

ROOM-TEMPERATURE COULOMB FINGERPRINTS IN THIN FILMS OF Cu+SiO₂ COMPOSITE MATERIAL

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We study the room-temperature electrical properties of thin (≈ 200 nm) SiO₂ films with inclusions of Cu globules with radius ≈ 1 nm and separation ≈ 20 nm. Current-voltage curves taken across the film in different experimental arrangements show "fingerprints" that are fully reproducible within each setup. We observe multiple peaks with a height of ≈ 2 pA against the Ohm's-law background. The typical peak width is consistent with single-electron recharging of Cu globules. We interpret these data as self-selection of energetically favorable quasi-1D chains of globules, along which the current is mainly concentrated.

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Thin films of granulated material have unusual electric properties. The material parameters can be chosen so that the electron transport is dominated by single-electron recharging of granules [1]. For this we should fulfill two main conditions [2]:

1) The typical granular radius r should ensure a single-electron charging energy E_C for a granule which is well above the level of thermal fluctuations. For $r = 1$ nm and a dielectric constant $\epsilon \approx 5$, we can estimate $E_C \approx e^2/2 \cdot 4\pi\epsilon\epsilon_0 r \approx k_B \cdot 2000$ K.

2) The typical intergranular separation ℓ should provide a tunneling resistance R_t between granules such that $R_t \gg R_K/2\pi$, where $R_K \approx 26$ k Ω is the quantum of resistance. To get a rough estimate of the necessary value of ℓ for this composite with contaminated material between granules, we can extrapolate the dependence $R_t(\ell, r)$ for lithographically fabricated aluminum oxide tunnel junctions, starting with the typical value $R_t \approx 100$ k Ω for a tunnel thickness of 2 nm and a tunnel area of $50 \cdot 50$ nm². Further, we expect that the intergranular material is contaminated (mostly by residual copper), which should reduce R_t another order of magnitude relative to the pure case. This leads to the conclusion that to get $R_t \approx 100$ k Ω with $r \approx 1$ nm, we need a value of ℓ in the range 10 nm $\leq \ell \leq$

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30 nm. This corresponds to a volume concentration $\rho_V \simeq (4\pi/3)r^3/(2r + \ell)^3$ of granular material (in relation to all the material of the system) in the range $1.3 \cdot 10^{-4} \leq \rho_V \leq 2.4 \cdot 10^{-3}$.

It has been noted [3] that the electrical parameters of such a material can be statistically reproducible functions of the material parameters and of the macroscopic geometry of the sample. The set of electrical parameters includes the Coulomb blockade thresholds, the threshold for the switching on/off of the quasi-1D current channels, and the typical gate voltages controlling the current through the sample. This electrical reproducibility is possible only if the fabrication technology provides reliable control of the mean radius r and separation ℓ , the spreads in these parameters, and the shape of the granules.

In this letter we report first electrical tests of thin SiO₂ films with inclusions of spherical Cu globules with full technological control of aforementioned parameters [4].

1. Preparation and characterization of the samples. Composite films were fabricated by a co-sputtering technique using two independent magnetron sources. One source had a target of pure (99.999%) Cu under dc bias. The other was loaded with a pure silica target and driven by an rf voltage generator at 12.58 MHz. The sputtering was performed in an atmosphere of Ar at a pressure of 0.3 Pa (the initial vacuum in the chamber was 10⁻⁵ Pa). During deposition the substrate holder was rotated above the magnetrons, and in each turn less than one monolayer of Cu and SiO₂ was deposited. The rates of sputtering of Cu and SiO₂ were chosen so that the volume fraction of Cu in the resulting composite was exactly 0.2. This condition was maintained for deposition on both the highly conducting (doped Si) and the perfectly insulating (quartz) substrates. The thickness of the resulting film was always fixed at 200 nm.

In some cases photolithography was employed to provide Au wiring atop a Cr sublayer for better adhesion.

The composite films thus fabricated were subjected to various diagnostics.

X-ray studies and mass-spectrometry of the film material lead to the conclusion that Cu is present only in a metallic state; no compounds of copper were detected.

Low-angle x-ray studies provide information about the size of the Cu clusters in the film material. We see a sharp and narrow peak interpreted as being due to the presence of Cu globules with radius $r = 1.0 \pm 0.5$ nm. There is another peak which is due to the presence of Cu clusters comprising fewer than 10 atoms. And it seems that Cu clusters of other sizes are absent completely.

By TEM and STM imaging we found the globules to be randomly (but evenly) distributed in the SiO₂ matrix and to be nearly spherical in shape. They are in fact ellipsoids with a long axis 1 to 3 times larger than the short axis and oriented with the long axis pointing towards the center of rotation of the substrate holder. The separation ℓ between globules was estimated from the images as $\ell \simeq 20 \pm 10$ nm.

Thus the volume concentration of metal in globules as a fraction of all the material of the film is as low as $\rho_V(\text{Cu}_{\text{globule}}) = 3.9 \cdot 10^{-4}$. With an overall concentration of metal equal to $\rho_V(\text{Cu}_{\Sigma}) = 0.2$, we see that as little as 0.002 part of the copper went into "large" globules with $r \simeq 1$ nm, while all the rest (0.998 part) of the copper went into "small" clusters of 1 to 10 atoms in size.

Let us stress that films being reported here were not subjected to any annealing procedure after deposition.

The fabrication process may be governed by the phenomenon of phase decomposition of the solid solution [4] of Cu in SiO₂. Being governed by thermodynamics, it guarantees the formation of perfectly spherical globules at a nearly equal separation, which is consistently determined by the initial concentration of Cu and the deposition conditions.

Thus we end up with a 200 nm thick film of Cu+SiO₂ composite on either a conducting (doped Si) or a perfectly isolating (quartz) substrate.

2. Vertical transport across the film. (Fig.1). The STM tip was pressed into the upper part of the film (to serve as a voltage and current probe), while the conducting substrate was grounded (see the inset in Fig. 1).

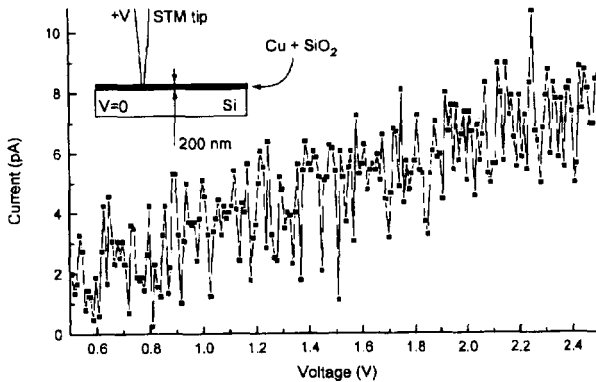


Fig.1. IV curve taken with STM tip pressed into surface across the film. $T = 300$ K. The squares are data points of single scan from left to right. The fine line is a guide for the eye

A current offset of 14.7 pA was subtracted from the data. We attribute this offset to the interface potentials and to the properties of the tip [5].

We were limited to a fixed voltage step of 10 mV. Figure 1 shows a portion of the data taken in a single voltage scan beginning at $V = -2.5$ V and ending at $V = 2.5$ V (scan range $\Delta V = 5$ V). The current-voltage (IV) curve exhibits nonlinear features, which are mainly reproducible for unidirectional scans, provided that the probe is not moved and the temperature is not changed. Similar data (with the STM in a contact mode) was obtained from our samples in another laboratory [6].

Each data point was read out with an averaging time of 30 μ s. When the voltage, temperature, and tip position were fixed, we never noticed any changes in the current during continuous readouts of as long as 1 min.

When we performed multiple successive cyclic voltage scans within the range $\Delta V = 100$ mV (i.e., 10 of our data points), the unidirectional scans produced data which appeared identical within our current resolution of 0.2 pA.

As the scan range ΔV is increased, we gradually lose reproducibility from one unidirectional scan to another. With $\Delta V = 5$ V we still see a definite correlation of the curves from different unidirectional scans.

Changing the direction of the voltage scan caused hysteretic behavior (very similar to that reported in [7] for systems of δ -doped 2DEG), which remains to be studied.

3. Lateral transport along the film. (Fig.2). Here we used a quartz substrate, with Au/Cr probes (100 nm thick) evaporated on top of the film. The lateral width of the probes was 400 μ m, and the gap L between them was 5, 10, 25, or 50 μ m. Such values of the width and gap are too large-scale to resolve

the recharging of separate granules. Here we can only hope to see residual effects and the most basic phenomena, such as the Coulomb blockade offset [8].

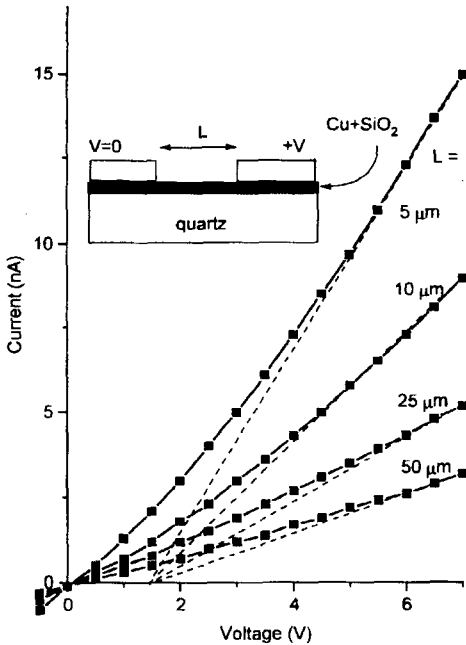


Fig.2. IV curves taken along the film. $T = 300$ K. The probes are $400 \mu\text{m}$ wide and separated by a gap of L (μm). The solid lines are guides for the eye. The dashed lines give the linear asymptotes with the same offset of 1.76 V. At voltages $7 \leq V \leq 20$ V all the curves are straight lines (not shown) coinciding with the indicated asymptotes

All the curves are exactly antisymmetric with respect to the point $V = 0, I = 0$. Note how each curve has a linear asymptote with the same offset of 1.76 V. For each 1D channel we would have an offset proportional to the number of granules involved.

The fact that the value of the offset is the same for each curve probably means that we are very far from a quasi-1D channel picture here, and that the current flow is essentially a three-dimensional net flow.

4. Discussion. Note that the curve in Fig. 1 has no long-range periodicity, and we argue that indeed it should not have. The typical peak width of $dV \simeq 200$ mV corresponds to single-electron recharging of granules with size $r \simeq 1$ nm, according to the rough estimate $dV \simeq e/(4\pi\epsilon\epsilon_0 r)$. Only the largest globules should contribute to this effect, as their single-electron charging energy is the lowest. We can therefore neglect recharging of small clusters of less than 10 atoms. It is energetically favorable not to charge them at all.

Each time the voltage grows towards a certain limit a *different* globule is being recharged, with a different size and at a different position. Thus the multiple peaks map the sequence of granules which are switched to a different steady charge state. It should be stressed that we are talking about the mean, steady charge state of the granules. During current flow their charge state can temporarily (for a very short time) switch to another neighboring (unstable) state [2].

That is why different peaks should *not* correlate with each other in position, height, and width, although they may look quite alike due to similar parameters of different globules. What *does* correlate here is the sequence of recharging events in different unidirectional scans. This means that the IV curve shows "fingerprints"

of the sample, characteristic of a given fixed position of the globules and of the probing tip.

The gradual loss of reproducibility for larger scan ranges ΔV can be understood as follows. Large voltages switch some of the granules (which are far from the current paths) to very long-lived (hours) charge states [9], which affect subsequent scans as a floating gate. In fact this loss of reproducibility for larger ΔV can serve as a basis for possible applications in electronics.

Any changes of tip position, temperature, or scan range ΔV immediately bring us to a different, but still steady, extremely nonlinear picture of the same general scene. In mesoscopic studies this phenomenon would be called mesoscopic fingerprints, which are characteristic of the positions of defects and the shape of the sample. In our case we can call it *Coulomb fingerprints*, which are characteristic of a single-electron recharging sequence involving the different conducting globules comprising our system.

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