

Arrays of Cu²⁺-Complexed Organic Clusters Grown on Gold Nano Dots

A. de Picciotto^{*,**}, A.D. Wissner-Gross^{**}, G. Lavallee^{**} and P.S. Weiss^{**}

^{*}Montclair State University, Upper Montclair, NJ, USA, depicciottoa@mail.montclair.edu

^{**}The Pennsylvania State University, PA, USA

ABSTRACT

Controlled growth of organic multilayers from periodic gold dot arrays on SiO₂ surfaces has been used to create complex overlayer structures. Nanosphere lithography was first used to produce uniform metal patterns with particle sizes of 40 nm, spaced by gaps of 110 nm. These particles served as the nucleation centers for layer-by-layer growth of organic/metal ion complexes. The resulting structures can either be isolated adsorbed dot structures on a continuous surface or continuous networks of the adsorbed materials with isolated arrays of SiO₂ surface dots. Step-by-step multilayer growth from small isolated centers enables us to monitor the process by direct surface imaging techniques.

Keywords: adsorption, nanostructures, nucleation, surface structure

The fabrication of periodic arrays of submicron structures on surfaces has potential applications in optical filtering [1], magnetic storage [2], biological probes [3], and molecular electronics [4,5]. Much effort has been directed toward finding methods for creating these structures. One particularly economical method is nanosphere lithography [6-13], which uses a monolayer or a bilayer of spheres as a porous deposition mask for a large set of materials. Nanosphere Lithography (NSL) has been used to produce several different classes of metal particle patterns with the smallest reproducible gap [9] of 165 nm between particles. The recent development of the molecular ruler nanofabrication process [14-17] has enabled the creation of very closely spaced metal structures with spacings of less than 20 nm. The introduction of molecular rulers for quantitatively scaling down the gap between neighboring structures offers a way to extend the capabilities of NSL.

Here we present a combined method for constructing an array of isolated Cu²⁺-complexed organic particles on a SiO₂ substrate and the extension of this array to a continuous network. A hexagonally packed monolayer of polystyrene nanospheres is used as a shadow mask for metal evaporation onto the substrate. After evaporation, dissolution of the nanospheres leaves an array of triangular metal particles on the SiO₂, which are then used as parent

structures for the molecular ruler process to create a new nanostructure pattern.

Suspensions of non-functionalized polystyrene spheres of diameter 240-400 nm (Bangs Laboratories) were diluted (1:2) by a 1:400 solution of Triton X-100 (Sigma-Aldrich) in methanol (VWR) [9]. After dilution, the nanosphere suspensions were spin-coated onto isopropanol cleaned oxidized Si wafers with areas between 0.5 and 2.0 cm². The nanospheres were deposited using a spin coater (Headway Research Inc., Model CB15) operated at ~500 rpm for 2 minutes. Excess fluid at the perimeter of the wafers was wiped dry. A 40-sec O₂/Ar Reactive Ion Etching (RIE) was performed (Plasma-Therm 720 RIE, SLR Series) to remove surfactant residues remaining in interstices of the sphere monolayer; this step is crucial to the adhesion of the metal deposited to the SiO₂ surface. The monolayer was then used as a mask (Figure 1), first for electron gun evaporation of a 6-nm Ti underlayer, followed by thermal evaporation of a 40- to 100-nm Au layer (Kurt J. Lesker E-gun/Thermal Evaporator). Subsequent removal of the nanospheres by sonication in CH₂Cl₂ (J. T. Baker) for 2 minutes [9] left a hexagonal array of ~40-nm-wide metal particles on the substrate (Figure 2).

Coordinated metal ion-organic multilayers [14-17] were adsorbed on the metal dots, by alternate deposition of a SH-(CH₂)₁₅-COOH (mercaptoalkanoic acid) molecules (1 mM in Ethanol) and Cu²⁺ ions (Cu(ClO₄)₂ (Aldrich), 1 mM in Ethanol) [18]. Adsorption times for the organic molecules ranged from 4h to overnight. Cu²⁺ adsorption time was 3 min. Samples were rinsed by ethanol and dried under a nitrogen stream between all adsorption steps and after adsorption was completed. Here, 10 or 20 such layers (each layer consists of one organic molecule plus one Cu²⁺ ion) were adsorbed on different samples, although we have successfully used this technique with 3-30 layers in prior work. The linear growth of the layers was verified using Ellipsometry: the thickness of each additional layer grown on gold thin films was measured and was identical to all other layers (2.0±0.2 nm) [18]. X-ray Photoelectron Spectroscopy (XPS) measurements were conducted as an independent characterization technique to verify the organic layer contents. The XPS atomic concentrations of the various chemical elements (i.e. C=84.2%, O=6.9%, S=4.7%, Cu=3.7% [±0.2]) reflects precisely the composition of the layers considering small (<1%) sulfur

contaminations that are always present in such samples. 0.5% of Au was found as well and is expected from the underlying gold surface. For FESEM imaging, the samples were coated by 2 nm evaporated gold. Field Emission Scanning Electron Microscope (FESEM) images were taken using a Leica LEO 1530 FESEM and a JEOL JSM-6300F FESEM.

Results and Discussion

Figures 3 and 4 show the selective assembly of the organic multilayers on the gold triangle array. Figure 3 shows a FESEM image of a sample coated with ten metal ion complexed organic layers. Ten complexed organic layers are expected to yield 20-nm thick coating since each layer thickness is 2 nm. The FESEM image reflects this expected thickness of *ca.* 20 nm grown off of the gold dots. Figure 4 is a similar image of a different sample coated with 20 layers of the complexed organic molecules. Here the thickness of the layers is *ca.* 40 nm, corresponding to the length of each molecular layer multiplied by the number of layers formed. In this image it can be seen that multilayers grown from adjacent gold patterns have reached each other and closed the gap completely. In some of these crossing areas, gaps of less than 10 nm appear to remain, although growth in other areas persists. This might be attributed to diffusion limitations of molecules into these thin gaps. The gold dots can be seen inside each structure. Note that in figure 4 the gold dots are not always centered within each structure, yet the organic multilayers follow a periodic array. It might be that the gold array in the imaged area was not totally symmetric prior to molecular adsorption (cf. irregular spacings between parent structures in some areas of fig. 2). Nevertheless the diffusion limitations of adsorption caused by neighboring growing clusters have the effect of healing this initial asymmetry.

The dark holes appearing in the images might be areas of incomplete growth between adjacent growing clusters. Structure deformation under the SEM beam is excluded by the evaporation of 2-nm gold layer on top of the structure prior to imaging (figures 3, 4 captions). Imaging of different samples without the 2-nm gold adlayer shows identical structures with lower image contrast. These nanostructures are further used as the basis for the molecular ruler process (figure 5). In this process, gold is deposited on top of the organic structures. Gold deposition is followed by the removal of the organic layers in an organic solvent. The result is an array of star-shaped structures that forms in between the original gold dot array. The shapes and sizes of these nanostructures can be easily controlled using organic molecules of various sizes and by choosing the desired number of organic layers deposited.

The growth of the organic layers from a well-defined gold dot array enables direct imaging of the organic multilayer formation in its initial steps. No deposition, extraction or manipulation of the material is needed. By reducing the dimensions of the gold nucleating centers and by using

various functional organic molecules with or without metal ions, a large number of organic nanoparticles can be created. Hybrid inorganic/organic or pure inorganic clusters can be similarly formed [19]. The organic nanoparticles formed complement the family of inorganic nanoparticles studied to date (see ref. [20] and references therein). The fabrication technique demonstrated here can help to create nucleation centers for studying growth mechanisms and for creating patterned surfaces for possible use in optical and electronic devices.

We have shown the controlled uniform growth of organic multilayers from a periodic gold dot array on SiO₂ surfaces. This special geometry enables imaging of the metallorganic structure formation in its initial steps. This process can be used to fabricate new organic/metal nanostructures for possible uses in electronic or optical devices. The layer-by-layer growth can yield an isolated organic dot structure on a continuous surface or a continuous organic network exposing only an isolated array of surface dots. The molecular ruler technique enables the formation of novel nanostructure arrays. The fine structure design depends on the initial dot spacing, the length of the organic molecule chosen and on the number of layers grown. Each of these parameters can be easily modified.

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1 ILLUSTRATIONS

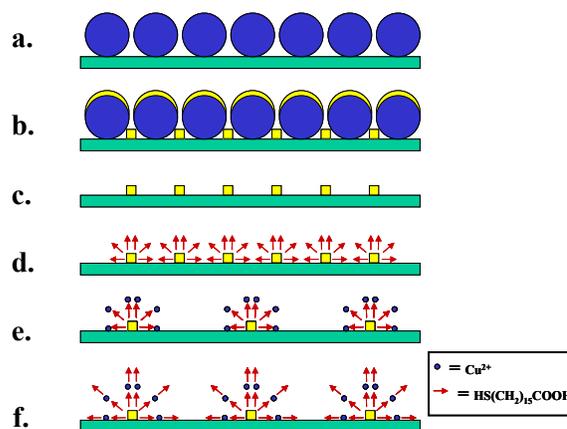


Figure 1: Fabrication scheme. **(a)** Nanospheres deposited on SiO₂ surface. **(b)** Metal evaporation onto the spheres and into the layer gaps. **(c)** Dichloromethane dissolution of the nanospheres. **(d)** Adsorption of SH(CH₂)₁₅COOH (arrows) monolayers. **(e)** Cu²⁺ ion (small dots) complexation to SH(CH₂)₁₅COOH monolayers. **(f)** Adsorption of a second SH(CH₂)₁₅COOH layer on top of a Cu²⁺ layer.

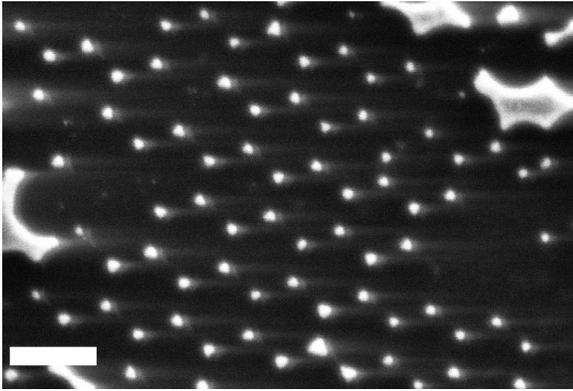


Figure 2: FESEM image of an array of Au/Ti particles formed by evaporating the metals through holes in a hexagonally packed 240 nm nanosphere mask. Particle shadow is formed by the FESEM detector position and is not inherent to the sample. Bar = 300 nm

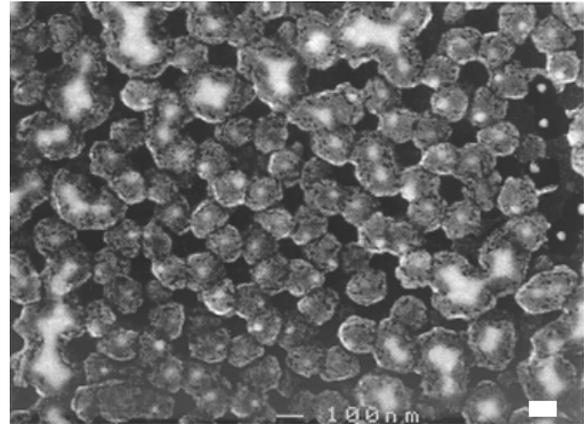


Figure 4: FESEM image of 20 layers of Cu^{2+} complexed mercapto-alkanoic molecular layers grown on a gold dot array: The sample was coated with 2 nm evaporated gold to enhance SEM contrast and to stabilize the organic structures that are otherwise sensitive to the electron beam. Nanospheres with diameters of 240 nm were used as a mask for this gold dot arrays. The scale bar indicates 100 nm.

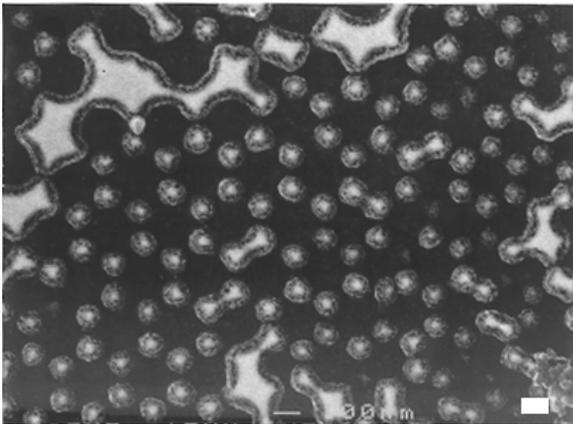


Figure 3: FESEM image of 10 layers of Cu^{2+} complexed mercapto-alkanoic molecular layers grown on a gold dot array. The sample was coated with 2 nm evaporated gold to enhance SEM contrast and to stabilize the organic structures that are otherwise sensitive to the electron beam. Nanospheres with diameters of 240 nm were used as a mask for this gold dot arrays. The scale bar indicates 100 nm.

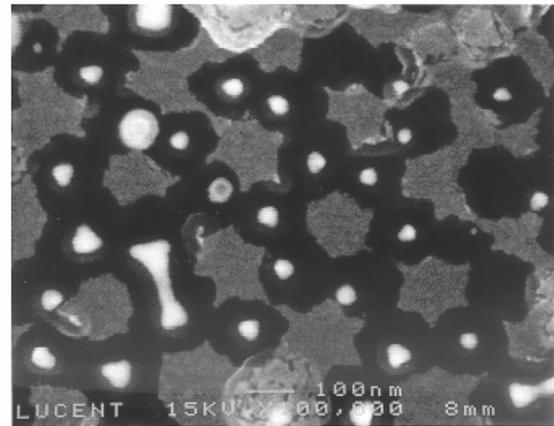


Figure 5: subsequent gold deposition on the sample shown in figure 4, followed by organic layers removal to form an array of star-shaped nanostructures within the original gold-dot array. Bar = 100 nm.

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