Electron tunneling through a monolayer of small metal clusters investigated by scanning tunneling spectroscopy

H Zhang, D Mautes and U Hartmann
Institute of Experimental Physics, University of Saarbrücken, P.O. Box 151150, D-66041 Saarbrücken, Germany
E-mail: h.zhang@mx.uni-saarland.de; u.hartmann@mx.uni-saarland.de

Abstract. We have investigated the current-voltage characteristic of monolayers of separated metal clusters of a size of 1.4 nm with a low-temperature ultra-high vacuum scanning tunneling microscope. Apart from the usual charge-quantization phenomena, such as Coulomb blockade and staircase, negative differential resistance was observed by performing measurements at distinct locations on the cluster layers. The latter phenomenon can be understood by a “leakage” current to a neighboring cluster and a nonclassical behavior of the nanojunction capacitances caused by electron tunneling.

1. Introduction
Metal clusters of nanometer size are considered to be potential candidates for quantum electronics. In such electronics electron tunneling plays a dominant role. We have investigated this phenomenon on a monolayer of small metal clusters by means of scanning tunneling spectroscopy (STS). The clusters we have chosen are the ligand-stabilized gold species \( \text{Au}_{55} [\text{P(C}_6\text{H}_5)_3]_{12} \text{Cl}_6 \) [1], since they can be produced almost monodispersely and can be self organized to regular structures under certain conditions [1,2]. The diameter of the metal core is 1.4 nm. The ligand shell consisting of 12 \( \text{P(C}_6\text{H}_5)_3 \) molecules and 6 Cl atoms, which acts as dielectric spacer, has a thickness of about 0.35 nm.

The mechanism of the electron transport through such small particles is single electron tunneling (SET) caused by Coulomb effects [3,4]. Scanning tunneling microscopy (STM) and spectroscopy (STS) [5] provide the ideal access for investigating transport phenomena. The imaging ability of STM allows one to observe the neighborhood of an individual cluster, on which current-voltage (I-V) curves are measured. This ability permits an analysis of the specific influence of the environment of a particular tunnel junction. In the following we report that in such small tunneling system not only conductance oscillation can be measured. Negative differential resistance (NDR) can also occur even without an explicit gate voltage. The observed phenomena are explained by assuming a nonclassical behavior of capacitances associated with the electron tunneling.

2. Experiment and discussion
We have investigated the clusters with a low-temperature ultra-high vacuum (UHV) STM [6]. For sample preparation the clusters were first dissolved in dichloromethane and then deposited on highly oriented pyrolytic graphite (HOPG) or Au(111) substrates from solution by spin coating. The STM images confirm that layers with a thickness of about one cluster were produced [7] (see Fig. 1(a)).
We performed numerous $I$-$V$ measurements at different sites on cluster layers of several samples. The measurements were carried out at 7 K. Independently of the substrate the $I$-$V$ curves exhibit some common features: Curves acquired above the center of a cluster show the ordinary Coulomb staircase (CSC) caused by SET. In Fig. 1(b) an example is represented (setpoint: $I_T = 0.7$ nA, $V_T = 2$ V) [7]. Curves taken from different clusters are not completely identical with respect to the Coulomb blockade (CB) range, the stair width and the asymmetry of the curve. This is because of the imperfect cluster monolayer and the varying tightness of the cluster-substrate junction. The latter causes small variations in the resistance and capacitance values, $R$ and $C$, of the respective double junctions. If the tip is away from the center of a cluster and relatively close to another cluster, then current oscillations and NDR can be observed in the $I$-$V$ curve, as shown in Fig. 1(c) (setpoint: $I_T = 0.7$ nA, $V_T = 2$ V). In the absence of a closely spaced neighboring cluster, no NDR could ever be observed. This actually proves that neither the electronic structure of the metallic cluster core nor that of the ligand molecules cause the NDR. If the measurement is performed on a cluster which is located within the second layer both stairs and NDR cannot clearly be recognized (e.g., Fig. 1(d), setpoint: $I_T = 0.1$ nA, $V_T = 2$ V). Only the enlarged CB range is evidently observable. The disappearance of fine structures in the $I$-$V$ curves with increasing number of cluster layers is expected from theory [8].

Figure 1. (a) STM image of Au$_{55}$[P(C$_6$H$_5$)$_3$]$_{12}$Cl$_6$ clusters deposited on HOPG, obtained at a scan range of 7 nm x 7 nm. (b) $I$-$V$ curve acquired above the center of a cluster, (c) away from the center and near a neighboring cluster, and (d) above a cluster which belongs to the second cluster layer, as marked in (a).

The CSC observed in Fig. 1(b) represents the usual $I$-$V$ behavior of a double tunnel junction [4] and can easily be understood from the orthodox SET theory [3]. Surprising at first sight is the appearance of NDR if the tip is fairly close to a neighboring cluster. In this case it is obvious that one cannot neglect the capacitance between the tip and the neighboring cluster [9]. This stray capacitance can evidently cause a significant change of the potential difference between the neighboring cluster and the substrate during the variation of the tunneling voltage which is applied between tip and substrate. This potential difference can be large enough for one electron tunneling from the neighboring cluster to the substrate. That could in turn cause an electron tunneling from the main cluster to the neighboring cluster and lead to a Coulomb blockade in the main current path. The neighboring cluster ultimately acts as a “gate”.

3. Simulation

We performed a modeling of the resulting $I$-$V$ curve (Fig. 1(c)) using a Monte-Carlo method [8] based on the orthodox theory. A scheme of the corresponding cluster arrangement and the ersatz circuit together with the calculated behavior is shown in Fig. 2. The $C$ and $R$ values are according to the experimental situation: First, the tip-cluster separation was determined from accompanying current-distance measurements. In these experiments the absolute distances were determined from the
onset of current saturation which occurs if the tip-cluster distance vanishes [7]. The $C$ values were then estimated from a straightforward calculation by assuming two metal spheres or a sphere and a slab [10] at the respective distances. The $R$ values can be obtained by tunneling through single ligand molecules, $P(C_6H_5)_3$, which can be prepared as monolayers on the substrates as well [11].

By modeling we found that current oscillations can only occur if the capacitance between the two neighboring clusters is larger than that between cluster and substrate. This situation is excluded in a treatment according to classical physics: The separation between the clusters (~ 7 Å) is larger than that between cluster and substrate (~ 3.5 Å). However, since we are dealing with tunnel junctions rather than with classical capacitors, electrons can overcome the dielectric or vacuum region through tunneling and thus effectively reduce the amount of accumulated charge on the electrodes. This mechanism thus leads to a reduction in capacitance. As a consequence, the capacitance decreases with decreasing separation of the electrodes in the tunneling regime because the tunneling current increases. This phenomenon can occur at separations smaller than about 1 nm because the electron transmission probability significantly increases with reduction of separation in this regime [5]. The capacitance completely vanishes if the electrodes come into contact with each other. It has to be mentioned that the quantum behavior of the capacitance of a nanojunction has already been theoretically described by Christen and Büttiker [12], and experimentally been observed by Hou et al. [13]. The latter reported on an unusual increase of CB regime by reducing the separation between the STM tip and an Au nanoisland.

Upon modeling of the $I$-$V$ curves, the potential changes of the cluster 1 and 2 and the tunneling current between the two clusters have been calculated as well (Fig. 3). At bias values close to 1.3 and 2.2 V (marked), for examples, the potential differences between cluster 1 and cluster 2 are evidently beyond the CB regime (Fig. 3(b)). Electrons begin to tunnel from cluster 1 to cluster 2 (Fig. 3(a)). The probability for one electron tunneling from cluster 1 to cluster 2 is now as high as that for one tunneling from cluster 1 to the substrate. Since the tunneling path tip - cluster 1 - cluster 2 - substrate possesses a much higher resistance than the main path, a current decrease occurs with increasing bias and the NDR results.
Figure 3. Monte Carlo simulation of the tunneling current from cluster 1 to cluster 2 (a) and the electrical potential (b) of clusters 1 and 2 in Fig. 2 as a function of the total tunnel bias.

From the modeling we found that the capacitance $C_{2T}$ between tip and neighboring cluster 2 (separation > 7 nm) is smaller than $C_{12}$ (see Fig. 2). The capacitance maximum occurs at a separation of about 0.7 nm for the Au$_{55}$ clusters. This is considerably larger than the value found for 2 nm 2-dimensional Au islands [13]. It has to be pointed out, however, that the density of states of the electrodes also significantly affects the $C$ values [12]. We have chosen proper $C$ values corresponding to the concrete situations of Fig. 1(b) and (d). The results are represented in Fig. 4(a) and (b), respectively. The characteristic features related to the CSC (Fig. 4(a)) or to the smeared-out stairs and enlarged CB range (Fig. 4(b)) are in good agreement with the experimental findings. A quantitative modeling of the experimental results is extremely difficult, since in reality the tunneling transmission probability (or $R$ value) depends on the bias voltage. On the other hand, also the $C$ values are voltage-dependent through the tunneling current. The strong asymmetry in the measured $I$-$V$ curves (Fig. 1) which is not expected from modeling is possibly due to tiny cluster movements since the clusters are charged depending on the tunnel voltage. This causes variations in the $R$ and $C$ values during a voltage scan by the exerted Coulomb forces. The satisfactory qualitative agreement between theoretical and experimental results confirms that the basis of the model is correct.

4. Summary

We have investigated the $I$-$V$ characteristics of monolayers of Au$_{55}$ clusters on well defined locations. Depending on the position of the STM tip with respect to the cluster center and on the location of neighboring clusters, CB and CSC as well as NDR have been observed. All results can be interpreted within the framework of the orthodox SET theory. One major condition for the occurrence of NDR in the $I$-$V$ curves is that the stray capacitance between the cluster underneath the STM tip and the neighboring cluster is larger than that along the direct tunneling path to the substrate. Only in this case the CB for a tunneling path through neighboring clusters is small enough to open this channel for an electron. The perfect equality of all clusters requires the assumption of a nonclassical behavior of the involved capacitances, i.e., due to electron tunneling the capacitance decreases with decreasing the separation of the nanojunction.
Figure 4. Schematic diagrams of the tip-cluster-substrate arrangements, the equivalent electrical circuits, and Monte Carlo simulation of I-V curves. (a) and (b) correspond to the cases of (b) and (d) in Fig. 1, respectively. The \( C \) and \( R \) values chosen for modeling are: (a) \( C_{IT} = 0.2 \) aF, \( C_{IS} = C_{2S} = 0.05 \) aF, \( C_{12} = 0.25 \) aF, \( R_{IT} = 5 \) G\( \Omega \), \( R_{IS} = R_{2S} = 100 \) M\( \Omega \), \( R_{12} = 100 \) G\( \Omega \); (b) \( C_{IT} = 0.08 \) aF, \( C_{IS} = C_{2S} = 0.05 \) aF, \( C_{12} = 0.25 \) aF, \( C_{14} = 0.25 \) aF, \( C_{24} = 0.27 \) aF, \( R_{IT} = 2 \) G\( \Omega \), \( R_{IS} = R_{2S} = 200 \) M\( \Omega \), \( R_{12} = 100 \) G\( \Omega \), \( R_{14} = 8 \) G\( \Omega \), \( R_{24} = 80 \) G\( \Omega \).

We thank Prof. G. Schmid from the Inorganic Chemistry Dept. of the University of Essen for offering the Au\(_{55}\) clusters and the ligand samples. This work was supported by the Deutsche Forschungsgemeinschaft.

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