Molecular Coulomb islands for single-electron tunneling in SiO 2 /molecular layer/ SiO 2 multilayers on Si(100)

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Molecular Coulomb islands for single-electron tunneling in SiO_2/molecular layer/SiO_2 multilayers on Si(100)

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We demonstrate the Coulomb blockade phenomenon by using organic molecules as Coulomb islands embedded in a metal–oxide–semiconductor structure. Staircases in current–voltage ($I-V$) curves are observed in an SiO_2/fullerene(C_{60})/SiO_2 multilayered structure on Si (100) substrates. The staircases in the $I-V$ curves can be attributed to the Coulomb blockade. The fullerenes serve as Coulomb islands and the SiO_2 layers serve as tunneling barriers. The same multilayered structure that includes a porphyrin derivative also exhibits similar staircases in an $I-V$ curve. These results reveal the potential of molecules to act as Coulomb islands of single-electron tunneling devices. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1605249]

Single-electron transistors (SETs) have undergone intense investigation as they have the potential of becoming one of the most promising components in future electronics devices. A crucial issue in developing SETs is to replicate identical nanostructures for both the Coulomb islands and tunneling barriers. Despite the recent progress in lithography techniques, room still exists for improvement in the nanostructure fabrication process. For example, a SET has been proposed that can be used for a standard current generator. Here, Coulomb islands, exactly the same size, must be fabricated to enable accurate current measurement. The charging energy (e^2/C) should be larger than the thermal energy (kT) during SET operation. To satisfy this requirement, the capacitance of the Coulomb islands should be as small as 10^{-19} F for operation at room temperature. Because of these conditions, nanometer-scale manufacturing techniques for SETs need to be precisely controlled.

Single-electron tunneling has been applied to the development of memory devices. Yano *et al.*[1] utilized Si crystallites as Coulomb islands and demonstrated that they worked as floating gates in a metal–oxide–semiconductor field effect transistor (MOSFET) memory device at room temperature. Yamashita developed a protein–nanoparticle hybrid material and prepared a well-ordered particle array.[2] This array has been proposed for floating gates, particularly to achieve stable operation. The importance of this work is that an organic material was used as a template to arrange the nanoparticle. A bottom-up technique was effectively applied to fabricate the nanostructures, utilizing the self-assembling nature of organic materials.

Organic molecules are key materials for precise nanostructure design, including island size, the interisland distance, and thickness of the tunneling barrier as well. Other advantages of organic molecules for SETs are their uniform structure and small size.[3–5] The main purpose of this study was to use these advantages to create the Coulomb blockade phenomenon. In our experiments, fullerene and porphyrin derivative molecules were sandwiched between two SiO_2 thin layers on a Si(100) substrate, which is comparable to a MOSFET device configuration. In this article, we demonstrate that organic molecules can serve as Coulomb islands and exhibit staircases in a current–voltage ($I-V$) curve.

Highly doped Si (100) wafers (n type, 0.01–0.10 Ω cm) were employed for the substrates. The substrates were cleaned using a typical Radio Corporation of America method. These were then dipped in diluted HF solution for 30 s to prepare the hydrogen-terminated Si surface. After being introduced into an ultrahigh vacuum (UHV) chamber with a background pressure of 1×10^{-8} Pa, they were thermally annealed at 500 °C for 30 min. Reflection high energy electron diffraction observation confirmed a clear (2×1) streak pattern.

The UHV equipment to prepare the multilayers had two chambers: One to heat the samples and deposit the SiO_2 and the other to deposit the organic molecules. A UHV-scanning tunneling microscopy (STM)/atomic force microscopy (AFM) system (Omicron VT deflection AFM/STM) was also connected to the chamber. Morphological characterization was performed with a STM under UHV conditions.

First, a SiO_2 layer was deposited from a quartz ingot with an electron-beam evaporator. The deposition rate was 0.07 nm/s. The SiO_2 layer was formed in an O_2 atmosphere at 1.3×10^{-2} Pa to suppress the oxygen deficiency. Next, C_{60} molecules of submonolayer thickness were deposited using resistive heating on the SiO_2 in a molecular deposition chamber. The molecules were then covered with the second SiO_2 layer deposited under similar conditions as the first. The first SiO_2 layer was 2.0 nm thick and the second was 1.2 nm. Finally, Au thin films were deposited on top of the samples

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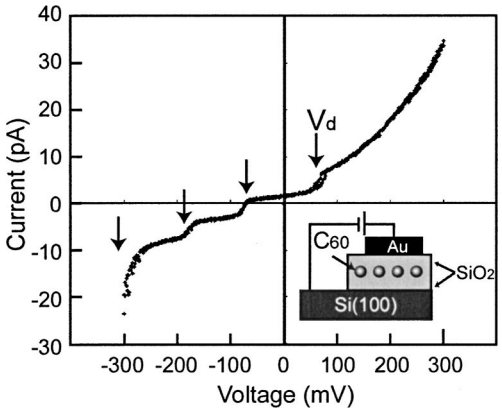

FIG. 1. $I-V$ curve of $SiO_2/C_{60}/SiO_2$ multilayer on Si (100) measured at 5 K. Staircases, due to Coulomb blockade, are clearly visible as indicated by arrows. Threshold voltage (V_d) appeared at 70 mV. Inset shows sample configuration.

through a shadow mask. The Si substrate was used as a lower electrode and the Au film was used as an upper one. The size of the Au electrode, i.e., contact area for measurement, was 1.8 mm^2. The $I-V$ curves were measured by using a two-terminal arrangement at low temperature in a cryostat (Nagase Electronics Cryokelvin CG308SCPR). The sample setup is illustrated in the inset of Fig. 1.

Figure 1 shows the $I-V$ curve of a $SiO_2/C_{60}/SiO_2$ multilayer obtained at 5 K. A periodic staircase in the $I-V$ curve can be clearly observed in Fig. 1 (indicated by the arrows). More than ten specimens were prepared for measurement. About 30% of them showed the staircases. Careful cleaning of the Si substrate seems to be critical for reproducible measurement. On the other hands, such $I-V$ characteristics were not seen in a 3.2 nm thick SiO_2 single layer without C_{60}. Thus, the presence of C_{60} molecules is responsible to the staircase in the $I-V$ curve. We concluded that C_{60} acts as Coulomb islands and the staircases in the $I-V$ curve result from the Coulomb blockade. Although no clear staircases were visible at a positive bias voltage above 100 mV, a differential curve, dI/dV-I (not shown here), indicated slight periodic peaks suggesting the presence of steps even in the range of bias voltage.

One of the advantages of using organic molecules for Coulomb islands is their small capacitance, which is due to their extremely small size. The capacitance C_j of a sphere conductor and a planar electrode can roughly be given by

$$C_j = 4\pi\varepsilon_r\varepsilon_0/\{(1/r)-(1/2d)\},$$

where ε_r is the relative dielectric constant (3.8 for SiO_2), r is the radius of the sphere (0.36 nm for C_{60}), and d is the distance between the planar electrode and sphere conductor. The C_j in our sample was estimated to be 1.7×10^{-19} F. Therefore, we anticipated that the threshold voltage ($V_d = e/2C_j$) would be above 400 mV. Instead, it appeared around 70 mV as indicated by the arrow (V_d) in Fig. 1. Estimated from the experimental value for V_d, r should be around 1.1 nm, which is three times larger than the C_{60} radius.

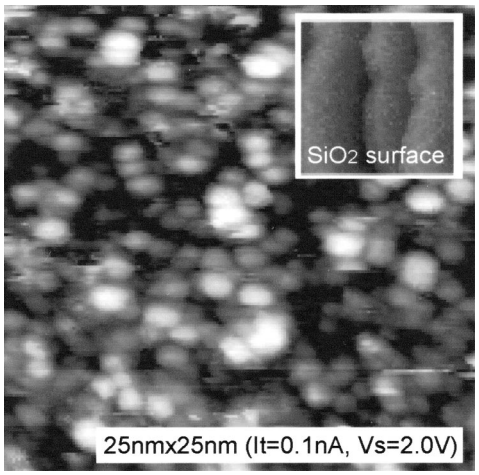

FIG. 2. STM image of C_{60} on SiO_2/Si (100) surface (25×25 nm, $I_t = 100$ pA, and $V_s = 2.0$ V.) Thickness of C_{60} layer is 0.25 monolayers. Molecules are next to each other, indicating that intermolecular coupling should be taken into consideration. Inset shows an STM image of SiO_2 layer before C_{60} deposition. Step edges of Si substrate are clearly observable, indicating that the surface of SiO_2 layer is flat.

Next, we observed C_{60} molecules by STM to monitor their distribution on the $SiO_2/Si(100)$ surface. Because the interaction among the Coulomb islands should be taken into consideration in a discussion on the C_j and V_d values.[6] Here, to enable STM observation, we used a thinner SiO_2 layer (0.4 nm) than that used in the sample shown in Fig. 1. Step edges of the Si substrate were observed when the molecules

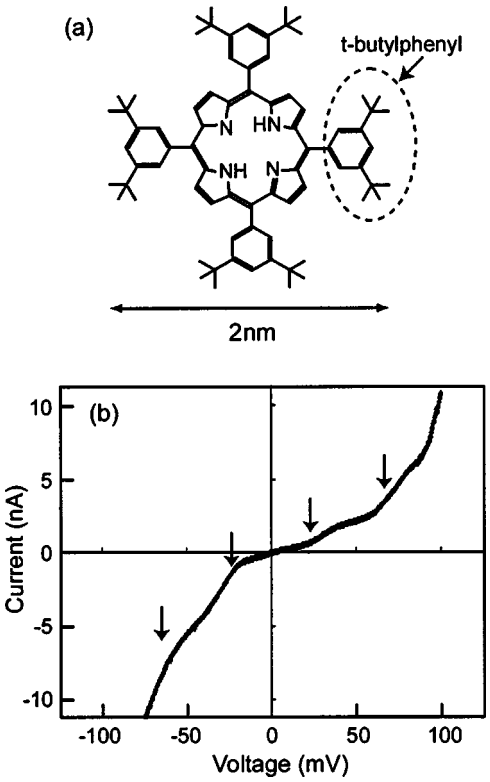

FIG. 3. (a) Molecular structure of H_2-TBPP. Four *t*-butylphenyls surround porphyrin ring. (b) $I-V$ curve of SiO_2/H_2-TBPP/SiO_2 multilayer on Si (100) measured at 5 K. $I-V$ curve with staircases indicates that H_2-TBPP can be used as Coulomb islands.

were not deposited, indicating that the surface of the SiO_2 layer was rather flat (see the inset in Fig. 2). Meanwhile, the deposition conditions for C_{60} remained unchanged. The thickness of the deposited C_{60} was approximately 0.25 of a monolayer. The STM image shown in Fig. 2 reveals that C_{60} molecules were not distributed homogeneously and some of them could not be observed as discrete dots. Consequently, we assumed that several C_{60} molecules aggregated to form clusters and each of these worked as a Coulomb island. We estimated that one cluster consisted of an average of seven to eight molecules from the value of r (=1.1 nm).

As a requirement for the Coulomb islands, organic molecules should have a certain capacitance value to keep tunneling electrons inside. Therefore, π-conjugated or dye molecules[3–5] are considered suitable. We used a porphyrin derivative, tetrakis-3,5 di-*t*-butylphenyl-porphyrin (H_2-TBPP), in a similar multilayered structure. The H_2-TBPP has four *t*-butylphenyls around a porphyrin ring [Fig. 3(a)]. These substituents are expected to isolate a central part of the porphyrin from other molecules to prevent aggregation.

Using the same experimental process as just mentioned, we prepared a SiO_2 /H_2-TBPP/SiO_2 multilayered sample on Si (100). The SiO_2 layers thicknesses were the same as those shown in Fig. 1. Figure 3(b) shows the $I-V$ curve for this sample. Staircases are visible in the $I-V$ curve at 5 K indicating that H_2-TBPP is also useful in forming Coulomb islands. The threshold voltage appeared at 25 mV. This is much smaller than the value expected (300–400 mV) for this molecular size (about 2 nm). H_2-TBPP molecules are considered to cluster similar to C_{60}. Compared with Fig. 1, the staircases in Fig. 3(b) are not as clear. The size of the clusters may be inhomogeneous, leading to threshold voltage distribution. In other words, molecular deposition needs to be optimized. Molecules should be isolated from each other[3,4] to make the most of their advantages; small size and uniform structure. Another advantage of H_2-TBPP is its self-assembling feature,[7] which enables a well-ordered molecular array to be formed with a constant intermolecular distance. We believe, therefore, that the appropriate molecular arrangement will allow further improvements to single-electron tunneling.

To summarize, we utilized C_{60} and H_2-TBPP organic molecules for Coulomb islands in a metal–oxide–semiconductor structure. The Coulomb blockade was witnessed in the SiO_2 /molecules/SiO_2 multilayers on the Si (100) substrates. We intend to optimize sample preparation so that it is accurately reproducible, resulting in an improved Coulomb blockade.

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