

# Fabrication of Arrays of Gold Islands on Self-Assembled Monolayers Using Pulsed Laser Deposition through Nanosieves

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## ABSTRACT

Sandwich structures of gold–self-assembled monolayer–gold were prepared by deposition of gold on alkythiolate self-assembled monolayers on polycrystalline gold, using pulsed laser deposition (PLD) through a nanosieve. The arrays of sandwiches, around 600 nm in diameter, approximately 10 nm high, and spaced 1.6  $\mu\text{m}$  apart, were analyzed using tapping mode atomic force microscopy. Electrochemical copper deposition experiments showed that of the islands deposited on octadecanethiolate monolayers about 15% were electrically insulated from the bottom gold electrode. This means that PLD is a suitable technique for the fabrication of metal–SAM–metal sandwich structures.

Despite some skepticism, the use of self-assembled monolayers (SAMs) in nanoscale electronic devices<sup>1–5</sup> remains a very important topic in nanotechnology. A perfect SAM would be one of the thinnest possible insulating layers between two electrodes for the preparation of nanoscale transistors, and moreover one that can be prepared in a simple low-cost process. To investigate the electronic behavior of a SAM (for example in a SAMFET), one needs to deposit a second electrode on a SAM without damaging it and creating electrical short circuits.<sup>6</sup> The majority of recently reported experiments on molecular electronics fall into one of three categories. First are single-molecule experiments such as measurements in break junctions. In these experiments the stability of the experimental setup, the number of molecules in the junction, and the contact between the molecule and the junction tips are critical issues. Recently, several examples of measurements through single molecules have been reported.<sup>7</sup> Nazin et al. used nanosized gold electrodes fabricated by STM manipulation to measure current through single copper(II)phthalocyanine molecules.<sup>8</sup> Molecules are often investigated for rectifying behavior, which would make them

useful in nanoscale electronic devices.<sup>9</sup> Second are “embedded” single molecule experiments in which a molecule of interest is inserted into an inert SAM and currents are measured using STM. These experiments have the advantage that a SAM is usually very stable and that the molecules of interest can be diluted to obtain genuine single-molecule data. Alternatively, measurements on a finite number of molecules can be reduced to single-molecule properties. STM was used to measure current through thiolate molecules assembled on gold and connected through evaporated gold clusters.<sup>10</sup> Conducting AFM has also been used to measure the conductance of thiolates on gold surfaces.<sup>11</sup> The techniques are usually able to distinguish between one or more molecules that are in contact at a time.<sup>12</sup> Third, attempts are made to measure the conductance of larger numbers of molecules at the same time. An elegant method was reported recently by Kushmerick et al. who used two gold wires, one functionalized with a SAM, which were brought in contact, making it possible to identify the number of molecules through which a current was measured.<sup>13</sup>

While contacting single or a few molecules is not quite straightforward, the fabrication of larger electrodes on SAMs seems even more challenging due to the limited ordered domain size in thiolate SAMs on gold. As several examples in the literature show, evaporated metals such as gold and

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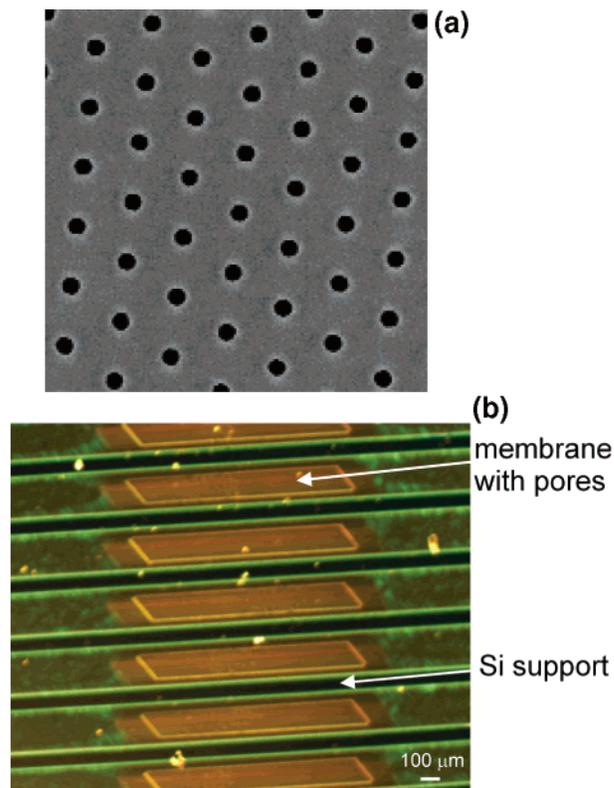
silver can diffuse through thiolate SAMs forming adlayers at the substrate–thiolate interface.<sup>14</sup> The use of SAMs with “sticky” headgroups, such as thiols or cyanides, with an affinity for metals might prevent diffusion of the metal through the SAM. Chen et al. used a nanopore to create a device in which the area of the gold electrodes at the contact point with the SAM was 30 to 50 nm in diameter.<sup>15</sup> The system makes easy measurement of the SAM possible; however, it is not quite easy to prepare, and the electrode size is still rather small. Austin et al. used nanoimprint lithography to construct diodes, using octadecanethiol as an insulating layer, and subsequent e-beam evaporation of gold while the substrate was cooled to liquid nitrogen temperature to prevent diffusion of the gold and damage to the SAM.<sup>16</sup> A technique recently reported to circumvent metal diffusion is nanotransfer printing in which a PDMS stamp, covered with gold, is used to print a pattern on a SAM with a thiol headgroup.<sup>17</sup> In this case the gold is already in solid bulk form and will not diffuse through the SAM.

Here we demonstrate a straightforward method to deposit gold on thiolate SAMs on gold in such a way that the gold does not diffuse through or damage the SAM, and without the use of lithographic process steps. This method yields arrays of Au–SAM–Au sandwich structures, which are nanoscale capacitors. In principle, this method readily allows variation of substrate, SAM composition, and deposited material, and hence can be a useful tool for the exploration of molecular electronics, in particular the role of molecule–metal contacts.

We present in this paper a mild gas-phase deposition technique for deposition of gold on SAMs. Pulsed laser deposition (PLD) enables low kinetic energy gold deposition on SAMs by controlling the kinetic energy of the atoms in the gas phase by means of a background gas and laser energy.<sup>18</sup> To create a pattern of islands we deposited gold through a nanosieve, which acts as a shadow mask. A nanosieve is a thin silicon nitride membrane on a silicon chip containing thousands of pores with diameters down to 300 nm.<sup>19</sup> By using the sieves it is possible to deposit many islands of the desired material in one deposition run.

Figure 1a shows an SEM image of the sieve used as a mask for this deposition. The pores have a minimum diameter of 300 nm. The diameter of the opening of the pores, which is in contact with the SAM during the deposition, is 500 nm. The thickness of the silicon nitride membrane is 1.5  $\mu\text{m}$ , and the center-to-center spacing of the pores is 1.6  $\mu\text{m}$ . The sieve consists of several silicon nitride membranes which span an area of 150  $\times$  1000  $\mu\text{m}$  each. These membranes are supported by a 0.6  $\times$  0.6 cm silicon chip (Figure 1b). Hence, deposition on a SAM through these nanosieves occurs only on the SAM directly below the membranes. In this way, most of the surface remains unaffected and is available as internal control to analyze both gold-SAM-gold structures and native SAM on one sample at the same time.

Gold was deposited on SAMs of octadecanethiol (ODT) and 1,9-nonanedithiol (NDT). These were chosen because ODT forms well-packed monolayers and because NDT has a second thiol group, which can immobilize gold that lands

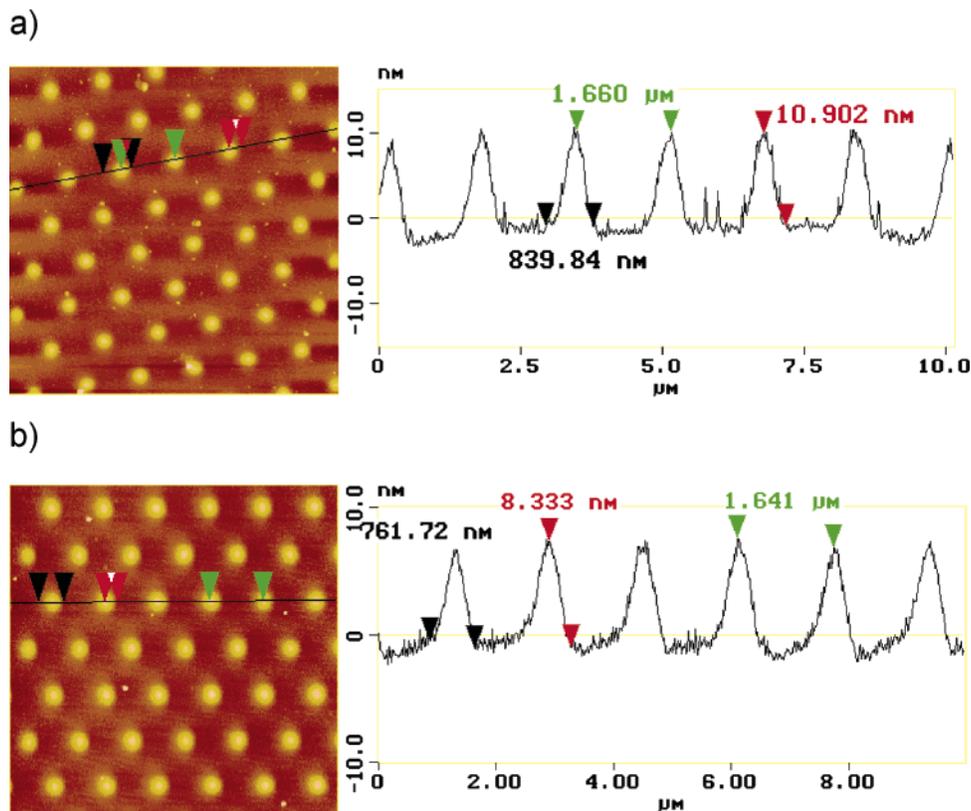


**Figure 1.** (a) SEM image of the silicon nitride membrane of the nanosieve (scale: 10  $\times$  10  $\mu\text{m}$ ). The distance between the pores is 1.6  $\mu\text{m}$ . The pore diameter is 500 nm near the opening and 300 nm inside the pores. (b) Light microscopy image of the nanosieve chip. The thin (black) bands are the supporting silicon, the broad lines are the silicon nitride membrane. Only the center parts of the membranes contain pores.

on the SAM.<sup>20</sup> As substrate, 20 nm polycrystalline gold on silicon (with a 2 nm titanium adhesion layer) was used.<sup>21</sup> ODT SAMs were prepared overnight from 1 mM ethanolic solutions and rinsed with dichloromethane, ethanol, and water. NDT SAMs were prepared from 1 mM hexane solution<sup>20b</sup> and rinsed with dichloromethane. The quality of the SAMs was verified with contact angle measurements before use.

The diameter and height of the deposited gold islands depend on the deposition conditions and the contact of the sieve with the SAM. As can be seen in Figure 2, a regular hexagonal pattern is obtained when using this type of sieve in which the islands have a center-to-center distance of 1.6  $\mu\text{m}$ . The monolayer has no significant effect on the shape of the gold islands or on the pattern in general. AFM images show no difference between islands deposited on ODT SAMs vs those deposited on NDT SAMs.

Different pressures and target-substrate distances were used for the depositions in order to find a compromise between the island shape and size and the kinetic energy with which the atoms or atom clusters reach the SAM. When higher pressures are used during deposition, less material reaches the substrate per pulse and the plasma is more diffuse, leading to larger island sizes. However, the gold reaches the substrate at lower speeds, reducing the possible damage to the SAMs. Deposition at lower pressure leads to better-defined islands,



**Figure 2.** (a) TM-AFM height image of pulsed laser deposited gold islands on an octadecanethiol SAM. The height of the islands is around 10 nm. (b) TM-AFM height image of pulsed laser deposited gold islands on a 1,9-nonanedithiol SAM. The height of the islands is around 8 nm. (Scale of both scans:  $10 \times 10 \mu\text{m}$ ).

but the chance that the SAMs will be damaged is higher. The experiments described in this paper were performed with a target/substrate distance of 40 mm, a laser fluence of around  $4 \text{ J/cm}^2$  (spotsize ranging from 2 to  $3 \text{ mm}^2$ ), and pressures of  $10^{-2}$  and  $10^{-3}$  mbar of argon. We have used a CompeX 205 KrF excimer laser of Lambda Physik, which emits pulses at a wavelength of 248 nm with a length of 20 ns. Depositions were done at a pulse frequency of 8 Hz for 2 to 4 min. The sieve was brought into physical contact with the SAM, while care was taken not to move the sieve and damage the SAM.

To demonstrate that the deposited gold islands were not covered by the SAM (as a result of diffusion of the gold through the SAM) a new SAM was prepared on the gold islands. The sample was immersed for 5 min in a 1H,1H,-2H,2H-perfluorodecanethiol solution ( $\sim 5 \text{ mM}$  in  $\text{CH}_2\text{Cl}_2$ ), after which XPS analyses<sup>22</sup> were performed to measure the relative fluorine concentration on the islands, compared to in the reference SAM. This is possible because of the design of the nanosieve, which gives a pattern of islands only on a limited part of the surface. Due to the spot size of the X-ray beam used in XPS, the islands cannot be analyzed individually. The XPS measurement is averaged over an area of several tens to hundreds of square microns, i.e., on the islands together with the native SAM between the islands. The analyses showed that the concentration of fluorine in the areas with islands was much higher than on the reference areas outside the patterned part of the sample (Table 1). We conclude that the surface of the gold islands remains exposed

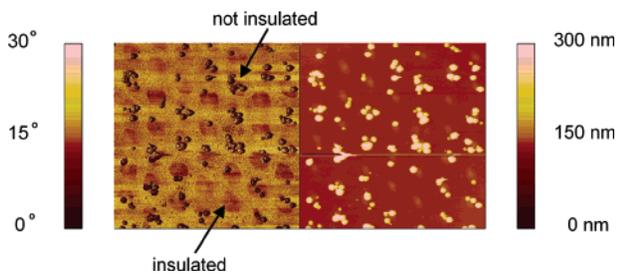
**Table 1.** Elemental Ratio of Fluorine to Carbon on Samples after Immersion in a Fluorinated Thiol Solution (as calculated from XPS measurements)<sup>a</sup>

SAM	[F]/[C] islands	[F]/[C] SAM	[F]/[C]islands/[F]/[C] SAM
NDT	0.88	0.19	4.6
ODT	0.15	0.006	25

<sup>a</sup> The fluorine-to-carbon ratio is given for areas of the SAM where gold islands were deposited ([F]/[C] islands) and for areas of the SAM where no gold islands were deposited ([F]/[C] SAM). See text for details.

after PLD and that a SAM of fluorinated thiols can be readily prepared on top of these islands. Some fluorine is also detected in the reference areas of the samples where no islands were deposited due to the insertion of fluorinated thiol molecules from solution into the existing SAM. The higher ratio of fluorine on the islands to fluorine on the reference SAM measured for the ODT SAM compared to that for the NDT SAMs is in agreement with this: insertion and replacement of thiolates is slower in SAMs that are well packed.

Electrochemistry was used to investigate whether the islands are electrically insulated from the bottom gold electrode by the SAM. A fast method to analyze thousands of islands in a parallel way is the electrochemical deposition of copper from solution on the islands. Provided that modest potentials are used, islands without short circuits behave as electrically insulated objects while islands with short circuits to the bottom electrode behave as small electrodes and hence will “grow” copper on them. The substrate after PLD was



**Figure 3.** TM-AFM phase and height image of an octadecanethiol SAM on gold after subsequent pulsed laser deposition of gold islands and electrochemical copper deposition. (Scale of both scans:  $10 \times 10 \mu\text{m}$ ).

used as working electrode and an aqueous solution of  $\text{CuSO}_4$  (10 mM) and  $\text{H}_2\text{SO}_4$  (10 mM) as the electrolyte. A Pt disk was used as a counter electrode and placed close to the working electrode in a parallel geometry. One cycle from  $-0.7 \text{ V}$  to  $-0.75 \text{ V}$  (vs  $\text{Hg}/\text{Hg}_2\text{SO}_4$  at  $0.01 \text{ V/s}$ ) was used to reduce copper(II) from the solution on the not-insulated islands. With ODT SAMs, part of the islands deposited at  $10^{-2} \text{ mbar}$  showed copper deposition while others remained unaffected (Figure 3). If a deposition pressure of  $10^{-3} \text{ mbar}$  or lower was used, no insulated islands were obtained: electrochemical experiments showed that all the islands showed copper deposition. When higher deposition pressures were used, the islands grew together laterally and could no longer be distinguished as individual electrodes. With NDT SAMs no insulated islands were found; in other words, all islands showed copper growth, irrespective of the deposition pressure.

Figure 3 shows that around 15% of the gold islands did not grow copper which would indicate that they are isolated from the bottom electrode by the ODT SAM. It also shows that, apart from on the islands, no copper grew on the SAM itself, indicating that there are no significant defects in the monolayer.<sup>23</sup> This demonstrates that copper deposition can take place only on areas where there is electrical contact with the gold substrate. From these electrochemical experiments it can further be concluded that the islands are not connected. When the electrochemical deposition experiment was performed on a sample on which a monolayer of fluorinated thiols had been formed on the islands, no copper growth took place at all. The height of the copper clusters is constant, in this experiment around 80 nm, indicating that the deposition starts at the same time on all the not-isolated islands.

In conclusion, PLD is a useful tool to deposit arrays of gold electrodes on top of SAMs of ODT. Electrochemical copper deposition experiments and AFM measurements show that part of the islands is not in electrical contact with the bottom electrode. NDT SAMs gave no insulated islands, so it seems that the packing of the SAM is more important than the headgroup when depositing metal islands on SAMs. It should be noted that the dimensions of the electrodes are considerably larger than the average crystalline domain sizes in SAMs. When smaller electrodes would be deposited the number of isolated islands likely increases.

**Note Added after ASAP Posting.** This article was posted ASAP on 4/07/2004. Changes have been made to the author addresses and affiliations on the first page of the article. The correct version was posted on 4/13/2004.

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- (20) NDT SAMs were prepared from hexane solutions, rinsed quickly with dichloromethane, and stored in a nitrogen box. According to literature and our own findings this yields SAMs in which the dithiols are attached to the gold surface only with one thiol group while the other one sticks out towards the SAM/air interface. XPS showed the  $\text{S}(2p_{2/3})$  signal of the bound sulfur (162.13 eV) and the  $\text{S}(2p_{2/3})$  signal of the unbound sulfur (163.43 eV) which had equal intensities. The relatively low contact angle of  $85^\circ$  indicates a thiol-terminated surface. See also: (a) Chah, S.; Fendler, J. H.; Yi, J. *Chem. Commun.* **2002**, 2094–2095. (b) Kohli, P.; Taylor, K. K.; Harris, J. J.; Blanchard, G. J. *J. Am. Chem. Soc.* **1998**, *120*, 11962–11968.
- (21) Substrates were obtained as 4 in. wafers from Ssens B. V. Hengelo (Ov.), The Netherlands. Substrates were spliced into  $\sim 1 \text{ cm}^2$  chips and rinsed in dichloromethane or cleaned by oxygen plasma treatment before preparing SAMs.
- (22) XPS analyses were performed on a Quanter SXM, from Physical Electronics, equipped with monochromator. The X-ray source is Al with  $\text{K}\alpha$  of 1486.6 eV. The spot size is  $100 \mu\text{m}$  in maximum diameter.
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