Supplemental Information

Chemical Self-Assembly Strategies for Designing Molecular Electronic Circuits

Dustin Olson, Alejandro Boscoboinik and Wilfred T Tysoe *

Department of Chemistry and Biochemistry and laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA

Materials and Methods

Fabrication of Gold Nanogaps

The gold nanoelectrodes were fabricated using a JOEL model JBX-6300FS electron-beam lithography system at the Center for Functional Nanomaterials at the Brookhaven National Laboratory. A uniform film of a (1:2) ZEP520A:Anisole resist, was spin-coated on a SiO_2 wafer with a 300 nm-thick oxide layer at 2 krpm for 60s and then baked on hot plate at 180 ˚C for 3 min. Gold electrodes were defined using an electron dose between 300-600 $\mu C/cm^2$ using beam current of 1 nA with design gap of 0 nm.[1] The film was developed in cold hexyl acetate at -20 ˚C for 90 sec. Following development, nanogaps were fabricated by e-beam evaporating a chromium adhesion layer which was 3 nm thick and deposited at a rate of 0.5Å/s followed by a 30 nm-thick film of gold deposited at a rate of 1.0 Å/s, using a Kurt J. Lesker PVD-75 Evaporator. The final lift-off took place by sonication in pure acetone.

Contact pads were fabricated using photolithography that was carried out using a Karl Zeiss MA6 Mask Aligner using S1811 photoresist resist, which was spin coated at 4 krpm for 60s, then baked at 110 ˚C for 3min. A chromium mask was aligned with the previously fabricated nanogaps and exposed to UV radiation for 8.5 s, then developed in MF-312/H_2O 2:3 for 75s. A 3 nm thick chromium adhesion layer was deposited, followed by a 100 nm thick gold film using the conditions given above. The resist was then lifted-off in remover 1165 at 80 ˚C.

Fabrication of Gold Nanoparticle Arrays

The electrical characteristics were measured for larger-scale nanoparticles arrays to precisely monitor the change in current with 1,4-PDI dose. They were fabricated using gold electrodes deposited onto an oxidized silica substrate to create a gap of 0.25 mm between the gold

electrodes. The electrode gap was defined by a chromium mask. The pattern was developed using photolithography using AZ 1512 resist spun onto a silica substrate using a spin coater at ~3 krpm for 60 s. The resist was exposed using an ultraviolet lamp (TLC) for 30 min and then developed in 8% TMAH (tetramethyammonium hydroxide). A chromel adhesion layer (~5 nm thick) was deposited on the silica prior to evaporating a ~200 nm-thick film of gold in a vacuum evaporator. The film thicknesses were estimated from the total amount of material flash-evaporated and the distance from the source to the silica sample.

The sample was then attached to a sample manipulator in a high vacuum chamber operating at a base pressure of ~1×10^{-8} Torr. Gold was deposited from a home-built alumina tube furnace at a rate of ~0.02 Å/s and was monitored by a QCM (Sigma Instruments SQM-160) until the final desired film thickness was obtained.

Measurement of I/V Curves

The *I/V* characteristics were measured by applying a voltage between the gold electrodes *via* a D/A converter and the resulting current measured by means of a picoammeter that was monitored by an A/D converter to yield *I/V* curves directly. No changes were found in the I/V curves for repeated experiments indicating that the samples remained stable. The temperature dependence of the conductivity was measured by allowing a cooled sample to warm slowly to ambient temperature. 1,4-PDI was dosed onto the sample via a home-built Knudsen source [2] where the flux was gauged by the increase in background pressure in the vacuum chamber and was varied by changing the temperature of the 1,4-PDI sample.

Figure S1: Plot of $ln(\sigma)$, where σ is the film conductivity, versus $1/\sqrt{T}$ where T is the sample temperature for an array of nanoparticles grown by gold evaporation on a silica substrate dosed to saturation with 1,4-PDI in high vacuum. Shown are SEM images of the film where the top image shows the raw data and the bottom image is processed to more clearly show the nanoparticles.
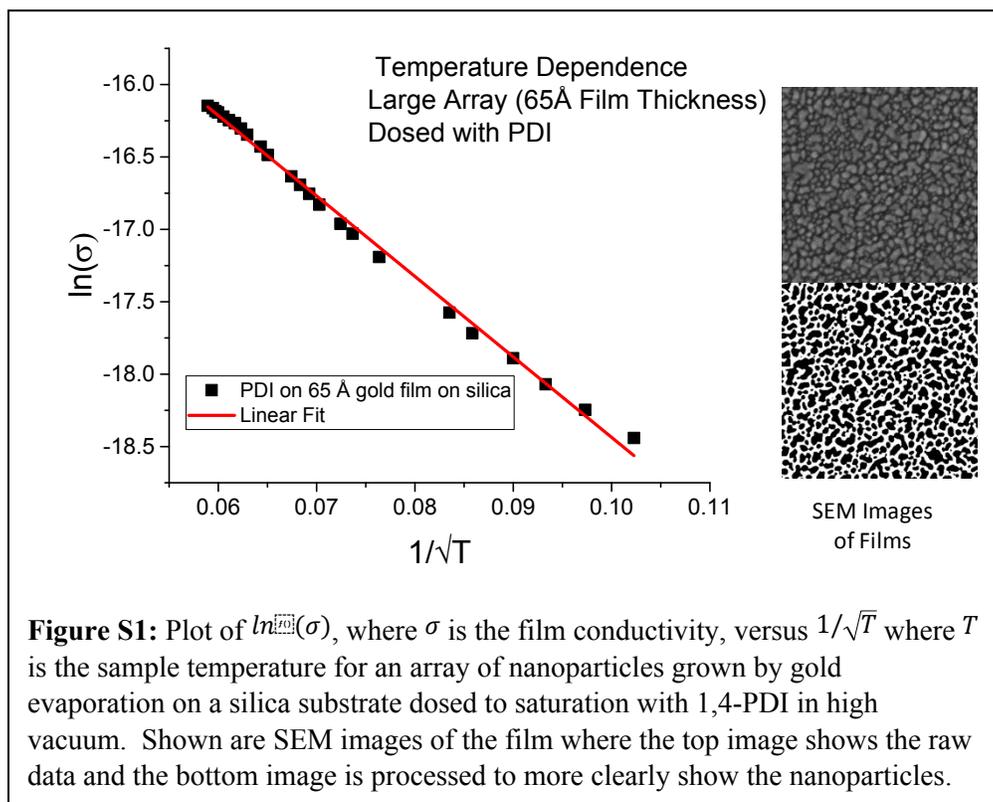
Estimate of Average Particle Separation s as a Function of Film Thickness, t for an Array of Gold Nanoparticles on Silica

Figure S2: Plot of the number of nanoparticles per unit area as a function of gold film thickness on silica.
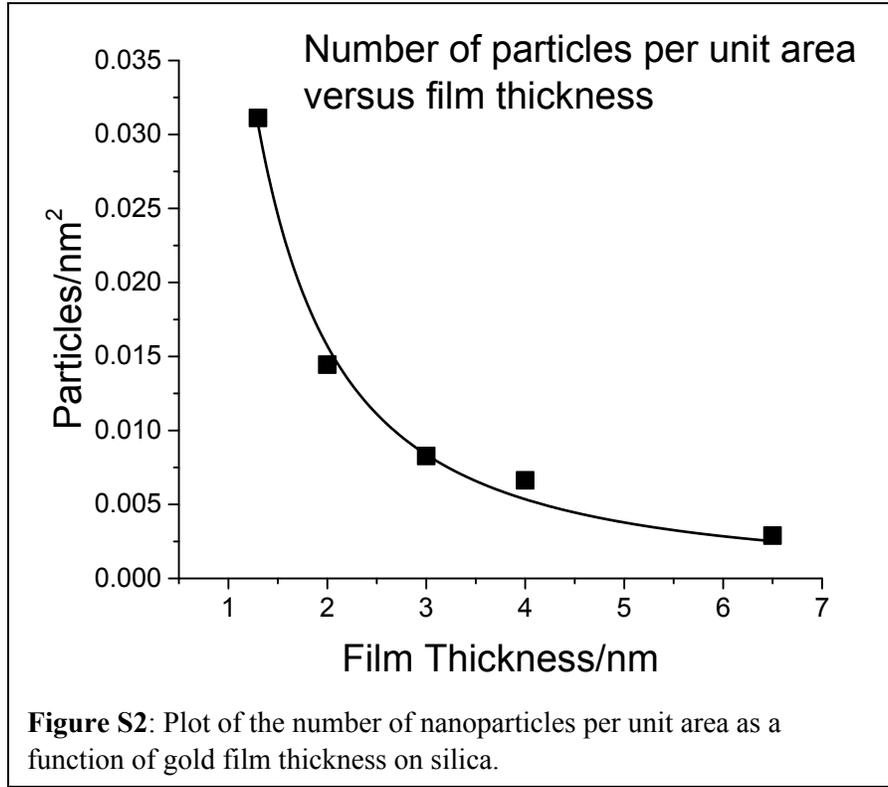
Secondary Electron Microscope (SEM) images of gold nanoparticles deposited in vacuo on silica are displayed in Figure 1 for various total film thicknesses, t, which are measured using a quartz crystal microbalance and are used as a basis for estimating the average particle separations as a function of film thickness. The SEM images were analyzed using ImageJ,[3] where the contrast is first enhanced to more easily identify the particles. The images were analyzed to count the number of particles per unit area and the results are shown plotted in Figure S2 (■) as a function of the thickness of the film, and fitted to a allometric function:

$$N(t) = N_0 t^n$$

(S1),

where $N_0 =$ $4.6 \pm 0.2 \times 10^{-2}$ particles/nm² and $n =$ -1.55 ± 0.10.

The SEM images were analyzed to measure the proportion of the surface covered by gold as a function of film thickness and the results are displayed in Figure S3 (■) and fits are also shown to an Allometric growth equation:

$$\alpha(t) = \alpha_0 t^m$$

(S2),

where $\alpha_0 = 0.29 \pm 0.01$ and $m = 0.36 \pm 0.03$.

Figure S3: Plot of the proportion of the silicon surface covered by gold nanoparticles as a function of total gold film thickness.
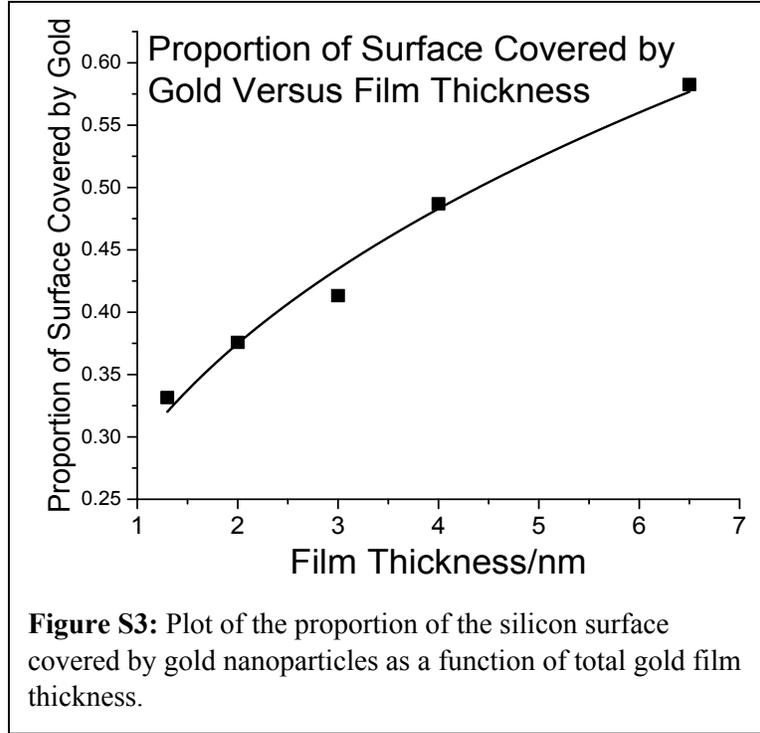
It is not possible to use image analysis software to measure the closest interparticle distances as a function of films thickness. However, an estimate of the variation in interparticle distance can be made from the measurements of $N(t)$ and $\alpha(t)$ as follows. It is assumed that circular particles with average diameter $d(t)$ are uniformly distributed on the surface with an average separation $s(t)$ so that the number of nanoparticles per unit area is given by:

$$N(t) = \frac{2}{\sqrt{3}(s(t) + d(t))^2}$$

(S3).

The area occupied by a particle is $\dfrac{\pi d^2}{4}$, so that the total area occupied by nanoparticles per unit area is given by:

$$\alpha(t) = \frac{\pi N(t)d(t)^2}{4}$$

(S4).

The value of $s(t)$ is obtained by eliminating $d(t)$ from Eqns. S3 and S4 to yield and estimate for the average particle seperation as a function of film thickness as:

$$s(t) \propto \frac{1}{\sqrt{N(t)}}\left(\sqrt{\frac{2}{\sqrt{3}}} - \sqrt{\frac{4\alpha(t)}{\pi}}\right)$$

(S5).

The results of Eqn. S5 are compared with those of direct measurements of the interparticle spacings measured manually from the SEM images of the nanoparticle coverages surface as a function of film thickness in Figure S4 (■), where the variation in particle separation

Figure S4: Plot of average particle separation obtained from Eqn. S5 (——) , using a scaling factor of 1.25, as a function of total gold film thickness compared with the results of direct measurements of interparticle spacings (■).
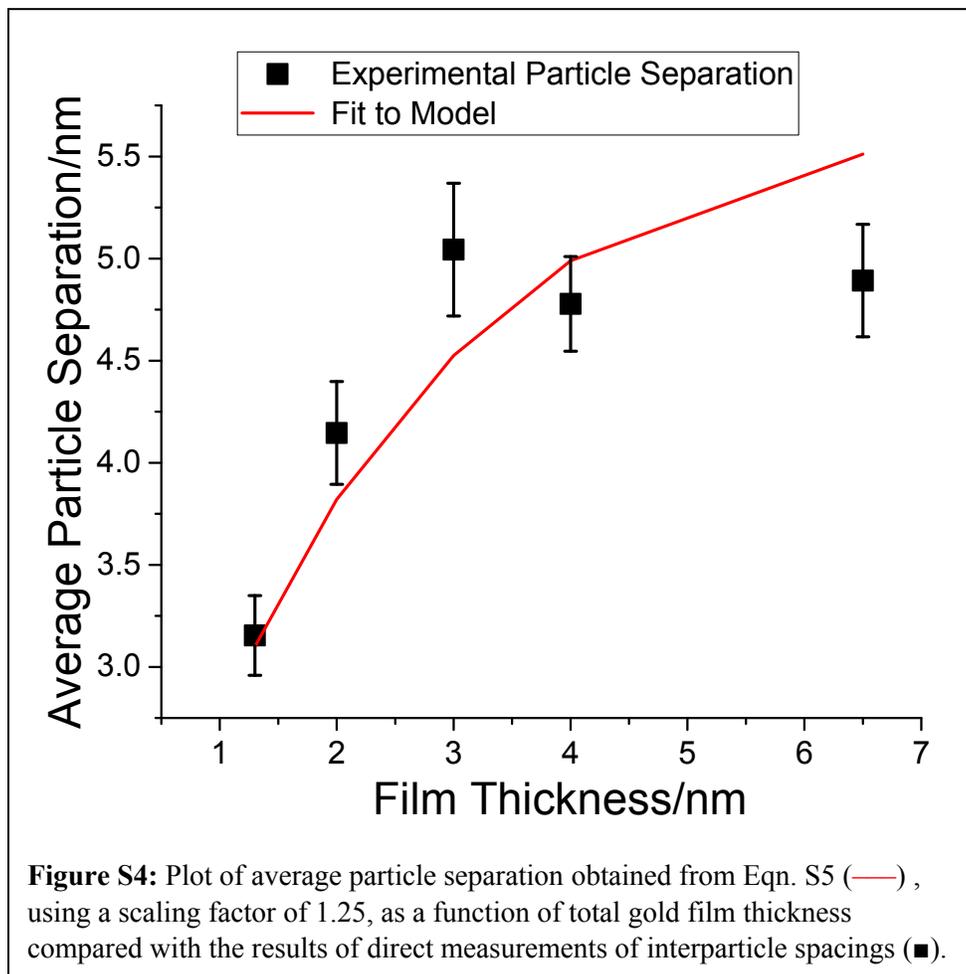
as a function of film thickness is in accord with the simple analytical model.

References

1.   M. S. M. Saifullah, T. Ondar uhu, D. K. Koltsov, C. Joachim and M. E. Welland, *Nanotechnology*, 2002, **13**, 659-662.
2.   C. J. Baddeley, M. Tikhov, C. Hardacre, J. R. Lomas and R. M. Lambert, *The Journal of Physical Chemistry*, 1996, **100**, 2189-2194.
3.   C. A. Schneider, W. S. Rasband and K. W. Eliceiri, *Nature Methods*, 2012, **9**, 671.