NANO
LETTERS

2001
Vol. 1, No. 8
405−407

Quasi One-Dimensional Arrangements of $Au_{55}(PPh_3)_{12}Cl_6$ Clusters and Their Electrical Properties at Room Temperature

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Received June 7, 2001

ABSTRACT

Short chains of $Au_{55}(PPh_3)_{12}Cl_6$ clusters were generated between tungsten tips on an SiO_2 surface, and their electrical behavior was studied. The clusters were deposited from solution by applying a voltage of 2 V between tips of 30 nm in distance. Current–voltage (I–V) measurements of the nanowires showed Coulomb blockades at room temperature in the region between –0.5 to +0.5 V, demonstrating quantum dot character and single electron transistor (SET) behavior, respectively.

Single-electron tunneling at room temperature in nanometer sized particles has developed to promising techniques for future nanoelectronics.[1−8] Independent of the kind of application, the three-, two-, or one-dimensional organization of the particles is an unrenounceable condition. Two-dimensional (2D) arrangements of perfectly ordered Au_{55} clusters have been described by us.[9,10] For one-dimensional (1D) arrangements we are just developing novel strategies by the use of functionalized polymers and DNA or by special procedures related to Langmuir−Blodgett techniques.[11] However, the generation of 1D arrangements of clusters in the 1−2 nm range is still a strong challenge.

To approach this goal we used an electric field to trap clusters between electrodes. The device consists of three tungsten electrodes, fabricated of a 25 nm thick tungsten layer on a silicon wafer with a 80 nm thick thermal oxide using an electron beam lithography process based on a negative resist and a SF_6−RIE etch technology (Figure 1). The minimum feature size is about 50 nm, and the distance between two contacts varies between 20 and 50 nm with a 80 μm × 80 μm contact pad on each lead.

$Au_{55}(PPh_3)_{12}Cl_6$ [Au_{55}] clusters[12,13] were used to generate cluster chains between the tips. These clusters consist of a 1.4 nm gold core, enveloped by a shell of 0.35 nm phosphine molecules, trapping the electrons in a quasi zero-dimensional (0D) volume, with the consequence that the physical behavior of such clusters follows quantum mechanical rules instead of classical physical laws. The quantum dot behavior of these clusters has been studied intensively since they were synthesized ca. 20 years ago.[1−8] The experiments were carried out by dipping the electrodes bearing wafer sample in a dichloromethane solution of [Au_{55}], followed by the application of a constant voltage ranging between 0.5 and 2.0 V for different time scales. Figure 2 elucidates the experiment.

As is known since 1986,[14] [Au_{55}] clusters in dichloromethane solution show electrophoretic behavior. Owing to this property, they can be positioned between the two contacts used in this experiment from the solution. The reason for this may be seen in the high density of π-electrons in the ligand shell and the presence of partially negatively charged chlorine atoms.

Numerous deposition experiments showed the reproducibility of the procedure. The cluster concentration in the solution, the applied voltage, and the deposition time turned out to be critical parameters to obtain cluster chains between the two nanoelectrodes. The concentration of the cluster solution can be measured by the current through a constant distance under a constant voltage. It is not possible to

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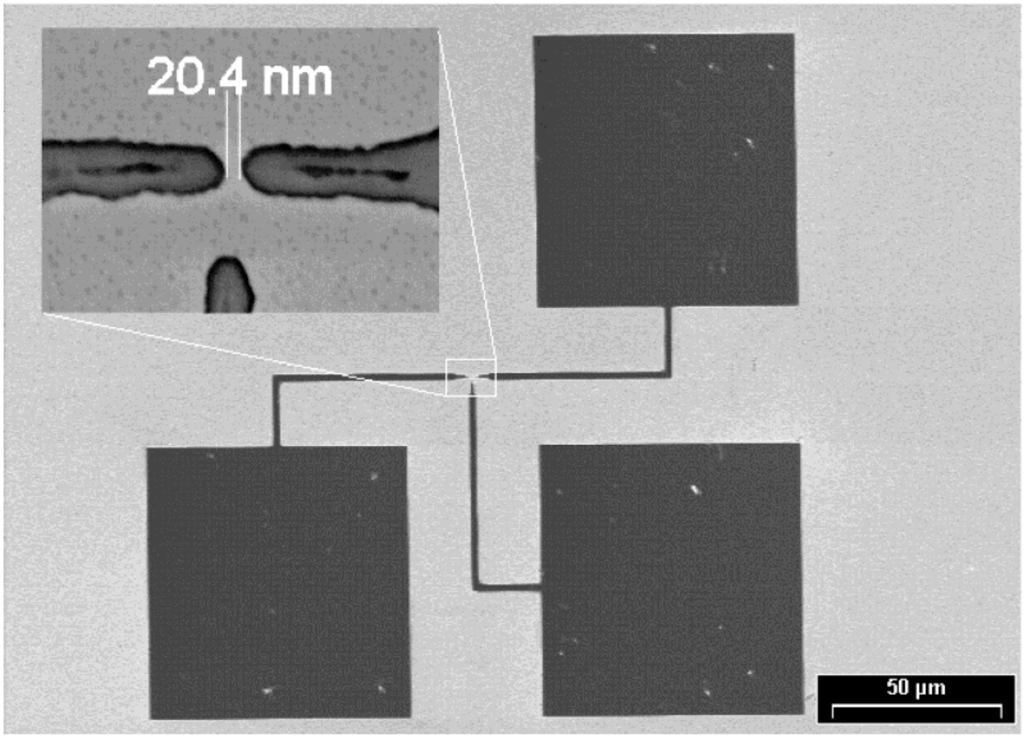

Figure 1. Complete nanostructure with contact pads (the inset is nanostructured with three nano tips).

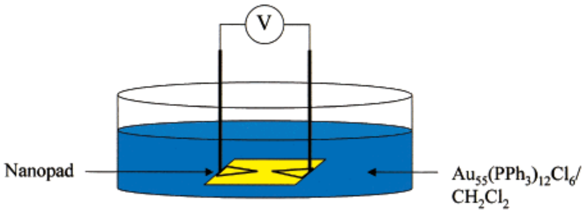

Figure 2. Sketch of the experimental conditions to deposit clusters from solution between contact pads.

calculate the cluster concentration due to the very low concentration. The optimum concentration was adjusted to give a current between 10^{-9} and 10^{-10} A between the contact pads. Higher concentrations resulted in the formation of cluster mono- or multilayers. Even the formation of microcrystals could be observed.

Figures 3a and 3b show SEM images of the tungsten tips before and after cluster deposition. Complete chains of up to 10 clusters between both electrodes can clearly be recognized, in addition to some not fully connected ones.

These cluster chains were obtained at 2 V, a deposition time of 240 s, and a tip distance of about 30 nm. SEM does not allow to determine the very exact particle size. However, the observed averaged particle size of ca. 3 nm is in relatively good agreement with the expected size of about 2.5 nm, regarding the strong noise on the SiO_2 surface.

The I−V curve of the sample shown in Figure 3b is displayed in Figure 4. All other samples showed equivalent Coulomb blockades in the region between −0.5 to +0.5 V, in agreement with results in other publications.[6,15]

In some cases we observed asymmetrical I−V curves, indicating a diode behavior as seen in Figure 5. This effect

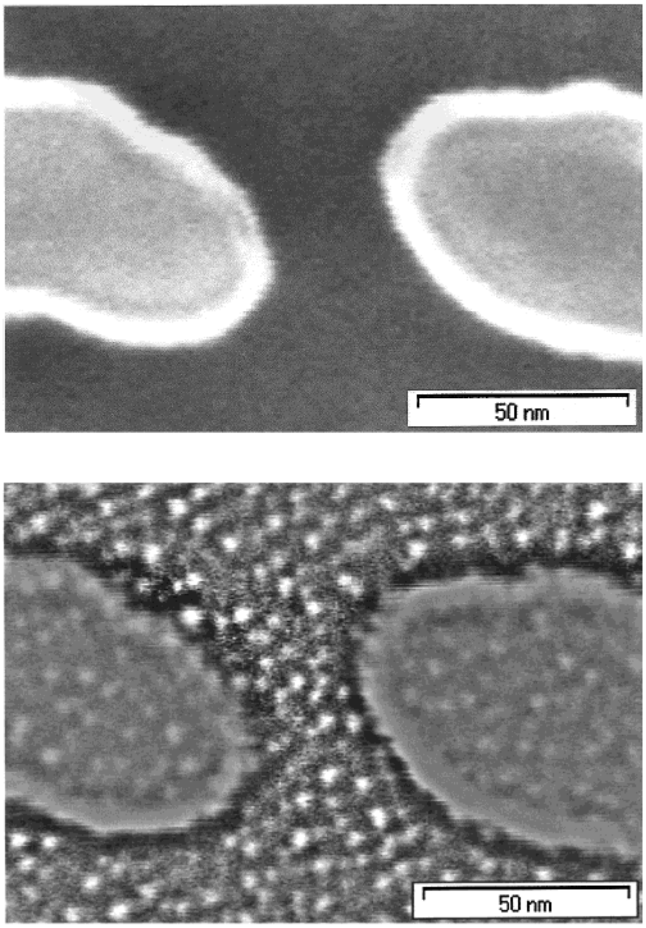

Figure 3. SEM image of the tungsten nanocontact before (a) and after (b) Au_{55} cluster deposition.

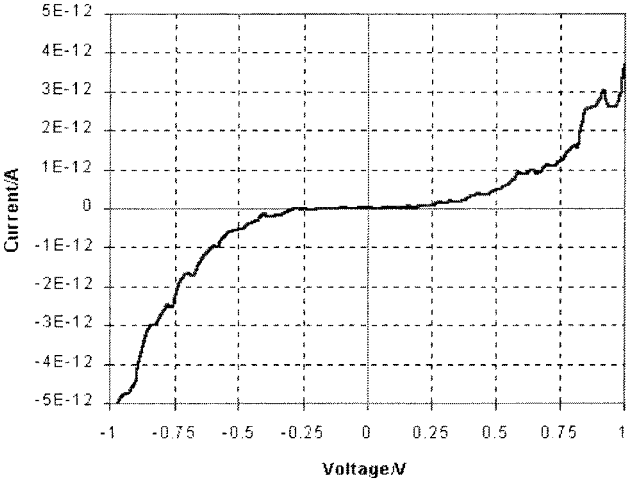

Figure 4. I−V curve at room temperature.

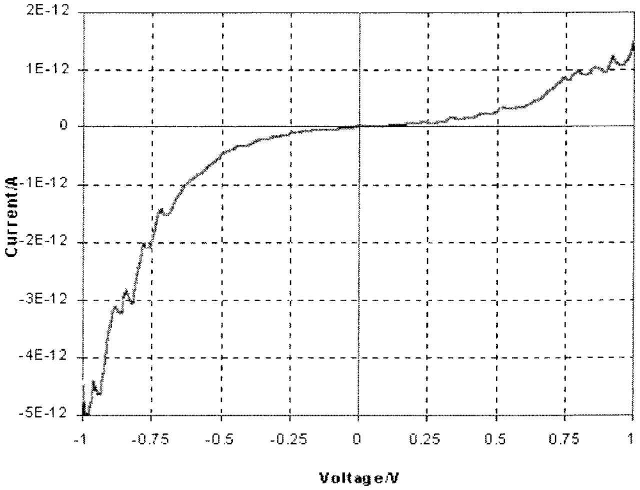

Figure 5. Diode behavior at room temperature.

probably is caused by charging clusters by the electron beam during SEM. Electron beam irradiation of clusters in 2D cluster monolayers between tungsten tips results in well-pronounced diode behavior.[16] Another reason could be the creation of one or more microcrystals consisting of only a few clusters.

We have demonstrated for the first time that short chains of $Au_{55}(PPh_3)_{12}Cl_6$ clusters can be organized between tungsten tips on an SiO_2 surface. The clusters are deposited from a CH_2Cl_2 solution by applying a voltage at the tips of 0.5 to 2 V for 40−120 s. These quantum dot wires exhibit well-pronounced Coulomb blockades between −0.5 to +0.5 V at room temperature. From these investigations it follows that Au_{55} clusters, which can also be equipped by ligand shells other than the one used here, act as single-electron transistors at room temperature, as has already been shown for single clusters of the same type.

Acknowledgment. We thank the Alexander von Humboldt Foundation for a grant (Y-P.L.). G.S. acknowledges support by the Deutsche Forschungsgemeinschaft (SFB 452) and the Fonds der Chemischen Industrie, Frankfurt.

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NL0100419