The Electronic Interaction Between $Au_{55}(PPh_3)_{12}Cl_6$ Monolayers Through SiO_2 Films

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Keywords: Monolayers / Gold / Multilayers / Electronic tunnelling / Current-voltage characteristics

$Au_{55}(PPh_3)_{12}Cl_6$ monolayers embedded between 5-nm SiO_2 barrier films have been successfully generated. The cluster monolayers were obtained by spin coating of very dilute solutions. The SiO_2 films were prepared by means of a special anodic plasma arc technique. Systems of one up to eight cluster/SiO_2 combinations on a gold surface have been generated and investigated. In the voltage region between –5 and +5 mV, all samples exhibited linear current-voltage characteristics. Control samples with only SiO_2 show very different I-U behaviour. We interpret the behaviour observed as a result of electronic tunnelling from the cluster monolayers through the SiO_2 barrier films.

Introduction

Monolayers of quantum dots are of general interest with respect to the electronic interaction between the dots in only two dimensions (2D). Whereas the electronic situation in individual quantum dots has been investigated by various researchers,[1–3] their interparticle behaviour is rather unknown. $Au_{55}(PPh_3)_{12}Cl_6$ and its derivatives are ideal quantum dots, since this compound is the only metal nanoparticle that shows well-expressed quantum behaviour already at room temperature.[1] Current investigations of the electric conductivity of 2D arrangements of $Au_{55}(PPh_3)_{12}Cl_6$ clusters over about 80 nm indicate that it is below the detection limit,[4] whereas the conductivity of only 20-nm areas shows a typical Coulomb blockade.[5] In this connection, there arose another interesting question, namely the ability of communication of extended monolayers in the vertical direction, separated from each other by insulating barriers. Variations of the insulating barriers (SiO_2) in thickness might provide evidence on the tunnelling limits. Furthermore, we might learn more about the storage capacities of cluster monolayers. Such information is of interest with respect to the development of novel floating gate transistors.[6–10] The corresponding behaviour of cluster double layers or thin films is the subject of another contribution in this issue.[4] There is a principal difference to be expected between thin films and monolayers. Dipolar interactions between cluster layers dominate the behaviour in thin films, whereas electronic tunnelling is observed in the case of monolayers.

In this contribution, we describe the current-voltage behaviour of multilayered systems consisting of $Au_{55}(PPh_3)_{12}Cl_6$ monolayers embedded between 5-nm SiO_2 films.

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Results and Discussion

Generation of Cluster/SiO_2 Multilayers

The generation of the cluster monolayers was performed by means of spin coating and for the formation of the SiO_2 films the same plasma assisted physical vapour deposition (PAPVD) procedure has been applied as is described in detail in the related paper of ref.[4] For the current (I)-voltage (U) investigations we used a novel kind of contacting technique that is shown in Figure 1.

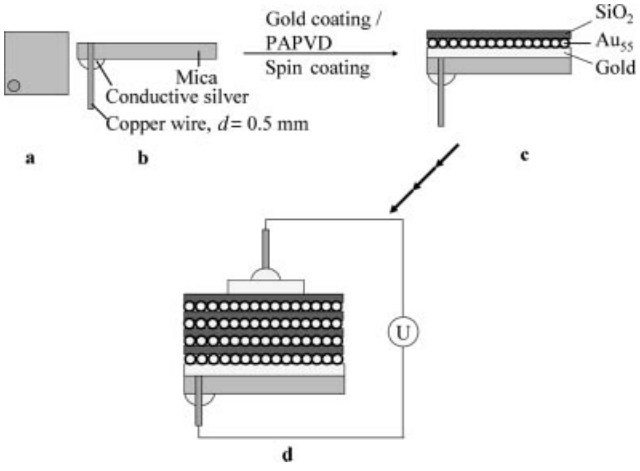

Figure 1. Construction of a $Au_{55}(PPh_3)_{12}Cl_6/SiO_2$ multilayer system.

A 1×1-cm^2 mica platelet was provided with a 0.5-mm borehole at the periphery (a). A 0.5-mm copper wire was plugged in in such a way that it ended exactly at the mica surface and was then fixed by conductive silver on the back side (b). A ca. 400-nm-thick gold film was then generated on the mica by means of PAPVD, followed by a first mono-

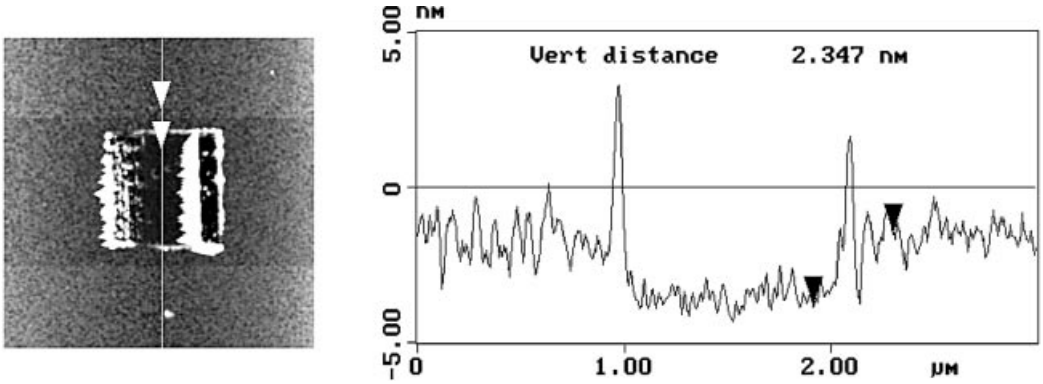

Figure 2. AFM image of a cluster monolayer with a scratched window (left) and the corresponding cross section (right).

layer of $Au_{55}(PPh_3)_{12}Cl_6$ clusters. This was produced by spin coating 50 µL of a 2.8×10^{-7} M cluster solution (c). The spin-coating process is described in detail in ref.[4] The next step consisted of the generation of a first 5-nm SiO_2 film by means of the anodic plasma arc process, also described in detail in ref.[4] Depending on the intended number of layers, the processes were repeated correspondingly. Figure 1d shows a system with four cluster/SiO_2 double layers. The final SiO_2 layer was contacted by a gold electrode 3 mm in diameter that was made by evaporating gold through a corresponding mask. Conductive silver was then used to fix a copper wire on top of the gold electrode. Control of the quality of the cluster monolayers was performed by AFM. Figure 2 views a cluster monolayer with a scratched window from above (left) and a cross section of that sample (right). The height of 2.4 nm agrees perfectly with the existence of a cluster monolayer containing randomly oriented clusters. The quality of the monolayers depends exclusively on the spin-coating conditions and the use of dichloromethane as solvent that has a distinct yield of moisture for improving the wetting conditions.[4]

As an example of the successful generation of cluster/SiO_2 multilayers, a transmission electron microscopic (TEM) image of a four-layered system is shown in Figure 3.

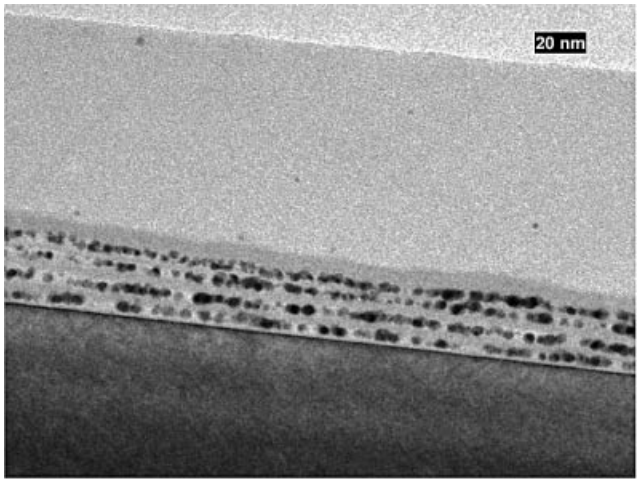

Figure 3. TEM image of a four-layered cluster monolayer/SiO_2 system.

As can be seen, the cluster monolayers are properly separated by the SiO_2 barrier films.

Electrical Measurements

Electrical measurements were performed by current-voltage registrations in the region from –5 to +5 mV. A control experiment with the gold layer alone showed the expected linear I-U characteristic, resulting in a current of 11 mA at 5 mV. Table 1 contains the measured values for four different-layered samples consisting of 1, 2, 4 and 8 cluster/SiO_2 combinations. In addition, two comparative values for 2 and 8 SiO_2 5-nm films are added. As can be seen from the values for the cluster/SiO_2 multilayers, the current values decrease with increasing numbers of layers; however, by far not to the same extent as SiO_2 films alone do.

Table 1. Current values of cluster/SiO_2 and SiO_2-only multilayer systems and of the pure gold surface.

Number of cluster/SiO_2 double layers	Current [mA] Cluster/SiO_2	Current [mA] SiO_2
0 (gold surface)	11	
1	8.8	
2	6.8	3.0
4	4.6	
8	2.9	0.9

Figure 4a shows a typical current-voltage plot for a two-layered cluster/SiO_2 array, resulting in 6.8 mA at 5 mV. The small steps are caused by the measuring technique and so are not system-immanent. In Figure 4b, the dependence of the current on the number of cluster/SiO_2 combinations is plotted and completed by the two SiO_2-only values.

Measurements at higher voltages were not possible because of the critical contact between the macroscopic wire and the nanoscopic part of the device.

These results can be interpreted as follows:

$Au_{55}(PPh_3)_{12}Cl_6$ monolayers, isolated from each other by 5-nm films of SiO_2, are electronically in contact with each other in the voltage region between –5 and +5 mV. This can clearly be followed from the significantly different behaviour of SiO_2 films without cluster monolayers in between. We assume that electronic tunnelling through the barrier

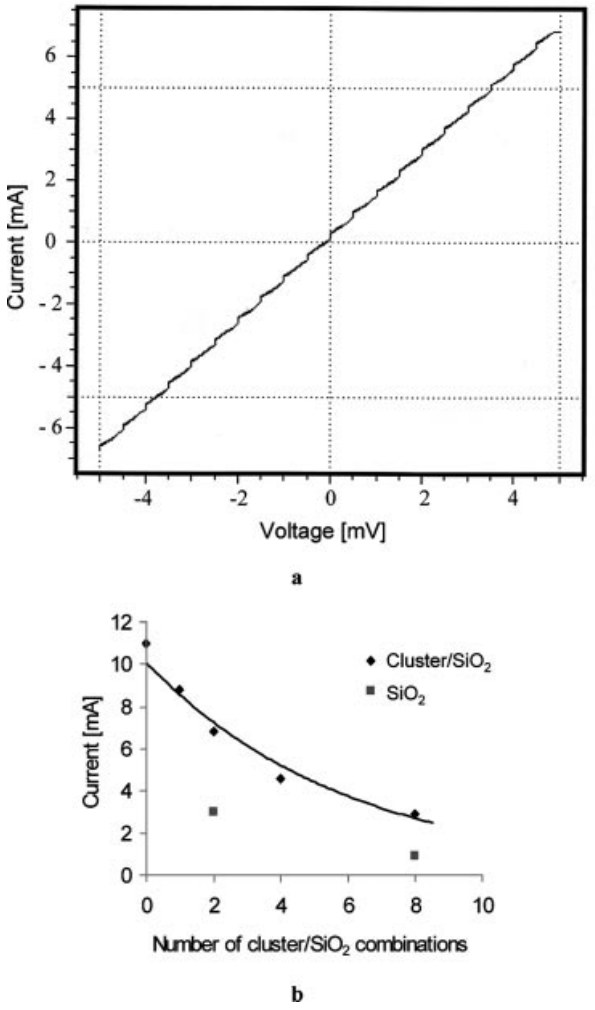

Figure 4. (a) Current-voltage plot of the two-layered $Au_{55}(PPh_3)_{12}Cl_6/SiO_2$ array; (b) dependence of current on the number of cluster/SiO_2 combinations and of SiO_2-only films. (The line serves only as a guide for the eye.).

layers occurs rather than electronic hopping, making the whole multilayer system an electronic unit. With increasing numbers of cluster/SiO_2 combinations, the currents decrease because of increasing tunnelling steps. The linear I-U characteristics, observed for all four investigated samples, indicate that there is no visible tunnelling blockade, which should have been observed in Coulomb blockades, in the layered systems. The tunnelling distance from cluster to cluster is, including the PPh_3 ligand shell, about 5.7 nm (5 nm SiO_2 + 2×0.35 nm for PPh_3). Figure 5 depicts the proposed process formally.

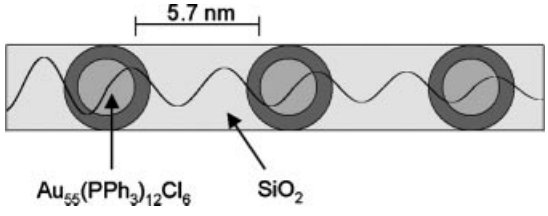

Figure 5. Illustration of the electronic tunnelling through a $Au_{55}(PPh_3)_{12}Cl_6/SiO_2$ multilayer system with decreasing amplitude.

An electronic wave, here arriving from the left, tunnels from cluster to cluster through the ligand shell and the SiO_2 film, however with decreasing amplitude leading to a kind of exponential decrease in current with increasing number of double layers, as can be observed in Figure 4b. The sloping curve approaches asymptotically the value zero for the current at a double-layer number >10. Since arrangements with more than eight layers turned out to be unstable towards crystallisation,[4] they could not be used for reliable measurements.

Conclusions

Multilayer systems consisting of monolayers of $Au_{55}(PPh_3)_{12}Cl_6$ clusters, separated from each other by 5-nm-thick SiO_2 films behave electronically like a tunnelling system, altogether reaching a maximum of over 60 nm in the case of eight cluster/SiO_2 double layers. This is a very valuable result with respect to the question of tunnelling distances. Compared with the behaviour of cluster double layers between SiO_2 barrier films, described in detail in ref.[4], where dipolar interactions between cluster layers dominate, this is obviously not the case with strictly monomolecular cluster layers, where electronic tunnelling happens. These results must be seen in relation to former measurements at three-dimensional assemblies of $Au_{55}(PPh_3)_{12}Cl_6$ clusters.[12–14] Since the gold electrode on top of the multilayer samples has a diameter of 3 mm, the tunnelling process from one electrode to the other is nothing but a kind of 3D system with considerably increased tunnelling distances, namely from 0.7 nm, considering only the PPh_3 ligand shell, up to about 5.7 nm in the samples described here. Since for systems with more than eight cluster/SiO_2 combinations the conductivity approaches that of pure SiO_2, the tunnelling distance reached might somehow be a natural limit. The 5.7 nm tunnelling distance is, compared with distances in former investigations,[15,16] a maximum value.

Experimental Section

Reagents and Physical Measurements: $Au_{55}(PPh_3)_{12}Cl_6$ was prepared as described previously.[11] CH_2Cl_2 for spin coating was kept in contact with air over a couple of days to enrich it with moisture. Mica sheets from PLANO, Wetzlar have been used (0.2 mm). Before use, upper layers were removed by a tape. Current-voltage measurements were performed with an IM 6e from Zahner Meßtechnik GmbH & CoKG, Kronach. Tungsten evaporation boats were from Balzer Materials, Liechtenstein. AFM measurements were performed with a Nanoscope IIIa, Digital Instruments, Woodbury. For spin-coating processes we used Model 6700, Speciality Coating Systems, Indianapolis. The device for PAPVD is described in detail in ref.[4]

Formation of SiO_2/Cluster Double Layers: The generation of the 5-nm SiO_2 barrier layers was performed analogously to the procedure described in ref.[4] For the preparation of the $Au_{55}(PPh_3)_{12}Cl_6$ monolayers, a CH_2Cl_2 solution (50 μL, 2.8×10^{-7} M) was applied for spin coating on the gold surface, generated on 1×1 cm^2 mica

platelets. For the gold coating, the same PAPVD system was used as the one used for the preparation of the SiO_2 films. Current: 30 A, pressure: 5×10^{-5} mbar. The coating rate was 5 nm/sec. For the evaporation of gold we used tungsten evaporation boats.

Acknowledgments

This work was carried out as a project in the Schwerpunktprogramm 1072 of the Deutsche Forschungsgemeinschaft. We gratefully acknowledge the generous support. We also would like to thank U. Simon for very helpful discussions.

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Received: April 29, 2005
Published Online: July 12, 2005

