Discrete charging effects in gold nanoclusters grown on self-assembled monolayers

D. Fujita*, K. Ohnishi, T. Ohgi

Nanomaterials Laboratory, National Research Institute for Materials Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

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Abstract

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

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1. Introduction

During this decade, there has been significant enthusiasm among researchers to fabricate nanometer-sized structures and understand the new physical properties hidden there. One of the most fundamental nanostructures for miniaturized devices is a nanometer-scale particle, so called nanocluster. Especially, metallic nanoclusters have various potential applications as basic components for new catalysis, electron confinement devices, and single electron devices. We have developed several new techniques to fabricate metallic nanoclusters on atomically clean surfaces using scanning tunneling microscopy (STM) nanotechnology [1,2]. Recently we have also succeeded in fabricating uniformly sized and dispersed metal nanoclusters on thin insulating layers composed of self-assembled molecules [3]. When a few sub-nanometers of gold are deposited on a self-assembled monolayer (SAM) of dithiol molecules (SH(CH2)nSH) on an Au(111) substrate, we have found that the gold nanoclusters are formed uniformly on the top surface by STM observation. The schematic arrangement of the supported metal nanocluster system is shown in Fig. 1(a).

When the STM tip is positioned above a single gold nanocluster as shown in Fig. 1(b), the geometry of the tip/nanocluster/SAM/Au(111) is a metallic nanoisland sandwiched by two electrodes through tunneling barriers (the vacuum gap and the SAM). In this case, typical single-electron geometry is realized. Since the nanometer-scale smallness of the center island implies the very small self-capacitance (∼10⁻¹⁹ F), the electrostatic charging energy for a single electron injected in the center island becomes large enough (∼10⁻¹ eV) to be observable as Coulomb blockade in tunneling spectroscopy even at room temperature [4].

On the other hand, when the gold nanoclusters are irradiated by X-ray photons, it may be possible for the nanoclusters to be positively charged by photoelectron emission as shown in Fig. 1(c). If the lifetime of the single positive charge on the nanocluster is long enough, then the electrostatic energy of the small charged system in the ionized state will affect both the work function and the kinetic energy of the emitted photo-electrons [5,6]. Up to now, many efforts have been devoted to clarify the mechanism of core-level shifts for metal clusters supported on the substrates [7–9]. However, the clear explanation of the mechanism has not been offered because of the lack of information on size uniformity. In this article, we will report on our new findings related to the discrete charging effects manifested on the uniform 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 at 600 K at a deposition rate of 0.1 nm/s in high vacuum [10]. Then Au(111) substrates were subsequently dipped into 1 mM octanedithiol (SH(CH₂)₈SH) solution of ethanol, incubated at 55 °C for 1 day 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 in high vacuum at room temperature at a deposition rate of 0.01 monolayers (ML)/s. The surfaces were observed by an air-STM (JEOL, JSTM-4200S) using a mechanically cut PrIr (10%Ir) tip at room temperature and an UHV–STM (Omicron, VT-STM) using a gold-coated tungsten tip at low temperatures. The surfaces before and after gold deposition were analyzed by a UHV–XPS system (PHI 5400) using a Mg Kα X-ray source (1253.6 eV, 200 W). The spectra were acquired with a pass energy of 35.75 eV corresponding to the energy resolution of 0.85 eV.

3. Results and discussion

A typical STM image of gold nanoclusters deposited on the top of octandithiol-SAM on Au(111) is shown in Fig. 2(a). In this case, the total deposited amount of gold was 0.6 ML. The surface was found to be covered with gold nanoclusters of similar sizes. As shown in Fig. 2(b), these gold clusters were able to be removed from the central square area by scanning with less tip-sample distance than that of normal imaging. The appropriate condition of the cluster-manipulation was found to set the tunnel resistance ($R = V_b/I_t$) close to the resistance between the cluster and the substrate, where $V_b$ and $I_t$ are the applied bias and the tunnel current, respectively. Clear threshold resistance ($R_{th}$) was observed depending on the deposition amounts. Typically $R_{th}$ was 4 GΩ at 0.65 ML and 140 MΩ at 1.25 ML. Generally speaking, when the tunneling resistance $R$ is 10% larger than the threshold $R_{th}$, no cluster was removed, whereas scanning at the threshold $R_{th}$ made the most of the clusters removed from the scanned area. After the cluster removal, the gold clusters at the boundary were found to exist as stable as the others, which means that only gold nanoclusters were removed by this method. Inside the square area where the gold nanoclusters were removed by the tip, smooth Au(111) terraces with small gold islands were observed. The height profile (Fig. 2(c)) along the line indicated in Fig. 2(b) indicates that all of these small gold islands were of monatomic height. These gold monatomic islands were formed by the penetration of deposited gold atoms thorough the dithiol SAM. The amount of penetrated gold atoms was estimated to be less than 10% of the total amount. In contrast, in the case of monothiol SAMs, it was found that most of the gold atoms penetrated through the monothiol SAM. 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 0.2 nm. These gold nanoclusters were dispersed over the surface with a density of $\sim 1.2 \times 10^{13}$ cm$^{-2}$ for the coverage from 0.25 to 2.6 ML.

XPS analysis can offer the important information on gold nanocluster formation on the octanedithiol SAMs. Fig. 3 shows S 2p spectra for octanethiol, octanedithiol and gold-deposited octanedithiol SAMs. Two chemical states of sulfur were found for octanedithiol SAM on Au(111). One is the sulfur bonded to the Au(111) substrate (S 2p₃/₂ = 161.9 eV), which is the same binding energy as the octanethiol case. The other is the terminated S atom protruding to the vacuum side (S 2p₃/₂ = 163.7 eV). With deposition of gold on the dithiol SAM, the S 2p peak corresponding to the
Decoupling of the gold nanoclusters from the substrate 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.

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. 4. The gap size, \( \Delta V \), is closely related to the self-capacitance \( C \) of cluster or the radius of cluster \( (\Delta V = e/C, \text{ where } C = 4\pi\varepsilon_0 R) \). As the coverage increases, the average radius of gold cluster becomes larger, and the gap \( \Delta V \) becomes smaller. Due to the nanometer scale cluster size and the resultant small capacitance, large \( \Delta V \) in the range of 200–400 mV enables the observation of the Coulomb Blockade at room temperature.

Low temperature can enhance the fine structures of single electron tunneling characteristics observed by STS. Fig. 5 shows the \( I-V \) curve observed on gold nanoclusters grown on octanedithiol SAM by UHV scanning tunneling microscope at 30 K. Instead of Coulomb blockade observed at RT, Coulomb staircase has appeared. By comparing with the theoretical simulation, we can obtain the detail parameters for the nanometer-scale charged system.

Fig. 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, 87.7 eV). The binding energy shift \( \Delta E \) 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 $KE_{\text{cluster}}$ for the nanocluster is expressed as below if the core-level binding energy for the cluster is the same as bulk one.

$$KE_{\text{cluster}} = KE_{\text{bulk}} - \frac{e^2}{2C}$$

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

$$BE_{\text{cluster}} = BE_{\text{bulk}} + \frac{e^2}{2C}$$

This equation clearly shows that the apparent core-level binding energy for nanometer-scale clusters shift higher energy by the charging energy ($e^2/2C$). From the Au 4f core-level shift with XPS and the low-temperature STS measurements, almost similar values for the self-capacitance of the nanoclusters were obtained as shown in Fig. 7. The estimated values of the self-capacitance were ranging from $1.2 \times 10^{-19}$ to $8.5 \times 10^{-19}$ F, which correspond to the charging energies $e^2/2C$ ranging from 0.09 to 0.67 eV. Because these values are much larger than the thermal energy $k_B T$ at RT (0.026 eV), the single electron charging effects can be observed even at RT.

Fig. 4. Top: STM topographic image ($28 \times 12$ nm$^2$) of gold nanoclusters on octanedi-thiol-SAM/Au(111). Bottom: the $dI/dV$ image taken at around the zero bias, showing Coulomb Blockade appeared only on the gold nanoclusters at room temperature.

Fig. 5. $I$–$V$ curve obtained for a gold nanocluster on octanedi-thiol SAMs/Au(111) at 30 K. The gold apparent coverage is 3 ML. Theoretical curve fitting is shown by a solid line. The number of electrons ($N_e$) in the cluster at a specific bias is also shown.

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

Fig. 7. Core-level shifts of Au 4f doublet ($4f_{5/2}, 4f_{7/2}$) with various gold deposition amounts on the dithiol SAMs observed by XPS.
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 SAMs. 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 octanedithiol 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.

Acknowledgments

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Fig. 7. The values of the self-capacitance estimated from the Au 4f core-level shift using XPS and tunneling spectroscopy (TS) curve fitting using low temperature (LT) STS measurements.