Noble Metal Nanoparticles Deposited on Self-Assembled Monolayers by Pulsed Laser Deposition Show Coulomb Blockade at Room Temperature**

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In the last decade molecular electronics has become a key area of nanotechnology.[1,2] Important topics in this field are the use of self-assembled monolayers (SAMs) in devices such as nanoscale transistors (SAMFETs),[3] the analysis of macroscale electronic properties of SAMs,[4,5] and measurement of the electronic properties of single molecules.[6–8] One of the critical steps in device fabrication is the deposition of metal top "electrodes" that are larger than the crystalline domain sizes of the SAMs (in other words, larger than several tens of square nanometers) and have no electrical connection with the bottom electrode.[9,10] In general, unreactive metals (Au, Ag, Cu) that are deposited on inert (CF$_3$- or CH$_3$-terminated) SAMs diffuse through the SAM to the Au/S interface. More reactive metals will stick to SAMs with coordinating head groups to form organometallic complexes.[11] Bao et al. have demonstrated that Au and Al can penetrate a monothiol SAM whereas they stick to dithiol SAMs. Ti destroys both kinds of SAMs because of its high reactivity.[12] Ohgi et al. have investigated the difference between Au evaporation on reactive dithiol and unreactive monothiol SAMs by STM.[13] They found that with monothiols the Au penetrates through the SAM to form islands of monoatomic height under the SAMs, while with dithiols Au particles were formed on top of the SAM. Czan-

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derna et al. have found that when Cu is vacuum-deposited on a carboxylic acid terminated SAM, some Cu reacts with the carboxylic acid groups, although most Cu diffuses through the SAM.[14] When faster deposition rates ($>1\,nm\,min^{-1}$) were used and the substrate was cooled to 220 K during deposition, penetration of Cu could be slowed down or even stopped. Earlier STM measurements were done on Au clusters deposited by a cluster beam source on short dithiol SAMs.[15] Small noble metal clusters can be deposited on SAMs by evaporation of Au,[16] chemical reduction of silver nitrate,[17] or by self-assembly of hexanethiol-stabilized Au clusters.[18]

Recently, we described pulsed laser deposition (PLD)[19] in combination with nanosieves to deposit submicrometer-size Au islands on self-assembled monolayers.[20] Here we report a new fabrication method for nanometer-sized metal clusters on top of SAMs by PLD. The presence of a Coulomb blockade measured by STM on Pd clusters on a decanethiolate SAM on Au indicates that the clusters have nanometer dimensions and are insulated from the underlying Au substrate.

Au, Pd, and Pt were first deposited on TEM grids, in order to see if clusters are formed and to investigate the dependence of the cluster size on the deposition parameters. Laser pulses (10 pulses at a repetition rate of 4 Hz) gave a reasonable surface coverage without creating large aggregates of metal. For these depositions we used a laser spot size of about $3\,mm^2$ and a fluence of $4\,J\,cm^{-2}$ at different background pressures. TEM (Figure 1) showed that the metal is present as small clusters.
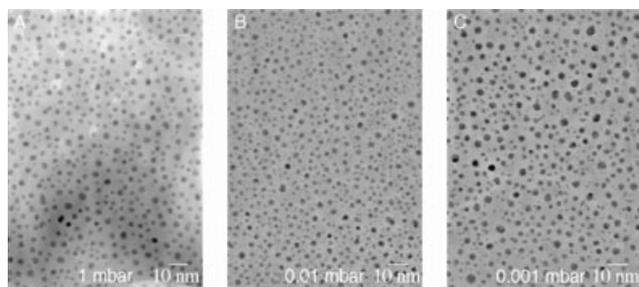

Figure 1. A–C) TEM images of Au clusters deposited with 10 pulses at a 40 mm target–substrate separation with a fluence of $4\,J\,cm^{-2}$ and decreasing Ar pressure. The sizes of the clusters are 2.67 ± 0.60 nm (A), 2.40 ± 0.50 nm (B), and 2.30 ± 0.94 nm (C).

The average diameter of the clusters is larger at higher deposition pressures than at lower deposition pressures (Figure 1). This result can be explained by the increased collision frequency of the metal atoms in the plasma with the argon atoms and with each other. The size distribution is narrower at higher pressures than at lower pressures. A possible reason for this might be that small clusters on the surface aggregate to form larger clusters. Aggregation into much larger metal particles does not take place, not even when 20 laser pulses are used instead of 10.

Pd and Pt were deposited in the same way (Figure 2). While the Au and Pd clusters are of similar size the Pt clus-
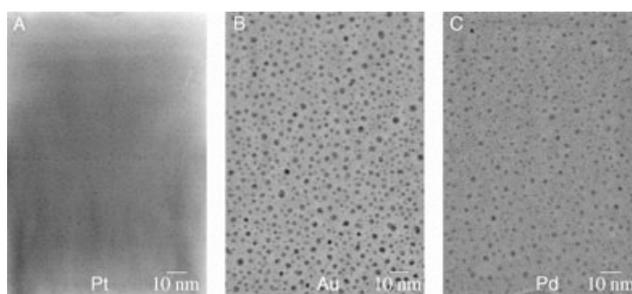

Figure 2. Clusters of A) Pt (cluster size: 1.06 ± 0.21 nm), B) Au (2.40 ± 0.50 nm), and C) Pd (2.29 ± 0.50 nm) deposited with 10 pulses, at 0.01 mbar with a target–substrate separation of 40 mm and a fluence of $4\,J\,cm^{-2}$.

ters are substantially smaller, probably due to the higher reflectivity of Pt toward the laser light (248 nm wavelength). This reduces the efficiency of the ablation so fewer collisions can take place in the plasma. At a fluence of $5\,J\,cm^{-2}$ larger clusters are formed.[21]

The main goal of this investigation was the deposition of clusters on SAMs in such a way that they are electrically insulated from the Au substrate without destroying the SAM. Depositions were performed directly on alkylthiolate SAMs on flame-annealed Au. AFM measurements showed that metal clusters were also present on these SAMs. Conducting probe AFM (CP-AFM) measurements in parallel with conventional AFM height measurements were performed to investigate whether the metal clusters were insulated on top of the SAM or buried in the SAM. CP-AFM was performed on samples of Au clusters on octadecanethiol (ODT) SAMs. The Au was deposited using six laser pulses (fluence $4\,J\,cm^{-2}$, spot size $3\,mm^2$) on an Au target at 0.01 mbar argon pressure at a distance of 40 mm from the substrate. Since the AFM tip has to be able to distinguish between single clusters fewer pulses were used in order to obtain a lower coverage.

The number of clusters (Figure 3 A) is lower than in the TEM images. On flame-annealed Au substrates deep (≈20–50 nm) trenches are present between the Au(111) islands. AFM indicates that the clusters are present in these trenches. This is likely caused by the mobility of the clusters on the hydrophobic SAM. The clusters seen in Figure 3 are stable and are not moved by the AFM tip despite not being
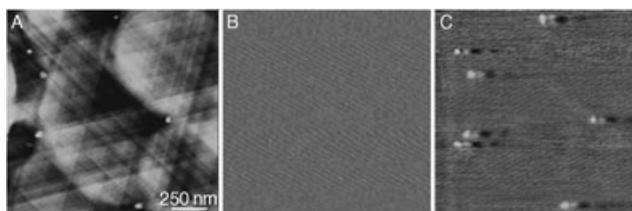

Figure 3. Simultaneous measurements of topography and current of Au clusters on an ODT SAM obtained by CP-AFM, acquired in air: A) height image (z-scale $=10$ nm); B and C) current images at a bias of 3 V and 7 V, respectively (z-scale $=0.5$ pA). Light region: conducting; dark region: dielectric.

chemically attached to the surface. The clusters only became visible in the current image if the bias over the tip and the sample was raised to about 5 V (Figure 3B,C). If the clusters were buried in the SAM, and thus in contact with the Au substrate, they would be visible at lower voltages. The fact that they are only visible at higher voltages indicates that these clusters are insulated on the SAM. The images were reproducible after changing the bias from higher to lower applied bias. Au clusters deposited on a shorter-chain thiol SAM showed the same behavior when measured by CP-AFM (Figure 4). Au was also deposited on
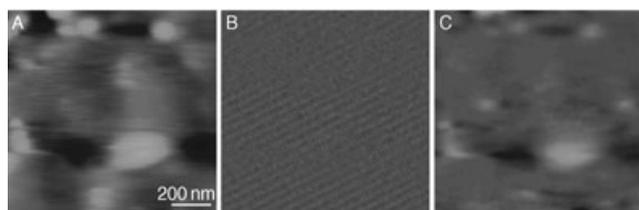

Figure 4. Simultaneous measurements of topography and current of a DT SAM obtained by CP-AFM, acquired in air: A) height image (z-scale = 10 nm); B and C) current images at a bias of 1 V and 3 V, respectively (z-scale = 0.3 pA). Light region: conducting; dark region: dielectric.

a decanethiol (DT) SAM using 10 laser pulses (fluence 4 J cm^{-2}, spot size 3 mm^2) on an Au target at 0.01 mbar argon pressure at a distance of 40 mm from the substrate. As expected for this thinner SAM, the clusters were visible at a lower applied bias than for the ODT SAM.

Pd clusters were deposited on DT SAMs by using 10 laser pulses (fluence 4 J cm^{-2}, spot size 3 mm^2) on a Pd target at 0.01 mbar at a distance of 40 mm from the substrate. The samples were measured in a high-vacuum STM directly after preparation. Figure 5 shows a typical STM image of a DT SAM with Pd clusters. It is quite clear from this STM image that Pd clusters are present on top of the SAM. Moreover, these clusters are distributed over the entire substrate and are not aggregated. The typical diameter of these Pd clusters is around 2 nm, which is in good agreement with the TEM measurements. I/V curves taken on the Pd clusters show Coulomb blockade, which provides proof of the insulated nature of the clusters. In order to observe Coulomb blockade the total capacitance of the Pd cluster should be smaller than $e^2/2kT$ and the resistances of the tunnel junctions should be larger than the resistance quantum $h/2e^2$.[22] If we assume that the Pd clusters are insu-
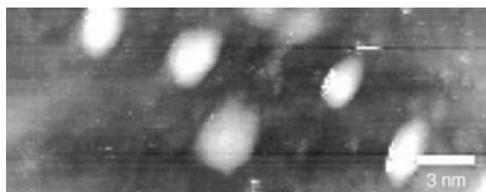

Figure 5. STM image (25 × 10 nm) of Pd clusters on top of an SAM taken at 300 K. The typical diameter of the Pd clusters is about 2 nm (V = 0.5 V, I = 0.1 nA).

lated from the surface by the DT SAM, we can model the system as a double-junction circuit where the first junction is composed of the STM tip and the Pd cluster separated by vacuum and the second junction consists of the Pd cluster and the Au substrate separated by the monolayer. Each junction is modeled by a resistor in parallel with a capacitor. At extremely low capacitance values (e.g. ≈10^{-18} F) and very large resistance values (e.g. ≈10^9 Ω), one can measure the Coulomb gap and the Coulomb staircase, even at elevated temperatures. The latter observation, however, requires an asymmetric double junction, i.e. both junctions should have different RC values.

Several I/V curves taken for the Pd clusters on the DT SAM and the uncovered SAM substrate at different temperatures are shown in Figure 6. The I/V curves of the individual Pd clusters invariably exhibit the characteristic Coulomb staircase and Coulomb gap. Although the Coulomb staircase is also faintly present at room temperature, equidistantly spaced steps in the I/V curve are clearly resolved at 80 K. I/V curves taken on the bare SAM do not show any evidence for Coulomb blockade effects. These observations clearly prove that individual Pd clusters are electrically insulated from the underlying Au substrate.[22]

In summary, we have used pulsed laser deposition of the noble metals Au, Pt, and Pd to fabricate nanometer-sized metal clusters. CP-AFM showed that insulated Au clusters can be deposited on DT and ODT SAMs, and STM showed that insulated Pd clusters can be deposited on DT SAMs. Room-temperature Coulomb blockade confirmed the small size of the clusters as well as the insulated nature of these particles, from the substrate and from each other. At 80 K, the I/V curves of these clusters show a very clear Coulomb blockade and staircase behavior.

Experimental Section

Self-assembled monolayers: *n*-Decanethiol (96 %, Aldrich) and *n*-octadecanethiol (98 % Janssen Chimica) SAMs were made from 1 mM solutions of the thiol in ethanol (p.a. Merck). Gold substrates (200 nm of gold on 5 nm of chromium on glass) were obtained from Metallhandel Schroer GmbH, Lienen, Germany. The substrates were rinsed with dichloromethane and directly flame annealed in a hydrogen flame (purity 6). After annealing the substrates were cooled down slowly in air and were then immersed in the ethanolic thiol solution. The substrates were kept overnight in solution after which they were removed and rinsed with dichloromethane p.a., ethanol p.a., and water (Q2 millipore)

Pulsed laser deposition (PLD): A Compex 205 KrF excimer 248 nm laser from Lambda Physik emitting 20 ns pulses at 4 Hz was used. Deposition pressures of between 1 mbar and 10^{-3} mbar were used with Ar as background gas. The Ar flow was varied from 0.2 to 26 mL min^{-1} depending on the pressure. A laser fluence of 4 J cm^{-2} was used, with a spot size of about 3 mm^2. The laser beam entered the vacuum chamber at an angle of 45° with respect to the target normal, and the substrate was placed parallel to the target at a distance of 40 mm. The Au
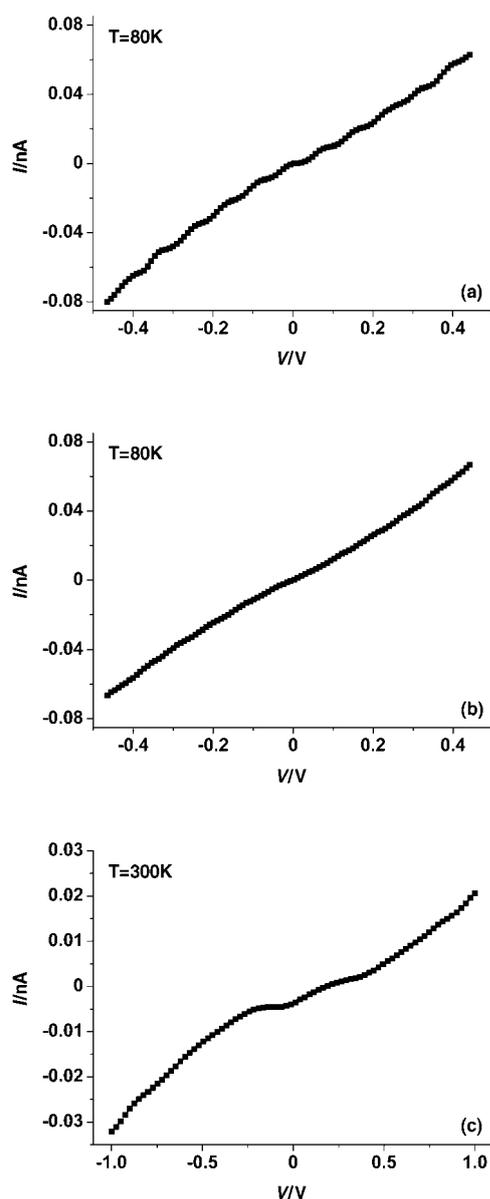
Figure 6. *I*/*V* curves taken for the Pd clusters on a DT SAM and in between the Pd clusters on the SAM at different temperatures: a) Pd cluster at 80 K, b) bare SAM at 80 K, c) Pd cluster at room temperature (298 K).

using the lowest applied load possible (approximately 1 nN). STM was performed under UHV conditions using an Omicron low-temperature STM.

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[21] Deposition of Au, Pd, and Pt on TEM grids was also performed at different target–substrate distances, different pressures, and through nanosieves. These experiments are not described here.

[22] A detailed analysis of the Coulomb blockade will be presented in a separate paper. N. Oncel, A. S. Hallbäck, H. J. W. Zandvliet, E. A. Speets, B. J. Ravoo, D. N. Reinhoudt, B. Poelsema, *Phys. Rev. B*, submitted.

target was 4N (99.99 % pure) and was obtained from Engelhard-Clal (Drijfhout) Netherlands. The Pd was obtained from Goodfellows, Cambridge, UK (99.95 % pure). The Pt was obtained from Engelhard-CLAL/Drijfhout B.V., the Netherlands (99.99 % pure).

Microscopy: TEM images were collected on a Philips CM 30 Twin/STEM, operating at 300 kV. The TEM was equipped with a Kevex EDX detector with a BN window and a Thermo Noran System Six Analyzer. Sample clusters were deposited directly on carbon-coated 200 mesh copper grids. Conducting probe atomic force microscopy (CP-AFM) was performed on a Nanoscope IV multimode equipped with a tuna extension. Gold-coated V-shaped silicon nitride cantilevers (Veeco instruments) were used. Measurements were performed under ambient conditions