Charging Effects in Gold Nanoclusters Grown on Octanedithiol Self-assembled Monolayers Observed by Scanning Tunneling Microscopy and X-ray Photoelectron Spectroscopy

D. Fujita, K. Ishige, and T. Ohgi

Nanomaterials Laboratory, National Institute for Materials Science
1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, JAPAN

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Single electron charging effects were observed for gold nanoclusters grown on octanedithiol self-assembled monolayers by scanning tunneling microscopy and X-ray photoelectron spectroscopy. Strong interaction of gold with the terminal sulfur atoms of dithiol molecules on Au(111) suppresses effectively the penetration of deposited Au atoms through the dithiol layer and results in the formation of homogeneous Au nanoclusters. Decoupling of the clusters from Au(111) by the octanedithiol layer and the small self-capacitance of the nanoparticles realize the observation the Coulomb blockade in scanning tunneling spectroscopy and the Au 4f core level shifts in X-ray photoelectron spectroscopy at room temperature. Both phenomena origin from a common physics, the Coulomb energy of charged particles.

1. Introduction

In this age of rapid miniaturization of science and technology, there is an increasing need among researchers to fabricate nanometer-sized structures and understand the new physical properties. One of the most fundamental nanostructures is a nanometer-scale particle, so called *nanoparticle*, *nanodot* or *nanocluster*. Nanoparticles have various potential applications as basic components for new catalysis, electron confinement devices, and single electron uses. Especially metallic nanoparticles have attracted much attention. We have developed several new techniques to fabricate metallic nanoparticles on atomically clean surfaces using STM nanotechnology [1,2]. Recently we have also succeeded in fabricating homogeneous metal nanoclusters on thin insulating layers composed of self-assembled molecules [3]. When a few Angstroms of gold are deposited on a self-assembled monolayer (SAM) of dithiol molecules ($SH(CH_2)_nSH$) on an Au(111) substrate, we have found that the gold nanoclusters are formed homogeneously on the top surface by scanning tunneling microscopy (STM).

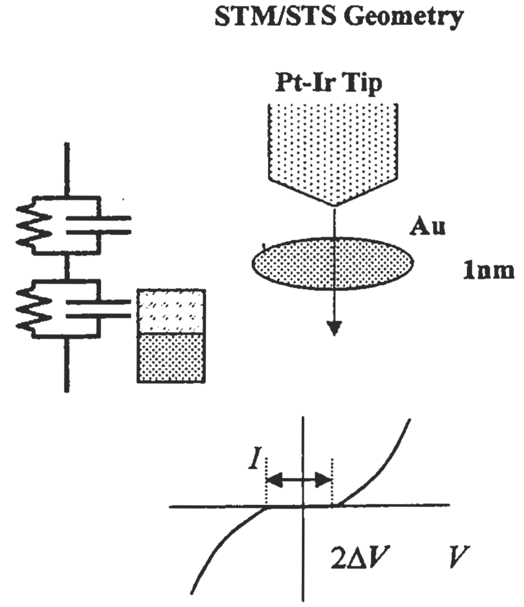

Fig.1 STM/STS geometry for a gold nanocluster on the dithiol SAM/Au(111), its equivalent circuit and possible single electron tunneling effect observable on STS.

As shown in Fig.1, the geometry of a gold nanocluster on the SAM is a metallic nano-island sandwiched by two electrodes through tunneling barriers (vacuum gap and the SAM), typical single-electron geometry. Since the nanometer-size of the center island implies the very small self-capacitance (~10^{-19}F), the electrostatic charging energy for a single electron becomes large enough (~10^{-1}eV) to be observable even at room temperature.

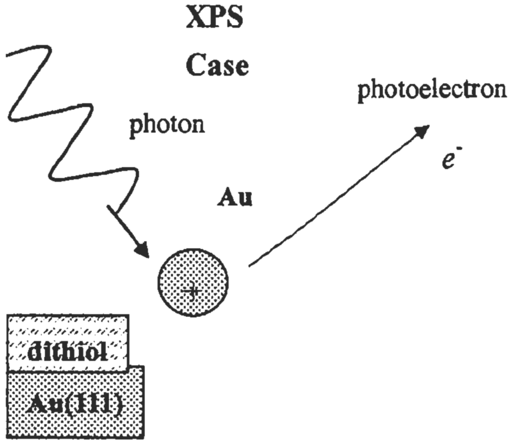

Fig.2 XPS geometry for Au nanoclusters on the dithiol SAM/Au(111). Incidence photons may make the nanocluster be positively charged by photoelectron emission.

On the other hand, when the gold nanoclusters are irradiated by X-ray photons, it may be possible for the metal clusters to be positively charged by photoelectron emission as shown in Fig.2. If the lifetime of the positive charge on the cluster is long enough, then the electrostatic energy of the small charged system in the ionized state will contribute the core-level binding energy [4]. Up to now many efforts have been devoted to clarify the mechanism of core-level shifts for molecules, clusters, and atoms at surfaces [5,6]. In this article, we will report on our new findings related to the charging effects manifested on the metal nanoclusters on the SAM using scanning tunneling spectroscopy (STS) and X-ray photoelectron spectroscopy (XPS).

2. Experiment

The Au(111) substrates were prepared by gold evaporation on a cleaved mica and the detail was reported elsewhere [7]. Then Au(111) substrates were subsequently dipped into 1mM octanedithiol ($SH(CH_2)_8SH$) solution of ethanol, incubated at 55°C for ~1day and then rinsed by ethanol. By this method the SAM of octanedithiol on Au(111) was routinely fabricated. Finally, gold was deposited onto the SAM substrate at room temperature at a deposition rate of 0.01 monolayers/s. The surfaces were observed by air-STM (JEOL, JSTM-4200S) using a mechanically cut PrIr (10%Ir) tip. The surfaces before and after gold deposition were analyzed by an UHV-XPS system (PHI 5400) using a Mg Kα X-ray source (1253.6eV, 200W). The spectra were acquired with pass energy of 35.75 eV corresponding to the energy resolution of 0.85eV.

3. Results and Discussion

An STM image of gold nanoclusters deposited on the top of octanedithiol-SAM on Au(111) is shown in Fig.3. The gold clusters were removed from the central square area by careful manipulation of an STM tip at appropriate conditions. Inside the square area, smooth Au(111) terraces with small gold islands of monatomic height are visible. The amount of penetrated gold atoms is estimated to be less than 10% of the total amount. In contrast, in the case of monothiol SAMs, most of the gold atoms penetrate through the layer.

Strong interaction of gold atoms with the terminal sulfur atoms of the dithiol molecules on the Au(111) substrate suppresses the penetration of the deposited gold atoms thorough the dithiol layers effectively. The size of the gold nanoclusters are 1~1.5 nm in diameter dependent on the deposition amounts. The standard deviation of the size distribution is less than 0.2nm. These gold nanoclusters were dispersed over the surface with a density of ~1.2×10^{13} cm^{-2} for the coverage from 0.25 to 2.6 ML.

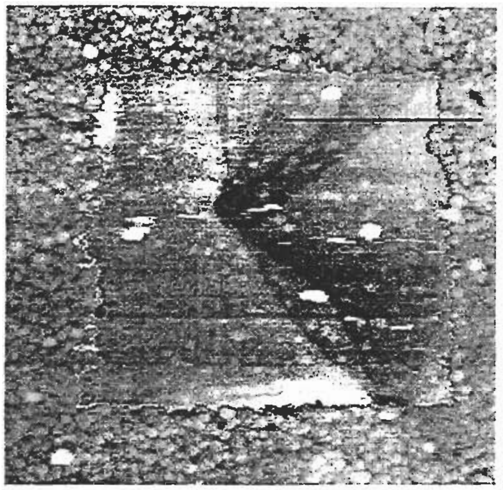

Fig. 3 An STM image (220nm×220nm, V=1.0eV, I=40pA) of gold clusters on the octanedithiol SAMs / Au(111) after 0.65 monolayer (ML) gold deposition.

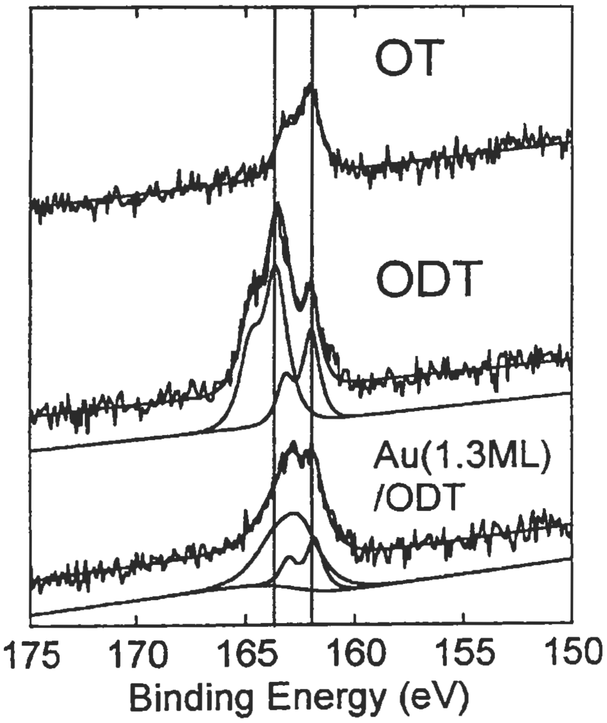

Fig. 4 XPS spectra of S 2p doublet ($2p_{1/2}$, $2p_{3/2}$) for various SAMs on Au(111); octanethiol (OT), octanedithiol (ODT) and 1.3ML-gold-deposited octanedithiol SAMs.

XPS analysis can offer the important information on gold nanocluster formation on the octanedithiol SAMs. Figure 4 shows S 2p spectra for octanethiol, octanedithiol and gold-deposited octanedithiol SAMs. Two chemical states of sulfur were found for octandithiol SAM on Au(111). One is the sulfur bonded to the Au(111) substrate (S $2p_{3/2}$=161.9eV), which is the same binding energy as the octanethiol case. The other is the terminated S atom protruding to the vacuum side (S $2p_{3/2}$= 163.7eV). With deposition of gold on the dithiol SAM, the S 2p peak corresponding to the surface protruding sulfur decreased rapidly on the increase of gold coverage, which suggests a high sticking probability of gold at the sulfur sites. The homogeneous growth and the high cluster density can be attributed to the high sticking probability and successive coalescence of gold atoms.

Decoupling of the gold nanoclusters from the substrate by the octanedithiol layer (~1.2nm in thickness) and the small self-capacitance of the nanoclusters (~10^{-19} F) enable us to observe the current suppression around zero bias (Coulomb Blockade) in tunneling spectroscopy (Fig.5).

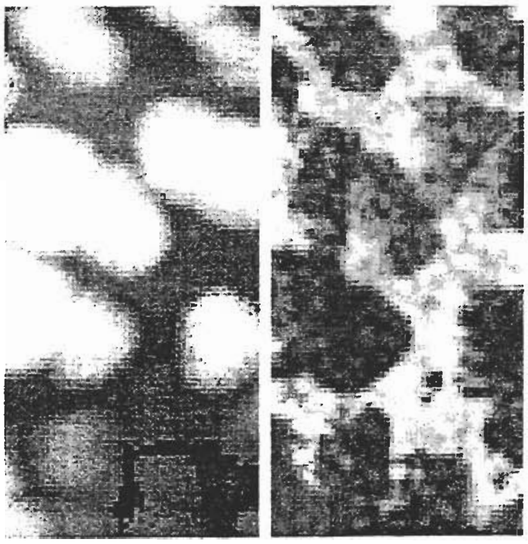

Fig.5 Left; STM topographic image (28nm×12nm) of gold nanoclusters on octanedithiol-SAM/Au(111). Right; the *dI/dV* image taken at around the zero bias voltage, showing the current suppression (Coulomb Blockade) appeared only on the gold nanoclusters.

When the tip is located above an area where gold clusters are absent, *I-V* curves show almost linear characteristics. In contrast, above a gold cluster, the current is strongly suppressed around the origin, as shown in Fig. 5. The gap size, ΔV, is closely related to the self-capacitance C of cluster or the radius of cluster ($\Delta V = e/C$, *where* $C = 4\pi\varepsilon R$). As the coverage increases, the average radius of gold cluster becomes larger, and the gap ΔV becomes smaller. Due to the nanometer scale cluster size and the resultant small capacitance, large ΔV in the range of 200-400 mV enables the observation of the Coulomb Blockade at room temperature.

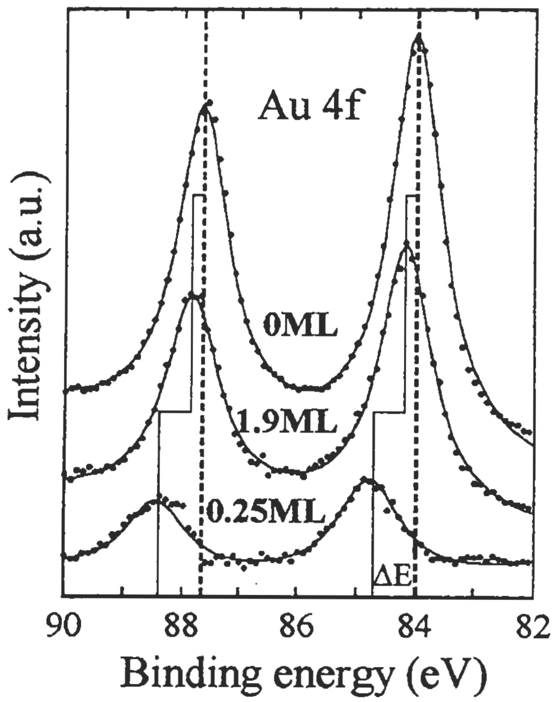

Fig.6 Core-level shifts of Au 4f doublet ($4f_{5/2}$, $4f_{7/2}$) with various Au deposition amounts on dithiol SAMs/Au(111).

Figure 6 shows the first direct evidence of the quantum size effect on the apparent binding energy of the Au 4f core-levels of the clusters. The Au $4f_{7/2}$ and $4f_{5/2}$ peak positions shift higher binding energies with respect to the original bulk positions (84.0 eV, 87.7 eV). The binding energy shift ΔE is more significant for the less deposition amount case, which means that the smaller the cluster, larger the shift. For a classical conducting nanometer-scale sphere, there are two contribution to the energy needed to remove an electron; one is the binding energy (BE), and the other is the electrostatic static energy for a small charged system, $e^2/2C$. Therefore, the kinetic energy $KE_{cluster}$ for the nanocluster is expressed as below if the core-level binding energy for the cluster is the same as bulk one.

$$KE_{cluster} = KE_{bulk} - e^2/2C \qquad (1)$$

Using this equation, the apparent core-level binding energy for the clusters ($BE_{cluster}$) can be expressed as below.

$$BE_{cluster} = BE_{bulk} + e^2/2C \qquad (2)$$

This equation clearly shows that the apparent core-level binding energy for nanometer-scale clusters shift higher energy by the charging energy ($e^2/2C$). Both the XPS and STS measurements, almost similar values for the self-capacitance of the nanoclusters were obtained.

4. Conclusion

Using STS and XPS, we have succeeded in the consistent observation of single electron charging effects for nanometer-scale gold clusters on octanedithiol self-assembled monolayers. Owing to the strong chemical interaction between gold of the cluster and sulfur of the octanedithiol molecules, penetration of the deposited gold atoms through the SAM was suppressed effectively. Electrical decoupling of the conductive clusters from the metal substrate Au(111) by the octandithiol SAM and the small self-capacitance of the nanoclusters realize the observation the Coulomb blockade in STS and the Au 4f core level shifts in XPS at room temperature. Both phenomena stem from the same origin, the electrostatic energy of small charged system.

5. References

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