Spontaneous Shape Distortion in Quench-Condensed Bismuth Clusters below 8 K

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We study single-electron transport in quench-condensed bismuth films. By lateral confinement, we select a specific cluster of about 10^3 atoms and use tunneling barriers that appear naturally during thin-film formation. A remarkable reversible increase of the sample conductance up to 5 times was found as the temperature was lowered from 11 to 4 K. We attribute this effect to a spontaneous distortion of the cluster shape and discuss its relation to a phase transition predicted for free metallic clusters.

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Metallic films prepared by vapor deposition on a cold (4–10) K substrate—quench-condensed (QC) films—have been used as model objects to study the effect of disorder on electron localization [1,2] and superconductivity [3]. Films condensed on inert substrates are believed to consist of small islands, although there is no clear picture of the island formation in extreme conditions where thermally activated diffusion is frozen [4]. The film structure was usually deduced from macroscopic electron transport measurements, providing information that is averaged over the whole sample. No direct measurements of the local transport have yet been performed.

As the structure of QC films is metastable, it can only be studied *in situ*. Recently, the morphology of these films has been studied by a cryogenic scanning tunneling microscope (STM) [5]. An unusual film growth scenario was found. The island formation happens suddenly by an avalanche in the amorphous precursor layer. The existence of islands in QC films was confirmed experimentally and charging energies as high as 0.2 eV were reported, indicating the presence of very small islands. However, an STM study does not provide information on the local transport. A macroscopic thin film built from such small clusters would be insulating. Therefore, the grain properties and the properties of tunneling barriers in QC films remain unclear.

During the last decade, a single-electron tunneling approach has been developed, opening new opportunities to study thin films. Single-electron phenomena are natural for thin-film studies at low temperatures: Giaever and Zeller noticed the first single-electron effects as early as in the 1960s [6].

In this paper we report the first measurements of tunneling through single clusters of an amorphous quench-condensed bismuth film [7] in a single-electron transistor geometry. Tunneling barriers, separating the central island of these transistors from the thin-film electrodes, appeared naturally during the QC film growth. Electrostatic gates, made of oxidized aluminum, had been prepared in advance, and used to tune the charge on the island.

The sample fabrication procedure has been described elsewhere [9]. We used electron-beam-defined shadow masks in combination with evaporation at an angle. By incremental depositions of bismuth through these masks controlled by *in situ* measurements of the sample conductance, we form bismuth quench-condensed films with (5–10) nm wide constrictions. A bridge of nanoparticles forms between the self-aligned low resistive electrodes at the initial stage of fabrication (see Fig. 1). The nominal film thickness in the bridge could be varied stepwise in the range (2–5) nm by *in situ* film depositions. Each deposition changed the grain size and the configuration of the tunneling paths. More than 30 samples, different in thickness and the properties of the bridge, were studied in every experimental run. Each sample was characterized by current versus source-drain and gate voltage patterns (see, for example, Figs. 2a and 2b). A multigrain nanoconstriction structure, formed at the initial deposition steps, was replaced by a single-electron transistor geometry (with one island dominating the transport) as the thickness increased. A single tunneling gap survived in further depositions. Eventually, a metallic nanocontact was formed.

Here we discuss representative data for transistors with well-developed Coulomb diamonds, obtained in different experimental runs, and compare them with the case when just one tunneling gap is left in the constriction.

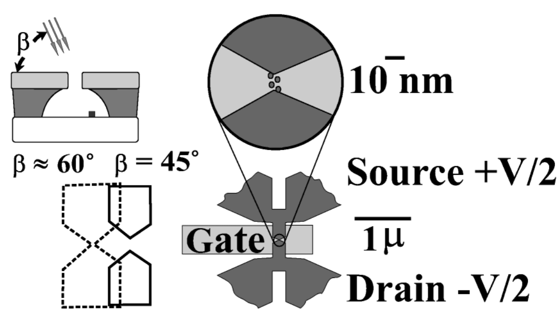

FIG. 1. Left—tuning the constriction width: starting from $\beta = 45°$ the tilt was incremented stepwise narrowing the gap between the leads by 10 nm at each step. After each step 2 nm of material was deposited and the sample conductivity was measured to check if a connection had been made. Right—resulting sample geometry. Substrate—oxidized silicon; gate—oxidized aluminum.

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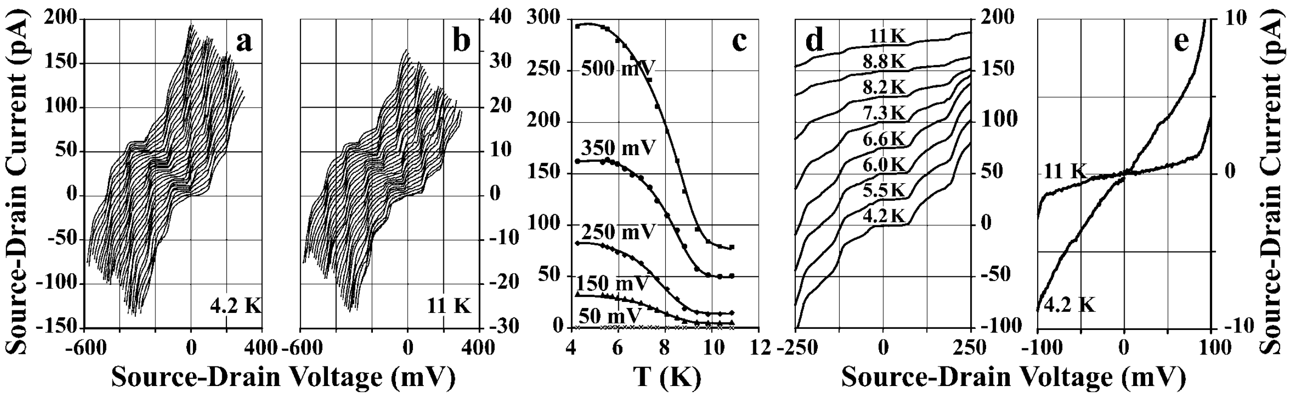

FIG. 2. (a),(b) Two sets of $I(V)$ curves for sample No. 1 taken at different gate voltages, equally spaced in the region from -900 to -280 mV, and at two temperatures, below and above the transition. Three gate periods are shown from 21 measured. Sample at zero gate voltage: (c) temperature dependence of the tunneling current at different biases; (d) $I(V)$ curves taken at different temperatures (shifted for clarity). Note a constant offset charge. (e) The open state of the transistor.

The samples were studied at different temperatures. In sample No. 1 with total charging energy $E_C = e^2/2C_\Sigma = 35$ meV [10], we observed a reversible transition around $T \sim 8$ K, between two states with up to 5 times enhanced conductivity on the low temperature side (Figs. 2a and 2b). Figures 2c–2e show the effect of temperature in more detail. We see that not only the sample conductance in the open state (Fig. 2e) but also the asymptotic behavior at high bias is changed by a factor of 5 (Fig. 2d). Figure 2c shows the current variation at different steps of the Coulomb staircase for gate voltages corresponding to the closed state of the transistor. These data demonstrate that the effect of temperature saturates at 4.2 and 11 K for this sample. Note that Fig. 2d indicates that the temperature variation did not change the charge distribution around the grain. It is clear that the temperature does not activate current in the closed state (as $T \ll E_C$), but causes a pronounced rise in current at the Coulomb steps.

A similar temperature dependence was found for sample No. 2 with a charging energy of 93 meV [11]—see Fig. 3. In Fig. 3b we can also see a fivefold increase of current around $T \sim 7$ K. Structures with more than one grain in the constriction demonstrated qualitatively similar, though less pronounced, temperature dependence.

QC bismuth films are superconducting. The critical temperature depends on the film thickness, but never exceeds 6.1 K [7]. By a two point measurement we have determined the critical temperature of the superconducting transition in the leads of the second sample. The result is presented in Fig. 3d. One can see a relatively sharp transition at 3 K, well beyond the region of interest. The low critical temperature of the leads is not surprising, taking into account the dependence on thickness [12]. A superconducting transition in the grain could affect only the transport by changing the tunneling density of states within a few meV around the Fermi energy and cannot increase current at biases as high as 500 mV. Thus superconductivity is excluded as a possible reason of the observed temperature dependence.

An addition of as little as 1.5 Å of evaporated metal made the transport through the grain insensitive to the gate potential. Apparently, at this moment the resistance of one junction became comparable to the quantum resistance $\hbar/e^2$, and the grain effectively merged with the electrode. The current-voltage characteristic for a single tunneling gap is shown in Fig. 3c [13]. All data for different gate voltages and different temperatures were close to this curve within the experimental accuracy. There was

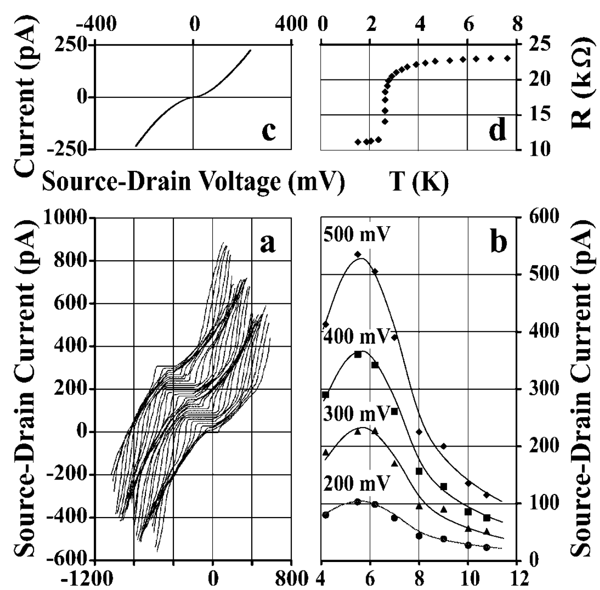

FIG. 3. (a) A set of $I(V)$ curves taken at different gate voltages equally spaced in the region ± 1100 mV at 4.2 K. (b) Temperature dependence of the tunneling current at different biases for the open state of the transistor; (c) an $I(V)$ curve of a single tunneling gap. (d) Superconducting transition in the leads.

no temperature dependence for all thicker samples that followed this one.

From a Coulomb energy of 93 meV we can estimate the cluster radius $R_C \approx 1.5$ nm [14]. This gives about 600 bismuth atoms and 3000 valence electrons in the cluster. We believe that cluster phenomena are important in our samples, being responsible for the observed anomalies.

The observed temperature dependence does not resemble the one that could be expected either from the classical orthodox Coulomb blockade [15] or from the quantum Coulomb blockade [16]. In the classical orthodox theory, the increase of temperature activates tunneling events in the Coulomb blockade region and smears out the Coulomb staircases. In the quantum case, the zero bias conductivity in the open state of the transistor increases as the temperature goes down. Any finite bias destroys resonant transparency. Both the quantum and the classical pictures predict that the asymptotic conductance in the high bias limit is determined by temperature independent tunneling transparencies. In our experiments, the large-scale asymptotic conductance up to bias voltages of (500–750) mV was reversibly affected by temperature in a very moderate window (4–8) K. The temperature dependence disappears when the island merges with one of the two macroscopic leads. This observation confirms that the barrier height and the density of states in the leads do not depend on temperature.

A natural way to explain this effect is a simple variation of the tunneling barrier width with temperature. A mechanical reduction of the tunneling gap by $\sim$1 Å explains the observed increase in the tunneling current even at high voltage [17]. The absence of the effect in the case of a single tunneling barrier rules out a thermal expansion of the leads. We conclude, therefore, that the observable change of the tunneling barrier conductance comes from the distortion of the grain itself. We believe that the reason for such a distortion is a phase transition in the grain, occurring around 8 K [18].

Indeed, a similar phase transition in free alkali clusters was predicted in [19]. A well-established model of free metallic clusters predicts that the ground state of a cluster with unfilled electron shells is not spherical [20]. However, thermal perturbations of the electron density recover the spherical symmetry at finite temperature. There is a phase transition associated with this scenario, where the cluster shape plays the role of the order parameter. For a cluster approaching a closed shell configuration, the transition temperature goes to zero as the ground state of a filled shell cluster is spherical. Despite the relatively high electron energies involved, the critical temperature T_c of the transition is rather low and decreases as the number of valence electrons N in a cluster increases: for a potassium cluster with $N \sim 10$–13 electrons, $T_c \sim 1400$ K, while for $N \sim 65$–85 it is already around 200 K. T_c is proportional to the square of the Wigner-Seitz radius r_S, which is a factor of 2 smaller for amorphous bismuth, as compared to potassium [21], lowering T_c even further. Therefore, we would expect T_c to be about 10 K for bismuth clusters with $N \sim 10^3$ electrons. Unfortunately, the estimate of the electron-phonon interaction, used in the theory, becomes too crude at such low temperatures. In addition, there are indications that the exchange interaction becomes important in small clusters at low temperature [22]. All these circumstances were neglected in the theory. Thus, the theory [19] cannot be applied quantitatively to our results, but it provides a clear picture of the physical situation.

An equilibrium cluster shape results from the competition between the electronic and ionic contributions to the cluster free energy [23]. For small clusters, like those measured in our experiments, the electron contribution to the energy is dominant and the electronic system governs the cluster properties [24]. The fact that the ionic structure of QC bismuth clusters is amorphous and relatively unstable [8] (our samples start to change their conductance *irreversibly* above 16 K) increases the role of the electronic system even further.

Tunneling in a lateral geometry allows the detection of extremely small variations of the cluster size. For a cluster with $N \sim 10^3$ electrons the relative ground state deformation $\delta/R_C \sim 0.1$ [25], which gives an expected shape distortion δ of about 1.5 Å for our cluster, in reasonable agreement with the observation. Since the probability of finding a cluster with a completely filled shell is virtually zero, it is not surprising that the effect is so robust and reproducible.

Generally, the cluster deformation may result in either opening or closing the tunneling gap. This may lead to nonmonotonic curves like in Fig. 3b. However, the sample conductance is always lower at high temperatures [26]. This is reasonable to expect when the cluster is rounded as a result of the phase transition—see Fig. 4. A small variation of the grain shape ($\delta \ll R_C$) does not change the grain capacitance noticeably, while the tunneling current is exponentially affected. The transitions are fairly gradual, taking place over several degrees. This is likely due to a finite system size—one can see that the transition region is wider for the smaller cluster.

Let us discuss the role of the substrate, as the theoretical results were obtained for free clusters in vacuum. The characteristic feature of our experiment is that most of

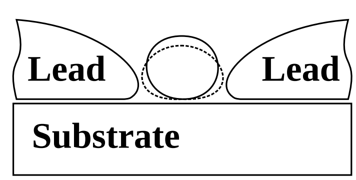

FIG. 4. The cluster tends to restore spherical symmetry at high temperature as a result of a phase transition. This leads to wider tunneling gaps above the transition temperature.

the cluster surface in a QC film remains free. A cluster experiences a relatively weak van-der-Waals interaction with the chemically inert substrate. Therefore, the fact that our cluster is suspended should not appreciably disturb the picture of electron shells and the phase transition scenario described in [19]. Then, the substrate influence on the cluster can be treated as an external field in the theory of phase transitions [27]. The result is that the phase transition survives in a weak external field, though with a lower critical temperature.

To summarize, we used a quench-condensed bismuth film as a source of clusters enabling tunneling through a dominating island in a well-defined single-electron transistor geometry. The cluster surface is essentially free and its shape is not fixed [28]. We observed a *reversible* change in current through the amorphous cluster within a temperature range below the one of *irreversible* crystallization. This may be attributed to a predicted phase transition associated with spontaneous distortion of the cluster shape.

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[11] $C_1 = 2.3 \times 10^{-19}$ F; $C_2 = 4.6 \times 10^{-19}$ F; $C_{\mathrm{Gate}} = 1.7 \times 10^{-19}$ F; $C_\Sigma = 8.6 \times 10^{-19}$ F.

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