Octanedithiol layer as tunneling barrier

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Abstract

Au deposited octanedithiol/Au(111) samples provide homogeneous Au nanoclusters, well defined tunneling barriers and atomically flat substrate, which enables us to observe single electron tunneling effects and the kinetic energy shifts of the photoelectrons on the same sample in tunneling spectroscopy and photoelectron spectroscopy, respectively. Through the manipulation technique and the observation of Coulomb staircase by tunneling microscopy and spectroscopy, it is shown that this system provides the uniform resistance ($\sim$ 140 MΩ) between clusters and Au(111) surface.

Key words: single electron charging effect; photoelectron spectroscopy; tunneling spectroscopy; nano-cluster

Gold deposition on Au(111) substrate covered with octanedithiol ($HS(CH_2)_8SH$, ODT) layer provides uniformly-sized gold nanoclusters, the size of which can be precisely controlled by the amount of the deposition [1]. These nanoclusters are separated from Au(111) surface by the homogeneous ODT layer with a thickness of $\sim$ 10 Å. This system, Au nanoclusters/ODT/Au(111), is suitable for the study of the single electron charging effects of nanoclusters supported on the substrate because the structure is well-defined in atomic scale and moreover, the photoelectron spectroscopy and tunneling spectroscopy can be performed on the same sample. Although ionization potential of the supported metal clusters has been extensively studied by photoelectron spectroscopy [2,3], it has not been clear how these clusters are coupled with metal substrate geometrically and electrically and also, how this coupling affects the photoionization of the clusters. By using above system we succeeded in observing the consistent size dependency of the charging effects of the supported clusters by both tunneling and photoelectron spectroscopy [1,4].

In this paper, we discuss the coupling amplitude of this system, especially the resistance between nanoclusters and Au(111) surface. Through the manipulation technique and the single electron tunneling phenomena by tunneling microscopy and spectroscopy, it is shown that the resistance between clusters and Au(111) surface on the same sample can be determined with small deviation.

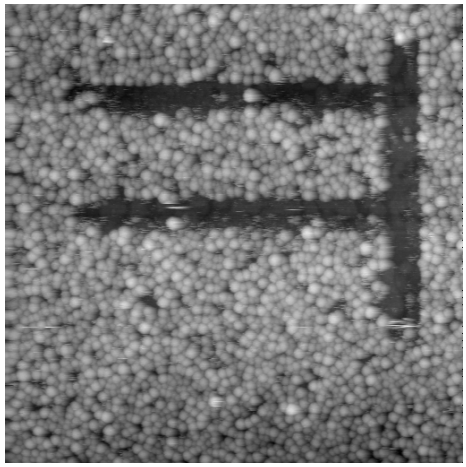

Fig. 1. STM image of Au nanoclusters grown on octanedithiol/Au(111) substrate after Au deposition of 1.3 monolayers (215 nm x 215 nm). The removals of the clusters were performed by the STM tip (see text).

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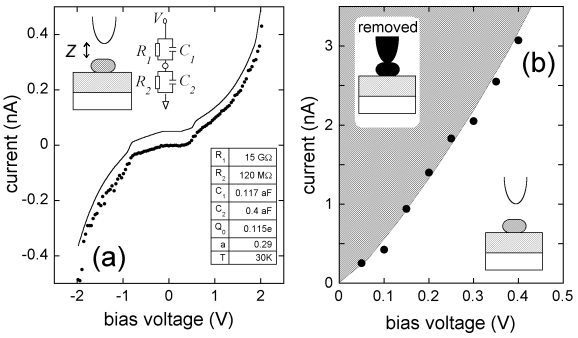

Fig. 2. (a) Tunneling spectroscopy of Au nanoclusters grown on octanedithiol/Au(111) substrate after Au deposition of 1.3 monolayers (ML), showing Coulomb staircase at temperature of 30 K. The solid curve and the parameters in the figure is the result of the curve fitting by the orthodox theory with barrier suppression. (b) Threshold of the bias voltage and tunneling current for the removal of the clusters (1.3 ML) grown on octanedithiol/Au(111) substrate. At the shaded area clusters are removed by the STM tip.

The preparation methods of the samples were the same as reported elsewhere [1]. The sample image of the scanning tunneling microscope (STM) is shown in Fig. 1. Due to the small self-capacitance of the clusters, single electron charging effects are observable in both tunneling spectroscopy and photoelectron spectroscopy at room temperature [1]. Tunneling spectroscopy at lower temperature reveals the coupling parameters of a cluster with the substrate through Coulomb staircase as shown in Fig. 2(a). The mean resistance and capacitance between Au(111) substrate and randomly selected clusters are 170 MΩ and 0.35 aF with the standard deviations of 70 MΩ and 0.07 aF, respectively.

The clusters can be removed by the STM tip under the appropriate conditions as shown in Fig. 1. The position of the tip during the scanning is determined by the bias voltage (V_b) and the tunneling current (I_t) kept constant by the feed-back loop. As shown in Fig. 2(b) there exists a critical boundary in I_t-V_b relation for the removal of the clusters. When the set impedance R_{set}, determined by V_b/I_t, is less than $\sim$ 140 MΩ (shaded area in the figure), most of clusters were removed. Since each point was obtained from the different position on the same substrate, the clear and smooth boundary indicates that the position dependency of this property is fairly small. The result is consistent with that of tunneling spectroscopy, clearly showing that the clusters are removed when R_{set} is set less than the resistance between clusters and Au(111) surface. The shape of the boundary would reflect the conductance property through the octanedithiol layer between a cluster and the Au(111) substrate. It seems unlikely that the existence of the Coulomb gap affects this boundary because the gap size becomes much smaller around the critical boundary due to the tip effect.

Compared with the deviation of the resistance obtained by the tunneling spectroscopy, the critical R_{set} can be determined with small deviations. For instance, when R_{set} is set to 10 % less (more) than the boundary, all clusters are (no cluster is) removed. This is mainly due to the fact that the resistance obtained from the spectroscopy is determined from the small features in I-V curves. In addition, the high sensitivity of the tip position around the critical boundary should be important as discussed below.

When the bias voltage is much larger than the Coulomb gap size, I-V curve becomes close to the asymptotic slope $V = (R_1 + R_2)I$ (see inset of Fig. 2(a) for the determination of the parameters). Due to the exponential dependence of R_1 on the barrier width (z), the relation between R_{set} and z can be expressed as,

$$R_{set} = V_b/I_t = R_{10} \exp(1.025\sqrt{\phi}z) + R_2, \qquad (1)$$

where ϕ is the work function of the tip and clusters in eV and R_{10} is a appropriate constant. If R_{set} is set much higher than R_2, the bias voltage has to drop mainly between the tip and cluster, which makes the tip far away from the cluster. On the other hand, the tip position is quite sensitive to R_{set} around R_2 due to the relation $\mathrm{d}z/\mathrm{d}R_{set} \propto (R_{set} - R_2)^{-1}$ derived from equation (1), to which the clear boundary for the removal would be attributable. This effect would make the cluster apparent height in STM image close to the height that includes the thickness of the layer underneath, which has been observed in previous study [1].

In addition to the uniformity of the cluster size, the resistance between clusters and Au(111) surface, where ODT layer exists, exhibited the distribution with fairly small deviation. This should be affected by the thickness of the layer, i.e., the length of the molecule and we believe that the systematic study of this well-defined barrier would be helpful for the development of the nanometer scale devices.

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