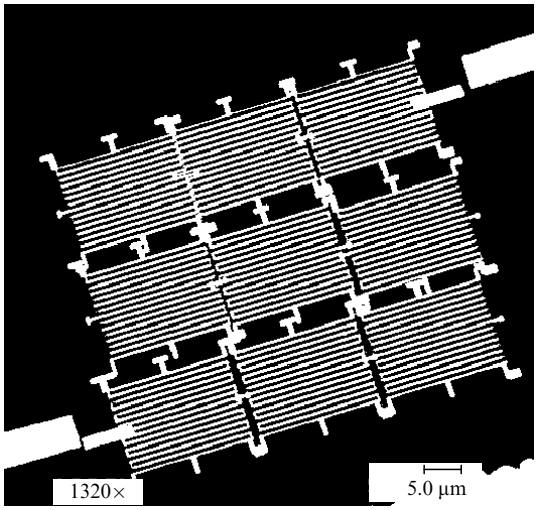

Figure 1. SEM image of the gate electrode fabricated before the monolayer deposition.

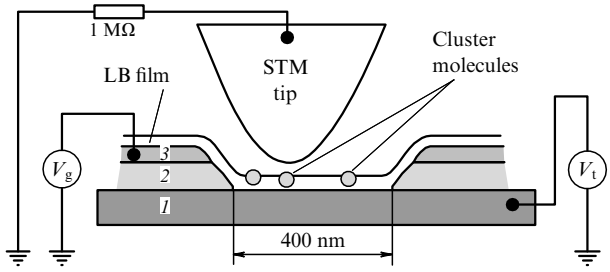

Figure 2. Schematic of the single-electron transistor based on a single cluster molecule. (*1*) HOPG substrate, (*2*) insulating layer (Al_2O_3), (*3*) gold gate electrode.

Electron transport through the film was studied at room temperature using a "NanoScope" STM with atomic resolution. First the films were imaged at a typical tip bias voltage of 0.5V and tunneling current of 0.5 nA. The images were stable and reproducible.

The carboran clusters were seen as elevated oval shape objects with a greater dimension of about 20 A and lesser dimension roughly half that. The average distance between clusters was about 20 nm. The size and shape were not strictly reproducible, but that can be explained, for example, by the different orientations of the cluster molecules in the monolayer.

After finding a cluster molecule, the STM tip was positioned above the cluster and a series of transport measurements with a disconnected STM feedback loop was conducted (the feedback loop was used between measurements to restore the vertical position of the tip). Actually the measurements were carried in 49 closely located points in the plane, so the points directly above the cluster as well as the points aside the cluster were studied. The typical dc $I-V$ curve in the case of tunneling via the cluster molecule is shown in Fig. 3. It has a clear staircase shape while there are no stairs if the STM tip is far from the cluster. Six equidistant steps with a voltage period of about 130 mV are visible in Fig. 3. Figure 3 also shows the results of the differential conductance measurement using the lock-in technique.

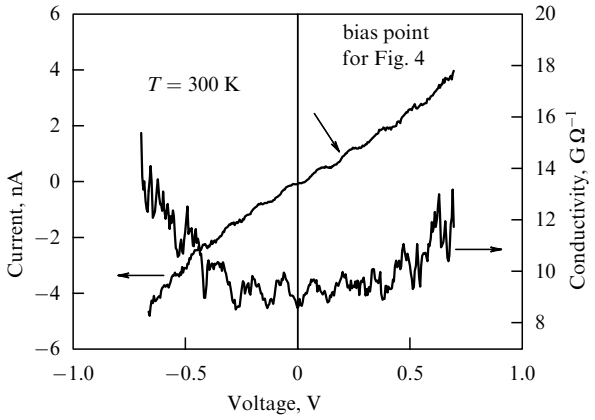

Figure 3. Typical $I-V$ curve and the differential conductance (as a function of bias voltage V) for the molecular single-electron transistor.

Curve *1* in Fig. 4 shows the dependence of the tunneling current I on the gate voltage V_g in the case when the STM tip is positioned above the cluster located about 100 nm from the gate electrode. The curve is clearly periodic with a period of about 0.8 V. In contrast, the $I-V_g$ curves do not show such an effect when the STM tip is positioned above the flat area of surface without clusters (Fig. 5, curve *2*). Assuming that each period of oscillations of the curve *1* corresponds to one additional electron, we can estimate the charge sensitivity of our molecular single-electron transistor as $10^{-3}e/\sqrt{\text{Hz}}$ (the measuring system has the bandwidth of 16 kHz). We suppose that mechanical vibrations give the main contribution to the total system noise (~150 pA peak-to-peak in Fig. 4). The modulation amplitude of the control curve depends on the dc bias voltage V. Qualitatively we have found that the amplitude is maximal for V corresponding to the points between the steps of $I-V$ curve while the gate control is almost negligible when V is within the plato range.

The experimental results qualitatively agree with the theory of the single-electron transistor [1], however, several issues are not clear yet. Single electron tunneling in a molecular system should be affected [2] by the discreteness of the energy spectrum. In this case the electric capacitance becomes not well-defined, and the Coulomb energy is converted into the energy of ionization and electron affinity. However, at the present time there is no independent information in the literature about the energy spectrum of the studied system. On the other hand, the simple 'orthodox' theory [1] which assumes a continuous energy spectrum for the electrodes is proven to work sufficiently well even for nanometer-size systems.

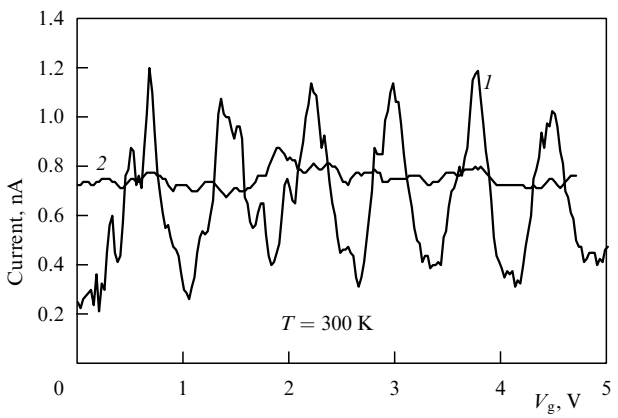

Figure 4. Curve (*1*): the dependence of the current through the molecular single-electron transistor on the gate voltage (dc bias point is shown by the arrow in Fig. 3. Curve (*2*): similar dependence when the STM tip is positioned above the stearic acid (without a cluster).

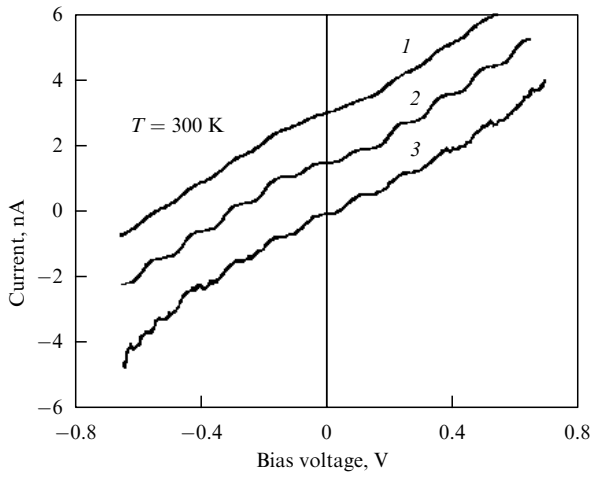

Figure 5. $I-V$ curves calculated using the 'orthodox' theory (curves *1* and *2*) to fit the experimental result (curve *3*). The curves are shifted vertically for clarity.

So, as a first approximation it is natural to try the explanation of the experimental $I-V$ curve shape using the 'orthodox' theory. Then taking the staircase period of $\Delta V \simeq 130$ mV from Fig. 3 we can calculate the capacitance of the junction with a larger resistance $C = e/\Delta V \simeq 1.2 \times 10^{-18}$ F. This figure is too large to be explained as the capacitance of the core of the carboran cluster which is 7 A in diameter. The STM image of the cluster molecule is also considerably larger (about 20 A). It is reasonable to assume that the effective size (in the sense of electrostatical energy) is larger that the core size†. A sphere of diameter $d = 20$ A has a capacitance $C \simeq \varepsilon \times 1.1 \times 10^{-19}$ F. Hence, the experimental capacitance of 1.2×10^{-18} F can be reasonably well explained if we take into account the effective dielectric constant ε (related to the substrate, stearic acid, and adsorbate) and the capacitance increase when the geometry is closer to the plane capacitor.

Figure 5 shows the $I-V$ curves calculated using the 'orthodox' theory (curves *1* and *2*) to fit the experimental results (curve *3*). One can see that the agreement between the theory and the experiment is qualitatively quite good but not perfect quantitatively. The calculations show that to have such a well pronounced Coulomb staircase the temperature should be at least 1.5 times lower than it was experimentally. The almost horizontal steps obtained in the experiment could be explained only assuming that the tunnel junction, which has a much higher resistance, also has a considerably larger capacitance. Though such an assumption does not seem quite

† We should note that in our earlier study of a similar system [11] (without a gate electrode) we did not observe the pronounced Coulomb staircase, but observed a considerably larger (~ 500 mV) Coulomb blockade. It is not excluded that an additional fabrication step has changed the chemical environment of the cluster molecules.

natural, it is the usual explanation of the almost flat steps in single-electron experiments using an STM.

The horizontal steps could be well explained if we assume a discrete energy spectrum for the central electrode of transistor [18], which is quite natural for a molecular system. However, at the present time we do not have the necessary information about the energy spectrum of our system.

The gate capacitance C_g calculated from the period of the control curve (curve *1* in Fig. 5) is about 2×10^{-19} F. The ratio $C_g/C \sim 0.15$ is unexpectedly large despite the distance between the cluster and the gate electrode (~ 60nm) being much larger than the typical distance between the STM tip and the cluster molecule. A possible explanation of this fact can be based on the fact that the graphite substrate is quite far from being a perfect conductor, and this considerably reduces the screening of the gate voltage by the bias electrodes. Theoretical fitting of the modulation amplitude of the control curve (using the capacitance calculated from Fig. 3) gives a discrepancy of 1.5 times in the temperature, similar to the discrepancy for the $I-V$ curve fitting. However, Fig. 5 shows the largest current swing obtained, and the typical control curves do not go beyond the limit explainable by the 'orthodox' theory.

In conclusion, we have demonstrated a controllable single-electron system based on a single cluster molecule. The clear Coulomb staircase and the transistor action were obtained at room temperature. The experimental results are in a good qualitative agreement with the 'orthodox' theory of the single-electron transistor, however, there are several quantitative discrepancies. Further studies of this subject are obviously necessary.

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Sensing of dynamic charge states using single-electron tunneling transistors

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1. Introduction

The SET transistor is a system of two ultra-small tunnel junctions attached to a small conductive island and supplied with a gate electrode that is capacitively coupled to this island [1]. When the energies of thermal and quantum fluctuations are small enough ($E_c \gg k_B T$, $R_{1,2} \gg R_q$) one can observe several specific features of the transistor:

(1) the Coulomb blockade region on the $I-V$ curve with a vanishing dc current;

(2) periodic variations of the $I-V$ curve with a change in the gate voltage.

One of the most important properties of the SET transistor is that its $I-V$ curve is quite sensitive to the charge of the central island. Theoretical estimates give a value for the sensitivity of about $1 \times 10^{-5}\ e/\sqrt{\text{Hz}}$. The experimental values appear to be about one order of magnitude higher at a frequency of 10 Hz and increase as $1/f$ at lower frequencies. Nevertheless it is the best value available for electrometers up to date. The SET transistor was successfully used as a sensitive readout electrometer in recent experiments with the SET box [2], pump [3] and trap [4].

Being a measuring device a SET-transistor is still not free from non-idealities in behavior, such as the back influence on the system monitored. The fact that the tunneling current in the transistor is realized via a random process of tunnel events gives rise to a fluctuation of the number of excess electrons on the transistor island. As a result the electric potential of the island fluctuates with a magnitude of the order of e/C_Σ, where C_Σ — is the total capacitance of the island. Thus the monitored node of another SET device nearby is subjected to the voltage fluctuations, in turn affecting the tunneling process onto and from the node. The stronger the coupling between the two central nodes the higher sensitivity of the electrometer. On the other hand, the stronger the coupling, the stronger the back influence. In this way, we arrive at a contradiction: to obtain a higher sensitivity the electrometer should be positioned closer to the object under study, but the closer the electrometer is to the object, the stronger is its back action. Another problem which can arise is local overheating of the object by the Joule heat dissipated by the electrometer. In the present paper we mostly consider these two factors. In addition, as can be seen in the system with the SET-trap, these two mechanisms of back action are not the only ones to exist.

2. Sample characteristics

Our experimental structure consists of three standard type transistors with Al based tunnel junctions. It was prepared using the usual conventional shadow evaporation technique on a thermally oxidized Si substrate. In our design, all three in line shaped transistors were formed without stray shadows of their islands (Fig. 1). We fabricated transistors with essentially different junction areas and, therefore, tunnel capaci-