

# ASSEMBLY OF NANOCCLUSERS ON SILICON SURFACES

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## ABSTRACT

The electrostatic association between mercaptosuccinic acid coated gold clusters, about 2 nm in diameter, and amine silane derivatized silicon was examined. Relatively good coverage takes place in the pH range between 5 and 6 that coincides with the dissociation of the acid coating on the gold clusters. The latter was established by infrared spectroscopy taking advantage of the typical carboxylate vibrations that differ from the protonated species. The dissociation of the gold bound acid takes place at higher pH values than that on the free acid. Such displacements are anticipated for monolayers of bases or acids but it is smaller in the spherical cluster than on flat surfaces. The microstructure of the films may be manipulated through control of pH, contact time and the nature of the crystalline substrate. Preliminary experiments were also conducted to assemble semiconductor quantum dots, cadmium selenide cores, on silicon surfaces containing a monolayer coating as in the case of gold. Assembly in this case did not involve electrostatic interactions since ions were not involved but the physicochemical affinity between the treated surface and the coating on the quantum dot.

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## INTRODUCTION

The preparation and manipulation of nanoclusters, particularly gold, is one of the leading areas spearheading efforts to develop and implement nanotechnology, which has become one of the main thrusts in current interdisciplinary scientific pursuits. A few representative examples are given to illustrate this assertion stemming from widely diverse fields such as catalysis<sup>1</sup>, electronics<sup>2</sup> and nanobiotechnology<sup>3</sup>.

The great affinity of gold for sulfur compounds proves to be a powerful tool that enables the preparation of nanoclusters coated with a wide variety of ligands and thus provides handles for further manipulation<sup>4</sup>. This characteristic is particularly useful in developing strategies for assembly following a bottoms-up approach. Assembly of a multi-particle system is a prerequisite to derive any technological benefit from a given device such as electronic components or sensors. Implicit in this is the ability to connect the assembly to the macroscopic world via electrical or optical means and herein resides the demanding challenges for work in this area.

We attempted in this study to assemble gold nanoclusters coated with thiols terminated with carboxylic acid functionalities to single crystal silicon surfaces derivatized with complementary functionalities, i.e. amines, as a preliminary step to span conducting macroscopic pads with the ultimate goal of observing nonlinear electronic conduction. Nonlinear electronic conduction is a consequence of single electron charging of metallic particles smaller than a few nanometers, which may be exploited for advanced computing.

The assembly strategy is based on the use of non-covalent electrostatic interactions as the driving force, which was anticipated to be pH sensitive. This approach is not novel in broad terms, having been examined by others<sup>2d, 2e, 5</sup>, but the specifics of the present study, not duplicated before, are the use of an amine monolayer bound on silicon and carboxylic acid terminated thiol bound to gold clusters. Variants of this, involving a flat gold surface coated with thiol terminated with a carboxylic acid interacting with volatile amines or an amine silane on silicon interacting with citrate coated gold colloids were previously studied<sup>6a, b</sup>. In addition to this we conducted preliminary studies to assemble quantum dots containing a cadmium selenide core on silicon surfaces treated as in the case of the gold particles.

## EXPERIMENTAL

*Colloid preparation.* Conducted according to a procedure described by Chen and Kimura<sup>7</sup> that involves mixing gold, 0.5 mmole as  $\text{HAuCl}_4$ , in methanolic solutions with either 1.25 mmole mercaptosuccinic acid or thioctic acid dissolved in about 100 mL methanol followed by reduction with  $\text{NaBH}_4$ . The isolated products are water-soluble sodium salts and were characterized by X-ray diffraction and FTIR, obtaining results in agreement with the published procedure. Average crystallite sizes were 2.0 and 3.5 nm for the succinic and thioctic acid coated particles, respectively, as calculated by the Scherrer equation. Chemical analyses showed 56.3 wt % Au and 9.5 wt % Na for the mercaptosuccinate coated gold while 70.2 wt % and 2.0 wt % were the corresponding values for the thioctic acid coated gold.

*Silicon derivatization.* Single crystal silicon covered with native silica and with  $\langle 100 \rangle$  as the direction of the surface normal was used. The silicon was cleaned by sonication in acetone followed by methanol and finally treated with piranha solution (7:3

volume mixture of concentrated  $\text{H}_2\text{SO}_4$  and 30 %  $\text{H}_2\text{O}_2$ . The cleaned silicon was placed, after rinsing with water and drying, in contact with a 1.0 % solution of (aminoethylaminomethyl)phenethyl-trimethoxysilane, PEDA in 95:5 methanol water containing 1mM acetic acid as catalyst, following the procedure of Dressick et al<sup>8</sup>.

*Instruments.* Infrared spectra of aqueous solutions of mercaptosuccinic coated gold and free mercaptosuccinic acid were obtained using a “Circle cell”. Microscopic imaging of surfaces was performed by AFM in the tapping mode with a Nanoscope III from Digital Instruments while ellipsometry was conducted with a model L117 C Gaertner ellipsometer. Additional microscopic imaging was obtained by transmission electron microscopy, TEM, using a Philip Tecnia 20 microscope operating at 200keV. Measurements of pH were conducted using a freshly calibrated Ross electrode connected to a Corning pH meter.

*Assembly procedure.* Aqueous solutions of the gold sol were prepared, containing 0.5 mg/mL of the solid thiol coated clusters that are initially present as the sodium salt and have a pH of about 9.5. For each run, the gold solution was acidified with 0.1 N hydrochloric acid to a desired pH while purging with argon to exclude carbon dioxide. The derivatized silicon pieces that had been baked at 120 C for 20 min were coated by contact with the gold solution under argon. A stream of argon was maintained above the solution surface, to exclude carbon dioxide, while the silicon was being coated.

The above procedure was modified for the assembly of films on TEM grids (lacey  $\text{SiO}_x$  on Formvar supported on 300 mesh copper, Ted Pella Inc. Redding, CA.). The grids were exposed to ozone and then soaked in the silane solution for 3 h., rinsed in methanol, baked at 120 C for 20 min and finally exposed to the gold sol, adjusted to pH 5.0 for 3 and 18 h periods for two different sets of grids.

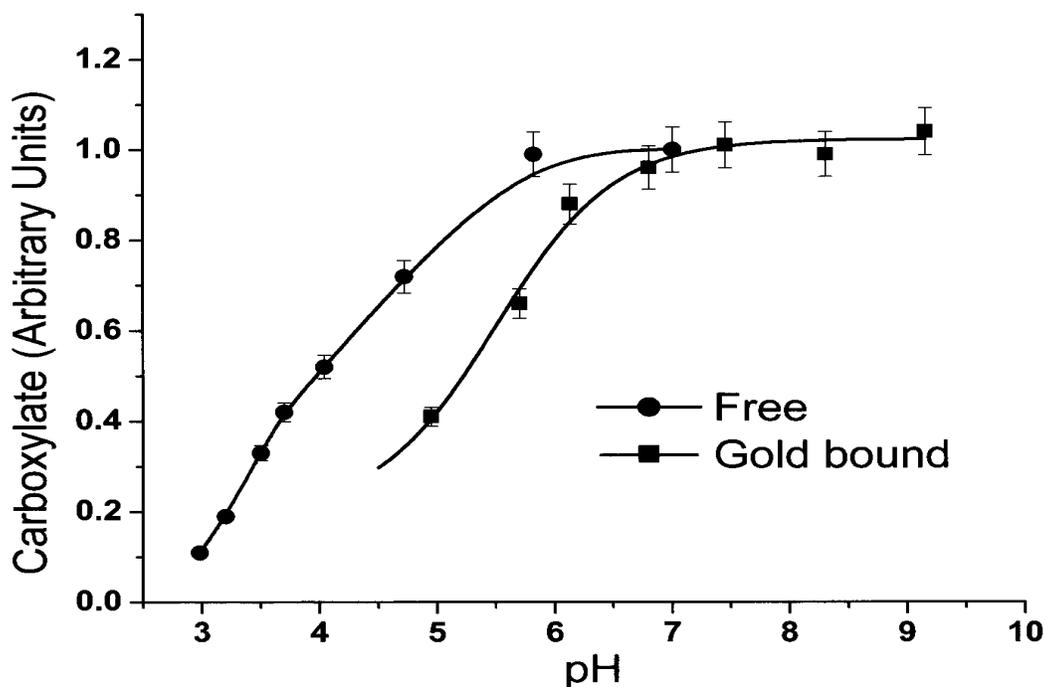


Figure 1. Carboxylate content, established by infrared spectroscopy, of mercaptosuccinic acid dissolved in water as compared with the acid bound as a monolayer to gold nanoclusters.

## RESULTS AND DISCUSSION

The presence of a monolayer of amine on the silicon was confirmed by ellipsometry, which revealed a film thickness of 10 Angstrom, in agreement with the observations of Dressick et al<sup>8</sup>. We also used a value of 1.508 (provided by Gelest) as the refractive index of the amine. Contact between the derivatized silicon and gold sol covering the pH range 4.0-7.3 revealed, as expected, a marked pH dependence on the extent of gold deposition with better coverage taking place in the middle of that pH range. This was assessed by the AFM images, which revealed different microstructures, to be discussed later. A pH dependence of the electrostatic association between the complementary carboxylate and alkyl ammonium ions was anticipated and is expected to maximize at a pH where each species reaches an optimum value corresponding to electroneutrality as observed in a number of studies<sup>9</sup>. For monolayer films containing ionizable moieties marked shifts take place in the dissociation as a function of pH of the ionic species bound on the surface as compared to the free species in solution. Under these surface-bound conditions both acids and bases become much weaker when bound in monolayers because of enhanced opportunity to form hydrogen bonds. This phenomenon has been repeatedly documented using a variety of techniques such as observation of wetting behavior<sup>10</sup>, capacitance measurements<sup>11</sup>, force measurements between a modified spherical tip in an AFM and a derivatized surface<sup>12</sup>, and *ex-situ* infrared spectroscopy of Langmuir-Blodgett films<sup>13</sup>.

In the present study an attempt was made, by means of infrared spectroscopy, to determine independently the optimal association range for the electrostatic association of the carboxylic acid and amine used. The ionization of a carboxylic acid may be readily detected by monitoring the carbonyl stretching vibration<sup>14</sup>, which in the protonated form of the carboxylic acid moiety appears as a single band in the range of 1650-1750  $\text{cm}^{-1}$ ; however, as the acid is ionized the carbonyl stretch becomes degenerate and appears as a doublet at about 1550 and 1410  $\text{cm}^{-1}$ .

The sodium salt of the mercaptosuccinate coated gold dissolved in water shows bands at 1571 and 1400  $\text{cm}^{-1}$ . Stepwise neutralization with acid (1:10 dilution of concentrated HCl) while monitoring the pH and IR spectra produced a profile of the acid dissociation as a function of pH, shown in Fig. 1 along with a profile of the free mercaptosuccinic acid neutralization with base. The data points represent integrated peak areas and are normalized for comparison for the two titrations. Error bars cover a  $\pm 5\%$  on the y values, which is an estimate of the errors involved in the determination.

There are a number of observations that may be gleaned from the data described above. The most significant is the pH displacement for dissociation taking

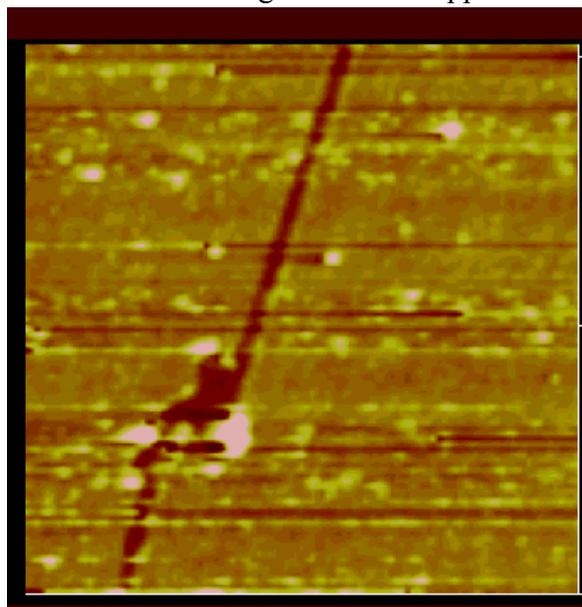


Figure 2. AFM micrograph, 2  $\mu\text{m}$  on the side, few Au particles on derivatized silicon.

place by attaching the acid to a gold nanoparticle. The acid bound to gold, in spite of being a monolayer, dissociates at 1.3 pH units higher than the free acid and thus it is shifted much less than in the case of monolayers in flat substrates<sup>10-13</sup>. A similar shift of an acid bound to gold nanoparticles has been observed<sup>15</sup> previously for the case of tiopronin as derived from the titration profile of pH versus volume of strong base.

The dissociation shifts in the case of the gold-bound acid on colloidal surfaces compared to those more pronounced on monolayers apparently reflect the transition of closely packed neighboring moieties on a flat monolayer with one that is forced into a more open structure projecting from a spherical surface.

The atomic force microscope is a very useful tool in observing microstructures but it lacks the analytical power to actually identify the features under observation and one must rely on independent information to interpret the nature of the images being collected. The present study is no exception but the dimensions of the gold particles as derived from the X-ray diffraction and TEM (to be discussed later) as well as the amino silane film thickness as obtained by ellipsometry are sufficiently different to allow a rational interpretation of a variety of microstructures observed. The AFM images of individual particles were in agreement with the x-ray determination; similarly, the thickness of the amine silane was also confirmed by the AFM. Advantage is taken of film imperfections that occur in the deposition or handling of the specimens. This is illustrated (image is 2  $\mu\text{m}$  on the side) in Fig. 2 that shows a silane film with a few gold particles. The silane is identified on the basis of its height, 1.1 nm, as observed by the profile of a scratch inadvertently made on the film that is quite similar to the ellipsometry derived value, while a particle appears as a 2 nm object on the surface.

Different microstructures were observed in the course of this study. The most attractive, from the point of view of device development, is that of a continuous monolayer with particles in close contact with each other. This is illustrated by the micrograph in Fig. 3 of a film deposited at a pH of 5.7, which includes a portion not coated, apparently the bare silicon substrate at a height difference of -3.2 nm with respect to the mercaptosuccinate coated gold. This height incorporates the amine layer thickness. Alternatively, the thioctic coated gold on a derivatized surface showed a height difference of 4.6 nm with respect to the silicon and thus it reflects in a consistent way the size difference, of about 1.5 nm, between the gold cores of the mercaptosuccinate and thioctic acid coated clusters. It has been found in the course of our work and that of others<sup>16</sup>, that the AFM derived dimensions of clusters do not incorporate the ligand shell.

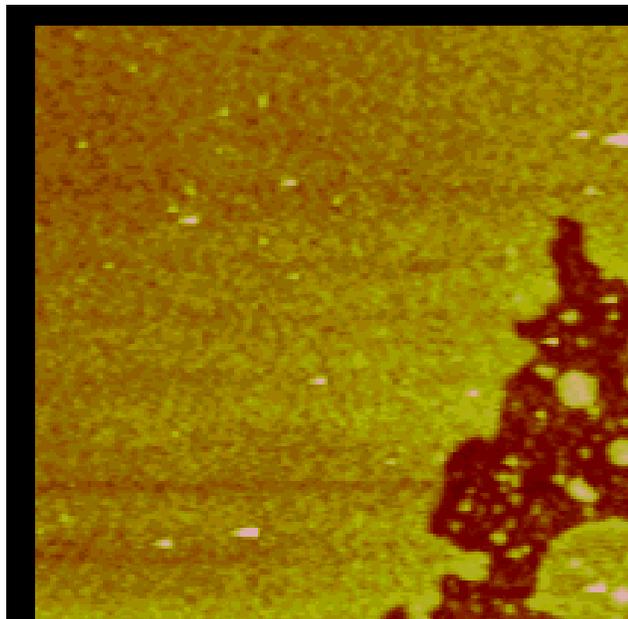


Figure 3. Smooth gold film on derivatized silicon. AFM micrograph, 2  $\mu\text{m}$  on the side

The gold surface shown in Fig. 3 is relatively smooth with a roughness of only 0.2 nm therefore it seems featureless other than a few gold particles appearing as light spots and the dark feature on the right bottom quadrant that is uncoated substrate. In contrast with this we have observed films that show less of a tight coverage such as the one shown Fig. 4, deposited at pH 5.0 that include some stacking of layers. The stacking of layers is interesting in that, evidently, it proceeds through a mechanism different from that of the initial layer, which is held by an electrostatic interaction between the clusters and the derivatized surface. It appears then that the stacking involves cluster-cluster interaction, which plausibly may arise through hydrogen bonding, more likely to occur at a lower pH that promotes less dissociation and less electrostatic repulsion among charged particles. The stacking of layers is observed as lighter features at the center of the micrograph and on a diagonal on the left bottom quadrant. The profile in Fig 4 shows heights of 4.0 and 2.0 nm for features that are apparently double and single layers respectively.

Additional microscopic characterization was conducted by means of transmission electron microscopy, TEM. In this case, sets of grids were exposed to longer periods in the silane derivatization reaction as well as contact with the gold sol following the practice recommended by Grabar et al<sup>5b</sup> to compensate for the fragility and lower reactivity of the lacey SiOx coating. The coverage obtained was quite tight for the grids exposed overnight to the gold sol and showed interparticle spacings that are similar to their diameters. This observation is consistent with the type of image obtained by AFM and shown in Fig. 3. On the other hand, a more open microstructure is observed at shorter contact times. The energy dispersive x-ray analysis of the films showed gold and silicon as well as copper but no sodium or chlorine which could appear as residues from the neutralization but evidently were rinsed away. The sulfur of the thiol coating could not be resolved because of overlap with the gold signals. An additional observation of interest during the TEM work is that of particle sizes coarsening upon intense exposure to the electron beam that in some cases produced larger particles but for the most part the particles were about 2 nm in diameter.

As previously mentioned the deposition of gold on amine-derivatized silicon is pH dependent. We observed no deposition at pH 4.0 and 7.3 and relatively good coverage in the pH range of 5.0 to 6.0 which coincides with the ionization range of the mercaptosuccinic acid bound to gold as established by the FTIR observations.

Additional experiments were conducted by coating gold through electrostatic interaction with amine treated silicon single crystal surfaces but in this case with crystals that had been cut a fraction of a degree off-axis from the crystal plane thus exposing terraces. The terraces were selectively coated with the gold clusters to produce a series of parallel arrays that would be of interest to certain electronic applications.

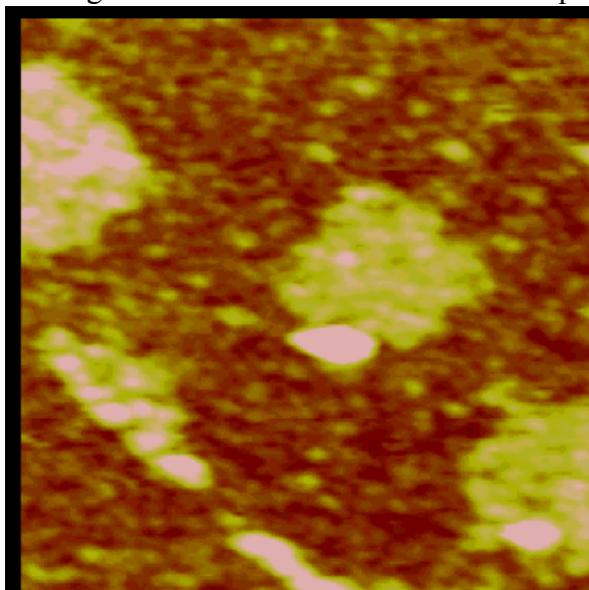


Figure 4. AFM micrograph. 1 $\mu$ m on the side, showing partial coating and stacking.

An experimental program was initiated to modify silicon surfaces used to build photonic devices by first treating the silicon with an amine terminated silane to be used similar to the gold attachment described above. The initial experiments were conducted using hydrophobic cadmium selenide quantum dots in a hexane medium in contact with the derivatized silicon surface. An interaction was expected although not electrostatic as in the case of gold. Films were prepared and examined for luminescence but none could be detected due to the relatively small amount of material present without considerable effort. Additional work with derivatized quantum dots that would make them hydrophilic is planned for the future.

## CONCLUSIONS

Relatively dense coverage of small gold nanoclusters as a two-dimensional film can be obtained between gold and derivatized silicon surfaces through the electrostatic interaction of complementary moieties with opposed charges. The microstructure of such films is influenced by the pH, contact times and surface morphology. The dissociation of mercaptosuccinic acid coating on spherical gold clusters is displaced less from the free acid than typical displacements of acids (or bases) present as monolayers in flat surfaces.

Significant findings of the present study are the determination of an optimum pH for a given coating on nanoclusters to maximize ionization and thus the opportunity for electrostatic driven association with a complementary moiety. Also of interest is the comparison in the behavior of monolayers on flat and spherical surfaces.

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