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Size-dependent single electron tunneling effect in Au nanoparticles

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Abstract

We investigated single electron tunneling (SET) behavior of dodecanethiol-coated Au nanoparticles of two different sizes (average sizes are 5 nm and 2 nm) using nanogap electrodes, which have a well-defined gap size, at various temperatures. The Coulomb staircases and the Coulomb gap near-zero bias voltage caused by the suppression of the tunneling electrons due to the Coulomb blockade effect were observed in the current–voltage (*I–V*) curves of both sizes of nanoparticles at a low temperature (10 K). At room temperature, the Coulomb gap was observed only in the *I–V* curve of the smaller nanoparticles. This result indicates that the charging energy of the smaller nanoparticles is enough to overcome the thermal energy at room temperature. This suggests that it is possible to operate the SET devices at room temperature using the smaller nanoparticles as a Coulomb island.

Keywords: Single electron tunneling; Coulomb blockade; Electrical transport; Self-assembly; Scanning electron microscopy (SEM); Gold; Nanostructures

1. Introduction

Single electron tunneling (SET) phenomena associated with the electronic transport properties of nanoparticles are of great interest from the view points of both fundamental research [1–5] and device applications [6–10]. In particular, ultra small nanoparticle of less than 2 nm provides physical interest in the coupling of the Coulomb blockade effect and the discrete energy level due to the quantum confinement [11–13]. They also can be used to operate the next generation low-power SET devices at room temperature.

Nanogap electrodes [14–16] are useful for measuring the electrical properties of nanoparticles and fabricating SET devices. However, there have been no reports on SET that uses ultra small metal nanoparticles placed in nanogap electrodes. This is because the experiment requires matching the gap and particle sizes in order to make the double barrier tunneling junction, which has not been achieved because of the difficulty in controlling the size of the nanogap to a range of sub-2 nm. Recently, we developed a new method of fabricating nanogap using a combination of electron beam lithographic (EBL) and self-assembled molecular (SAM) lithographic techniques [17], which enables us to control the gap size with an accuracy of approximately 2 nm. The gap size is well-defined by SAM films composed of multiple organic molecule and metal ion layers (thickness of the multilayer films is sub-2 nm per layer) as a size-controlled resist [18–21]. Moreover, we can control the position and the width of the gap electrodes in high-resolution patterning by using EBL.

We investigated the SET behavior of dodecanethiol-coated Au nanoparticles of two different sizes (average sizes are 5 nm and 2 nm) using the nanogap electrodes fabricated using the method we developed.

2. Experimental

The nanogap electrodes were made using the new method [17]. Fig. 1a–c are the scanning electron microscope

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(SEM) images showing the nanogaps formed using (a) three, (b) four, and (c) seven layers of the SAM films as a size-controlled resist. The gap sizes estimated from the SEM images are approximately (a) 6 nm, (b) 8 nm, and (c) 14 nm, and these values correspond well to the thickness of the SAM films.

We used Au nanoparticles with two different sizes (average diameter of the particles: 5 nm and 2 nm) for measuring the SET using the nanogap electrodes. The Au nanoparticles were covered with a monolayer of organic ligands (dodecanethiol:$CH_3(CH_2)_{11}SH$) as an insulator layer. The details of the preparation of the dodecanethiol-coated Au nanoparticles can be found in Refs. [22,23]. Since the average particle sizes including dodecanethiol are estimated to be approximately 8 nm and 5 nm, respectively, we prepared two different-size gaps of 10 nm and 6 nm using five and three layers, respectively, of SAM films. The nanoparticles were dispersed on the nanogap electrodes by spin casting at 1000 rpm for 60 s. By using the spinner, isolated single nanoparticles could be placed in the nanogaps. Fig. 1d shows such a typical nanogap electrode after the dispersion of 5 nm Au nanoparticles.

The measurements of the current–voltage (I–V) curves were performed in a multi-probe system (NAGASE & Co., Ltd.) in the sample temperature range of 10–300 K. Before the dispersion of the dodecanethiol-coated Au nanoparticles on the nanogap electrodes, we observed no tunneling current at the bias voltage $V = \pm 0.5$ V, meaning there was sufficient separation between the two metal electrodes.

3. Results and discussion

The I–V curves (open circles) and the differential conductance spectra (dI/dV: solid lines) at 10 K taken from the Au nanoparticles of the average size of 5 nm and 2 nm are shown in Fig. 2a and b. Each I–V curve exhibits strong suppression of the tunneling electron around zero bias voltage. This strong suppression means that the electron tunneling is suppressed because the energy spacing of the current steps (as denoted by ΔE in Fig. 2) is higher than the thermal fluctuation ($\sim$0.86 meV) at 10 K. Moreover, it is obvious that the spacing increases with a decrease in the particle size.

We also show the enlarged I–V curves around zero bias voltage measured at 10 K (open circles) and room temperature (solid lines) in the inset of Fig. 2a and b. The energy spacing in the I–V curve for the larger particle measured at room temperature completely disappeared and a linear increase of the current with respect to bias voltage was observed. On the other hand, the energy spacing for the smaller particle measured at room temperature was still ob-

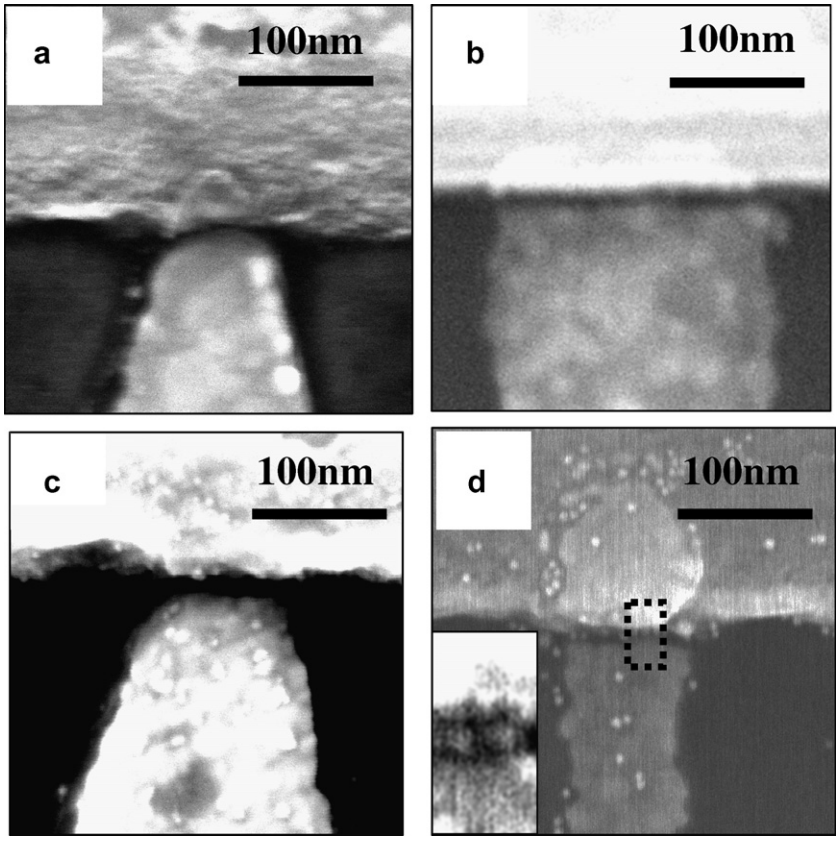

Fig. 1. SEM images of the nanogap electrodes fabricated using a combination of EBL and SAM lithographic techniques. Nanogaps were formed using (a) three, (b) four, and (c) seven layers of SAM films. (d) After the dispersion of Au nanoparticles (average size is 5 nm).