Chemisorbed Gold Nanoparticles by Dithiol Molecules Inserted in Alkanethiolated Monolayer Characterized by Scanning Tunneling Microscopy (STM) and Spectroscopy (STS)

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1. Introduction

devices in nanometer scale with high Electronic performances and low consumption energy are highly desired, which have attracted scientists to explore and develop the devices scaled down to molecular regimes. Mechanical single electron devices will be one of promising solutions. Recently, we have reported our experimental results for potential applications in Coulomb blockade electron shuttle devices [1]. In the above case, single electron is transferred one by one in accordance with the nanomechanical vibration of a nanoparticle, and the nanoparticles were physically-adsorbed in a double barrier tunneling structure. We have also established a fabrication process for nanogap gold electrodes by electroless gold plating. By using the nanogap electrodes, we have demonstrated Coulomb staircases on Au nanoparticles [2]. However, in order to realize such Coulomb blockade electron shuttle devices, it is important to stabilize the nanoparticles and to control their density. Here, we report an approach of inserting dithiol molecules in an alkanethiolated monolayer as a linker for chemically anchoring the nanoparticles on the substrate and thus controlling the particles density by modulating the density of dithiol molecules. By using scanning tunneling microscopy (STM) and spectroscopy (STS), factors influencing the density of dithiols and subsequent Au nanoparticles, i.e., chain-length dependence and dithiols solution concentration dependence, are studied. The resistances between the gold core and the metallic substrate for both of chemisorbed and physisorbed particles are estimated.

2. Experimental section

A typical fabrication procedure is shown in the following. The Au(111)/mica substrates were immersed in a 1.0 mM octanethiol ethanol solution for 12 hours for forming a closely-packed self-assembled monolayer (SAM). And then these SAM-covered substrates were immersed respectively in 5 mM octanedithiol or decanedithiol ethanol solutions for 7 hours, during which the monothiol molecules were partially displaced by dithiol molecules. The above substrates were then put into a 0.5 mM octanethiol-protected Au nanoparticles chloroform solution for 7 hours. Those samples were characterized in an ultra high vacuum chamber by STM at 65 K. The height dependence of I-V characteristics of the nanoparticles was evaluated by STS and the resistances between the gold core and the metallic substrate were then estimated for both of chemisorbed and physisorbed particles accordingly.

3. Results and discussion

The STM images of Figs. 1 show on the octanethiol monolayer with a ($\sqrt{3} \times \sqrt{3}$) R30° structure as shown in Fig. 1a, both the octanedithiol (Fig. 1b) and decanedithiol (Fig. 1c) molecules are well dispersed as protrusions. Octanedithiol's density is 18 (±10%) and decanedithiol one is 35 (±10%) per 100×100 nm², revealing a chain-length dependence of the

dithiol density. The chain-length dependence is attributed to the reactivity difference and different steric hindrance. Figs. 2 are STM images of the octanedithiol molecules made at different solution concentrations. The densities of octanedithiol molecules are 1, 18 and 39 at 0.5, 5, and 50 mM per 100×100 nm². This implicitly indicates a solution concentration dependence of the dithiol density, further confirmed by decanedithiol molecules (not shown). As a result, the density of the surface functional moiety can be controlled by simply tuning their solution concentration. In the following, Figs. 3 give a distinct difference of the density of the subsequent adsorbed Au nanoparticles on the surfaces with different dithiol molecules also on the surfaces made at different solution concentration. By comparing Fig. 3a of C8S2 with Fig. 3b of C10S2, the density of Au particles in 3b is two times more than that in 3a. They were carried out under the same conditions but different dithiol molecules. And hence, this is in good accordance with the chain-length dependence. By comparing Figs. 3b and 3c, at different solution concentration of the same dithiol molecules, the density of the Au particles increases as with the increase of the dithiol solution concentration. The height-dependence of I-V characteristics of the Au particles was conducted and the coulomb staircases are fitted by using orthodox theory [3], the resistance (R₂) between the Au core and Au substrate was then estimated for both chemisorbed and physisorbed Au particles, as shown in table 1. The R_2 of the physisorbed particles is ca. 6 G Ω , one order larger than that (ca. 300 M Ω) of the chemisorbed particles. By comparing with the R₂ value of the physisorbed particles directly docked on the Au substrate, we found that the protecting molecules of the Au particles are interdigited with the octanethiolate molecules. Moreover, the obtained resistances (R_2) are the same as those between the core of the particles and nanogap electrodes in single electron transistors.

4. Conclusion

Factors influencing dithiol density, i.e. chain-length dependence and dithiol solution concentration, have been characterized. The subsequent Au nanoparticles density shows a dependence on the density of the dithiol molecules. So we have succeeded in controlling density of chemisorbed Au nanoparticles. We also found that the resistance of the chemisorbed nanoparticles between the Au core and the Au film is one order smaller than that of physisorbed particles. These values are found to be the same as those obtained in single electron transistors consisting of chemisorbed Au nanoparticles in nanogap electrodes.

References: [1] Y. Azuma, T. Hatanaka, M. Kanehara, T. Teranishi, S. Chorley, J. Prance, C. G. Smith, and Y. Majima, *Appl. Phys. Lett.* 91 (2007) 053120.

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Fig. 1 (a) STM image of the C8S SAM ($20 \times 20 \text{ nm}^2$), (b) STM image of the C8S SAM inserted by octanedithiol molecules ($100 \times 100 \text{ nm}^2$) and (c) STM image of the C8S SAM inserted by decanedithiol molecules ($100 \times 100 \text{ nm}^2$). The averaged densities for octanedithiol molecules and decanedithiol molecules are 18 ± 2 and 35 ± 4 per $100 \times 100 \text{ nm}^2$, respectively.



Fig. 2 STM images $(100 \times 100 \text{ nm}^2)$ of the C8S SAM inserted by octanedithiol molecules at different dithiol solution concentration. (a) 0.5 mM; (b) 50 mM. The averaged densities for octanedithiol molecules are 1 (left), 18±2 (Fig. 1b) and 39±4 (right) per 100×100 nm².



Fig. 3 STM images $(100 \times 100 \text{ nm}^2)$ of the adsorbed gold nanoparticles on different surfaces. (a) on C8S2 made at 5 mM; (b) on C10S2 made at 5 mM; (c) on C10S2 made at 50 mM.

Adsorption Type	Chemisorbed Au nanoparticles	Physisorbed Au nanoparticles
Resistance between the Au core and the Au substrate	323±43 MΩ	6.4±1.1GΩ

Table 1 Estimated resistances between the Au core and the Au substrate for chemisorbed and physisorbed Au nanoparticles