Molecule Corrals as Templates for the Formation of Metal and Silicon Nanostructures

Jennifer D. McBride, Ben Van Tassel!, Rebecca C. Jachmann, and Thomas P. Beebe, Jr.*
Department of Chemistry
University of Utah
Salt Lake City, UT 84112
August 29, 2000

*Author to whom correspondence should be addressed:
Dr. Thomas P. Beebe, Jr.
University of Delaware
Department of Chemistry
175 Brown Laboratory
Newark, DE 19716
Phone: (302) 831-1888
Fax: (302) 831-6335
e-mail: beebe@udel.edu
Abstract:

Gold and silicon nanostructures have been produced by condensing vacuum-evaporated materials and semiconductors onto nanometer-sized etch-pit templates preformed on the surface of highly oriented pyrolytic graphite (HOPG). Billions of monodispersed monolayer-deep etch-pit templates, or “molecule corrals” can be produced in a range of diameters from a few to hundreds of nanometers due to the linear etch rate of carbon atom removal as a function of time. Evaporation and subsequent annealing of gold and silicon has resulted in the formation of metal and semiconductor nanostructures on the graphite basal plane. The size and shape of the nanostructures were examined using scanning tunneling microscopy (STM), and the total coverage of the nanostructures and other chemical properties were examined using x-ray photoelectron spectroscopy (XPS). By varying the ratio of the total amount of material evaporated to the diameter of the etch-pit templates, three distinct types of metal nanostructures were observed to form on the molecule corral templates: rings, disks, and mesas. This method of producing nanostructures is a process that is inherently parallel and allows direct control over the final diameters and shapes (in two and three dimensions) of the nanostructures formed.

Introduction

Nanometer-sized clusters of metallic atoms have been widely investigated due to the size-dependent structural and electronic properties that differ from those of the bulk metal, and from those of isolated single atoms. These nanostructures offer novel ideas for applications in catalysis, microelectronics, sensors, biological interfaces, and
advanced material design. By confining or growing nanometer-sized structures, interesting properties due to quantum confinement effects have been observed. Tailoring these effects by controlling the island growth has generated much interest in the field of quantum dots. 1-7

A number of methods have been developed for the production of metal nanostructures. Several groups have employed scanning probe microscopes to deposit various metal nanoparticles onto the highly oriented pyrolytic graphite (HOPG) basal plane.8-16 These probe techniques offer the benefits of site-directed deposition, but suffer from the inherent serial drawback of producing nanostructures one at a time. Optical methods such as lithography can produce structures in a parallel fashion, however they are limited in feature size to ~180 nm due to diffraction.17 There are also at least three parallel processes used to generate nanoscale arrays: nanosphere lithography,17 nanochannel glass replica masking,18,19 and porous-membrane template-based synthesis,20-23

Vacuum evaporation of metals onto HOPG has been a widely studied topic. These previous works were carried out in order to determine the structure, aggregation, and nucleation of metals on the graphite basal plane. Previous research8,24-27 has found that clusters of metal atoms gather in and around defects on the surface of HOPG under specific conditions to form metal nanostructures. Edge defects, steps or terrace edges in the basal plane of graphite, have been observed to anchor metal nanostructures during STM and AFM imaging. Hövel et al. capitalized on this observation, and have used monolayer etch pits as high-density anchoring sites in the vacuum deposition of gold and silver,28,29 in order to study the three-dimensional structure of the clusters by STM.
Control of molecule corral density can be accomplished actively or passively. Active control has been accomplished by use of high-resolution ion-beam lithography in a time-of-flight secondary ion mass spectrometer employing a Ga or Cs ion gun (the former with nominally 60-nm spatial resolution). Exposure of the HOPG surface to controlled doses of ions has been used to create defects. These high-defect graphite substrates are then subjected to the oxygen etching procedure described in the experimental section below. Ion dose density controls the overall pit density, whereas ion energy controls the defect penetration depth and the ensuing pit depth. Active control of patterning using ions is the subject of a forthcoming paper and will not be discussed further. Passive control of etch pit density is accomplished by selecting HOPG samples having specific, previously characterized, intrinsic defect densities. These intrinsic defects are the starting sites for carbon etching reactions, and thus passive control of pit density can be used by selecting HOPG samples with known (i.e. previously characterized) defect densities. Unlike active control, passive control cannot be used to control where etch pits are located on the graphite basal plane, and regular arrays are not possible.

“Molecule corrals,” monolayer-deep etch pits which form on the basal plane of graphite, have been used in a number of applications and investigations in our group. They have been used to isolate ensembles of liquid crystal molecules in order to study the nucleation rates of self assembly in various sized corrals. They have also been used to investigate the formation and dynamics of domain boundaries in self-assembled molecular films, and to study chiral “information transfer” between nearby domains of self-assembled monolayers. Molecule corrals have also been used to investigate the
ordering of adsorbed self-assembled monolayers and the effect of tip interaction on these self-assembled films while imaging by STM. In this paper, we have now combined the vacuum evaporation of materials with “molecule corrals,” and have used them as templates in the formation of metal and semiconductor nanostructures. By varying the ratio of the template diameter to the amount of metal deposited, we have observed the formation of three distinct types of nanostructures: rings, disks, and flat-topped mesas.

Experimental

Highly oriented pyrolytic graphite, ZYB grade, was generously supplied by Dr. Arthur W. Moore of Union Carbide/Advanced Ceramics. A piece of tape-cleaved HOPG was etched in air using a Lindberg Hevi-Duty quartz tube furnace, producing CO₂ (g) and removing C atoms. Samples were heated to 650°C inside the furnace and etched for various times to produce monolayer-deep (3.35 Å) etch pits (typically 20 minutes etch time to produce 700-Å-diameter templates). The etching procedure is described in further detail elsewhere. The template structures were then imaged by STM (typically 0.80 V – tip positive, 160 pA, 3.07 µm sec⁻¹ tip scan rate) prior to metal deposition in order to determine the pit density, etch-pit diameter, and pit depth. The STM used in these studies is custom built and has been described elsewhere. Images were acquired in both constant-height and constant-current (topographic) mode, using tips mechanically cut from Pt/Ir (80:20) wire. All images were acquired at room temperature under ambient conditions.

Etched HOPG samples containing molecule corrals were attached to a tantalum sample holder fitted with a chromel/alumel thermocouple and placed in a commercial
vacuum evaporator (BOC Edwards Auto 306). Samples were resistively heated to 350°C under vacuum with a base pressure of $2 \times 10^{-6}$ Torr for two hours, in order to remove surface contaminants from the freshly cleaved HOPG surface. Immediately before material deposition, the temperature of the sample was raised to the intended annealing temperature of 350°C or 400°C, as indicated. Varying amounts of gold from 4 to 25 monolayers ($1 \text{ ML} \approx 1 \times 10^{15}$ atoms cm$^{-2}$), were deposited onto the pre-etched HOPG samples containing molecule corrals with a deposition rate of 0.08 to 0.4 ML s$^{-1}$ by heating 99.9% gold shot (Alfa Aesar) in a tungsten boat (Edwards). The total amount of gold deposited and the deposition rates were monitored using a quartz-crystal microbalance (Inficon XTC/2). After deposition, the samples were annealed at 350°C and $2 \times 10^{-6}$ Torr for two hours. Once the annealing was complete, and the sample temperature cooled below 100°C, the vacuum chamber was vented with high purity nitrogen, and the samples were removed from the chamber. The samples were then characterized by STM in air, and images were compared to those obtained prior to metal deposition. Scanning conditions for gold-coated HOPG templates varied, but were typically 0.60 to 0.85 V sample bias (tip positive), 70 to 100 pA tunneling current, and 1.22 to 2.04 µm sec$^{-1}$ tip scan rate.

In order to use the STM tip to intentionally remove gold from the sample surface, the scanning conditions were adjusted to 0.1 V sample bias, 1 nA tunneling current, and a scan rate of 6.0 µm s$^{-1}$. The latter experiments were necessary to examine the relationship between nanostructure size and molecule corral template size.

Silicon wafer fragments were cleaned with methanol, then placed in 49% hydrofluoric acid for 30 min. (CAUTION: Extreme care must be taken when
handling HF; please refer to MSDS for proper procedures. Use proper safety equipment and clothing when handling). The cleaned silicon fragments were placed in a tungsten boat and were vacuum evaporated in a manner similar to that used for gold. Annealing temperatures were similar to those used for gold: 450°C for two hours. The STM scanning conditions for silicon-coated HOPG templates varied, but were typically 14 mV to 0.99 V sample bias (tip positive), 50 to 80 pA tunneling current, and 1.02 µm sec⁻¹ tip scan rate.

HOPG samples coated with gold and silicon were also analyzed using x-ray photoelectron spectroscopy (XPS). XPS was performed with a VG Scientific 220i-XL instrument equipped with a monochromatic Al Kα x-ray source. Typical operating conditions for the x-ray source were 400-µm nominal x-ray spot size (FWHM) operating at 15 kV, 8.9 mA setting and 100 W for both survey and high-resolution spectra. A 2-micron thick aluminum window was used to isolate the x-ray chamber from the sample analysis chamber, in order to prevent high-energy electrons from impinging on the sample. Survey spectra, from 0 to 1200 eV binding energy, were collected at 100-eV pass energy with an energy resolution of ~1.0 eV, a dwell time of 100 ms, and a total of two scans averaged. High-resolution spectra were collected at a pass energy of 20 eV, energy resolution of ~0.1 eV, dwell time of 100 ms, and a total of 7 scans averaged in the respective binding energy ranges for C 1s (275 – 295 eV); O 1s (522 – 542 eV); Au 4f (76 – 96 eV); and Si 2p (94 – 108 eV). The C 1s peak, centered at 284.6 eV did not require charge shifting, therefore no charge shifting of other elemental peaks was necessary. Peak areas were fitted using VG Eclipse software with component peaks assigned by the authors. Quantification was performed using previously published
methods, and atomic sensitivity factors (C 1s: 1.00, O 1s: 2.93, Au 4f7/2: 9.58, Si 2p1/2: 0.28, Si 2p3/2: 0.54, and Si 2poxide: 0.82).

**Results and Discussion**

Flat-bottomed monolayer-deep (3.35 Å) etch pits are produced from the high-temperature etching of HOPG in air. Because the diameter of the etch pits varies linearly with the time the graphite is exposed to reaction temperature, one can directly and conveniently control the diameter of the etch pits by varying the amount of time the substrate is heated, as seen in Figure 1. The etch rate for these ZYB grade samples was determined to be 30.8 ± 2.7 Å min⁻¹ for monolayer-deep etch pits. The y-intercept of this plot is zero within error limits (23.7 ± 43.1 Å).

Additional information about the production of monolayer and multilayer HOPG etch pits has been reported previously by this group. Due to the fact that pit growth (i.e. carbon removal) begins and ends at the same time for all of the pits, this process is inherently parallel, and a narrow gaussian distribution of pit diameters is produced, as seen in Figure 2. Etch pits were analyzed using scanning tunneling microscopy to gather information about the etch pits (i.e. diameter, depth, and density of pits on the surface). An example of these etch pits is shown in the constant-current STM image in Figure 3. The narrow distribution of pit diameters (817 ± 86 Å in this case) is typical. The HOPG substrates used as templates in this study had a surface pit density ranging from 3×10⁸ to 8×10⁹ pits cm⁻² or 3 to 80 pits µm⁻², with the majority of the samples falling at the lower end of this range. It is interesting to note that this corresponds to an initial defect density of 3×10⁻⁸ to 7×10⁻⁷ monolayers.
Gold was evaporated onto pre-characterized graphite etch-pit templates. Following vacuum evaporation, the graphite template surface was heated to allow the adsorbed gold to diffuse across the graphite basal plane. This results in the nucleation and growth of gold atom islands along edges of the molecule corrals and steps on the HOPG surface. Figures 4a and 4b depict an unusually high density of gold nanostructures that have collected along step edges and inside etch-pit templates. We have observed the gold structures to be fixed inside the molecule corrals, essentially surrounded and enclosed within a circular step edge, where the monolayer-deep wall acts as a collection site for gold nucleation and growth. As seen in Figures 4a and 4b, this collection at step edges occurs at all step edges, including non-corrall step edges. A region with an unusually high step population was selected to illustrate this collection of gold. A white line drawn by hand in Figure 4b indicates such a non-corrall step edge decorated with gold disk nanostructures.

Control of nanostructure shapes

By varying the ratio of the total average thickness of deposited gold to the average etch-pit diameter, three distinct types of gold nanostructures have been observed. These structures are gold rings, gold disks and gold mesas, as shown in Figure 5. Smaller ratios of gold to etch-pit diameters (∼0.02) resulted in gold diffusion and adsorption at the rims of the monolayer-deep etch pits. This produces an array of gold-ring nanostructures. An example structure can be seen in Figure 5a (total z-scale is approximately atomic). Similar graphite edge decoration has been observed with silver and platinum deposited electrochemically.\textsuperscript{8,43,44}
As the ratio of average gold-thickness to pit-diameter increases (∼0.04), gold rings are added to, gradually filling in the entire corral template with gold, producing an atomically flat circular disk having the diameter of the molecule corral on which it formed. The filling in of the etch pits with gold is apparently due to the favorable gold cohesive packing energy in comparison to the low gold-carbon adsorption energy on the open HOPG terraces. An example of a partially filled gold disk structure (referred to later as “pre-mesas”) is depicted in Figure 5b (z-dimension 40 Å). At slightly higher annealing temperatures or longer annealing times, the six atomically flat gold island pre-mesas shown would typically merge together to form a low-profile, flat-topped gold disk. The fact that the inner diameters of these pre-mesas were smaller, and the outer diameters were larger than the molecule corral templates indicates that the gold ring pre-mesa structures are anchored on the molecule corrals. The pre-mesas essentially straddle the monolayer-deep steps which act as collection sites for gold nucleation and growth.

With an even larger gold-thickness to template-diameter ratio (∼0.3), the disks begin to grow upward, and then begin to expand outward from the original etch-pit diameter. These structures are similar to the structures produced using tip-induced scanning probe deposition of gold and silver,8-11 although the latter must be produced one at a time. The vertically growing disks resemble a pillar or desert mesa. The tops appear to be nearly atomically flat with a (111) surface orientation, as evidenced by their hexagonal structure and step intersection angles. It does not appear that the gold mesas adopt the same epitaxial relationship, if any, with the underlying HOPG, since hexagon edges from different hexagons are not always parallel, as also seen by Hövel et al.29 We have grown mesas with heights varying from 20 to 100 Å. An example of a gold-mesa
structure is shown in Figure 5c. The line scan across the tops of these nanostructures, Figure 5d, shows that the left and right mesas are 44 Å and 38 Å high respectively, and atomically flat except for some adsorbed gold atoms on top. The etch pits on which these mesas formed were ~140 Å in diameter.

While most structures were formed on pieces of graphite with a lower density of pit templates than that shown in Figure 4, we wanted to see if it was also possible to form nanostructures on substrates of higher pit-density without completely coating the graphite with a thin layer of gold. The following analysis focused on forming mesa structures. Deposition of 25 ML of gold and annealing at a temperature of 530°C for two hours resulted in nanostructures evenly distributed on molecule corrals on the surface of the graphite template. Figure 6 shows the gold mesa structures formed on this etch-pit template. As expected a high density of mesa structures has collected along a step edge running diagonally through the image, highlighted by the two arrows. Prior to gold deposition, the density of etch pits was determined to be \((8.2 \pm 0.5) \times 10^9\) pits cm\(^{-2}\), and the diameter of these pits was \(194 \pm 49\) Å. After gold deposition, the density of the gold nanostructures was found to be \((1.04 \pm 0.20) \times 10^{10}\) pits cm\(^{-2}\), 1.3 ± 0.2 times that of the etch-pit templates, essentially equivalent within error limits. The diameters of the mesas were \(429 \pm 73\) Å, 2.2 ± 0.3 times larger than the molecule corral templates on which they are located. This indicates that the gold mesas straddle the monolayer-deep steps, similar to the pre-mesa growth, supporting the hypothesis that the pre-mesas gradually fill in to form the flat-topped mesa nanostructures.

In addition to hexagonal nanostructures, many triangular gold mesa nanostructures have also formed on this high-pit-density graphite template. This provides
additional evidence for the formation of well-ordered, crystalline gold nanostructures. This transition from hexagonal to triangular nanostructure shapes has been a widely studied topic in two-dimensional metal-on-metal growth.\textsuperscript{45-47} From the evidence shown in the STM images of gold nanostructures, it would appear that the equilibrium hexagonal shape of the nanostructures\textsuperscript{45} is the predominant crystalline structure. However, the presence of non-equilibrium triangular nanostructures suggests a temperature-dependent effect. The effect of annealing temperature on nanostructure shape and size will be further investigated for this system.

XPS analysis of three separate spots on a gold-coated HOPG template (24 ML gold deposited) indicates approximately 10.1 ± 3.7\% surface coverage with gold, as shown by the survey scan in Figure 7. Oxygen was also present on these samples (\textasciitilde2\%) primarily due to adsorption of oxygen onto the graphite surface.

Silicon nanostructures were formed by vacuum evaporation of 60 Å of silicon onto 120-Å-diameter molecule corrals on the HOPG basal plane. The samples were annealed at 450°C in a vacuum of 2\times10^{-6} Torr for two hours prior to STM analysis. Immediately following deposition, the samples were transferred through air to be analyzed by XPS, as shown in Figure 8. Oxygen is present on the graphite as a result of both the etching process and surface adsorption (also seen in Figure 7 for gold). Therefore, although oxygen was present with silicon in a 2:1 atomic ratio, a direct 2:1 ratio of oxygen to SiO\textsubscript{x} can not be assumed since some oxygen is associated directly with the carbon. It was found that the silicon nanostructures consist of both the oxidized and metallic forms of silicon, as shown in the high-resolution Si 2p XPS spectra of Figure 9. The peak-fitted data displays a 6.3 ratio of metallic to oxidized silicon, indicating that the
majority of the silicon in the nanostructures exists in the metallic form. Given the vacuum pressure and transfer through air, it is expected that the silicon would form an oxide layer, either during evaporation or immediately following evaporation.

These samples were then analyzed by STM and found to contain silicon nanostructures centered on molecule-corral templates, shown in Figure 10. It can be seen from this figure that the silicon nanostructures consist of a layered terrace structure. Pixel height histograms values of four silicon mesa areas, outlined in black (A-D), have been plotted and are shown in Figure 11 (region A in Figure 10 corresponds to plot 11a, etc.). Typically, cursor line profiles or line scans between two points have been used to analyze the topographic information contained in STM images. For such a line scan, the number of data points analyzed depends on the number of pixels in the image. In addition, the random error in a line scan must be estimated from the standard deviation of data obtained from many different line scans, or by estimating the random noise in a single line scan. However, by plotting a histogram of height values for each pixel within a defined region, we increased the number of data points analyzed by a factor of 10 (Figures 11b and 11d) to 24 (Figure 11a). This histogram approach clearly takes advantage of the large amount of information contained within an STM image, is more robust to noise, and is superior to a single cursor profile.

In order to bin the data properly, slope correction must be performed on the small area of interest in order to level the area independently in both in the x and y directions. This was performed using a first-order slope compensation function applied on a HOPG terrace area near the nanostructure in question, and selected by the authors. The histograms of the four silicon nanostructure regions (Figure 11) have been analyzed by
fitting the data with multiple (two to four) gaussian peaks in order to determine the peak
center values and error. These silicon terraces are, on average, 4.7 ± 0.1 Å high. The
interplanar spacing of the silicon (111) terraces have been determined previously to be
3.1 Å.48 It has also been shown that the silicon (100) surface displays a bilayer domain
reconstruction where the surface periodicities are (2×1) and (1×2) alternating, with
terrace heights of 1.36 Å.49,50. Further analysis of the layering behavior of these
nanostructures is planned in order to determine the orientation of these terrace layers.
Atomic resolution was not possible on the Si terraces, probably due to the oxide layer.51

Nanostructure heights and diameters

Gold ring nanostructures begin at low gold coverages as single-atom rings (see
Fig. 5a), and grow with increasing gold coverage to eventually be made up of individual
“pre-mesa” structures in a circular pattern surrounding the etch-pit templates. Each
corral contains between five and eight individual pre-mesa structures. The heights and
diameters of these individual pre-mesa gold nanostructures were compared to the heights
and diameters of a separate HOPG template sample containing “final” mesa (i.e. not pre-
mesas) nanostructures. Analysis of these two HOPG template samples resulted in the
distributions shown in Figure 12. Pre-mesa gold-ring structures have heights of 111 ±30
Å, and diameters of 329 ± 78 Å, while final gold mesa nanostructures have heights of
116 ± 35 Å, and diameters of 429 ± 73 Å. This indicates that regardless of the total
amount of gold deposited (8.5 ML for pre-mesa gold rings and 25 ML for final gold
mesas), the annealing temperature (450ºC for pre-mesa rings, 530ºC for final gold
mesas), or the diameter of the etch pits (818 ± 86 Å for pre-mesa rings, 193 ± 49 Å for
final gold mesas), there exists an optimal height of ~114 ± 46 Å for gold nanostructures regardless of the nanostructure diameter. Therefore, any additional gold results in horizontal expansion of the nanostructures, causing pre-mesa gold rings to gradually fill in, and final gold mesas to expand beyond the diameter of the original etch-pit templates.

Gold Nanostructure mobility

During STM imaging of the gold nanostructures, it was found that some of the nanostructures could be removed by the STM tip as it was scanned across the HOPG surface. This removal of metal structures was also observed by others. In agreement with those observations which in general were not made on corral-based nanostructures, the sweeping away of the gold structures occurs primarily to nanostructures that do not have an anchoring etch pit or a step edge beneath them, or are incomplete pre-mesa gold ring structures with hollow centers. By varying the STM imaging conditions (decreasing the bias, increasing the tunneling current, and increasing the scan rate) we were able to remove gold from the underlying etch pits. It was this ability to remove discs and mesas that allowed us to compare corral template diameters to nanostructure diameters accurately. Figures 13a and 13b depict the same two etch-pit templates decorated with pre-mesa gold-ring structures. Figure 13b shows that gold contained within the molecule corral templates has migrated slightly (top arrow) due to tip-induced movement while obtaining the image for Fig. 8a. The gold on the lower pit has been removed or pushed to the center of the etch pit, as shown by the bottom arrow. Figures 13c and 13d show line scans of the pre-mesa gold ring nanostructures and of the monolayer-deep etch pit. As discussed above, pre-mesa gold ring structures are made up
of individual gold mesas. Line A shows the flat-topped, vertical-walled structure similar to that seen for final gold mesas (Fig. 5d). The molecule corral template is also apparent in this line scan, since the center of the ring structure (between the two gold-ring pre-mesas) is 3.35 Å lower than the HOPG basal plane on either side of the two mesa structures. Line B is a typical line scan of a 3.35-Å monolayer-deep molecule corral.

Conclusions

Gold and silicon nanostructures have been produced by condensing vacuum evaporated materials onto nanometer-sized etch-pit templates preformed on the surface of HOPG. Monolayer-deep etch-pit templates or “molecule corrals” can be produced in a range of diameters from a few to hundreds of nanometers due to the linear etch rate of carbon atom removal as a function of etch time. Evaporation and subsequent annealing of varying amounts of gold onto these molecule corral templates has resulted in the formation of metal nanostructures. It was found that by varying the ratio of the total amount of metal evaporated to the diameter of the etch-pit templates, three distinct types of nanostructures, rings, disks, and mesas, were observed to form. Smaller ratios of gold-thickness to etch-pit diameters (0.02) resulted in gold diffusion and adsorption at the rims of the monolayer-deep etch pits, producing arrays of gold-ring nanostructures. At a slightly higher ratio (0.04) the small gold rings are added to, and gradually fill in the entire corral template with gold, producing an atomically flat circular disk. With an even larger gold-thickness to template-diameter ratio (0.3), the disks begin to grow upward, and then begin to expand outward from the original etch-pit perimeter.
The tops of the gold nanostructures appear to be nearly atomically flat with a (111) surface orientation, as evidenced by their hexagonal structure. Further evidence of the formation of gold nanocrystals is the production of triangular nanostructures. It does not appear that each gold mesa adopts the same epitaxial relationship, if any, with the underlying HOPG, since hexagonal and triangular edges from different hexagons are not always parallel or quantized in multiples of 60 degrees.

Regardless of the total amount of gold deposited, the temperature of annealing, or the diameter of the molecule corral templates, it appears that there exists an optimal maximum height (~114 Å) for gold nanostructures. Any additional evaporation of gold results in horizontal expansion of the structures, causing gold rings to fill in and mesas to expand beyond the diameter of the original etch-pit templates.

Tip-induced movement of nanostructures proved a problematic issue for imaging silver nanostructures. However, the ability to remove gold discs and mesas allowed an accurate comparison of the diameters of the corral templates and resulting nanostructures. This tip-induced mobility also helped to confirm that gold nanostructures are centered over the graphite etch-pit templates.

Silicon nanostructures were also formed by vacuum evaporation of silicon onto HOPG etch-pit templates. These nanostructures were found to consist of both the oxidized and metallic forms of silicon, either as a result of silicon oxidation during evaporation, or due to formation of a thin oxide film encapsulating the nanostructures. It was found that the silicon mesas formed multilayered, terrace structures. Scanning tunneling spectroscopy is planned to further investigate the electronic properties of multilayered silicon nanostructures.
Acknowledgments

This work was supported by the National Science Foundation (CHE-9814477), IPMI Student Award for Precious Metal Research (JDM), and the Alfred P. Sloan Foundation. TPB acknowledges John T. Yates, Jr., to whom this volume is dedicated, and who served as the author’s graduate advisor, for his mentoring and friendship.

References


(30) Zhu, Y. J.; McBride, J. D.; Hansen, T. A.; Beebe, T. P., Jr. to be submitted.


(51) In addition, an exciting continuation of this project is to examine the individual silicon nanostructure mesas using scanning tunneling spectroscopy (STS). Differences in the I-V plots of multilayered terrace structures as compared to single-layer terrace structures will be examined, as will a comparison between the STS of both silicon nanostructures and similarly sized metal nanostructures.

Figure captions

Figure 1. Plot of pit diameter vs. etch time for monolayer-deep pits produced at 650°C. One standard deviation for each data point is shown as error bars. The etch rate of 30.8 Å min⁻¹ is in agreement with previously published results.⁵⁷

Figure 2. Histogram of typical etch-pit template diameters produced on ZYB-grade HOPG. Solid line shown is a gaussian distribution centered at 607 Å. Mean diameter of pits on this sample was 607 Å with a standard deviation of 53 Å (~9%). The number of pits analyzed was 244.

Figure 3. 1.00-µm² constant-height image of monolayer-deep etch-pit templates. Image acquired with a sample bias of -0.60 V, tunneling current of 160 pA and scan rate of 6.08 µm sec⁻¹. Notice the narrow distribution of pit diameters. This image depicts typical pit densities used for nanostructure production (ca. 1×10⁹ pits µm⁻²).

Figure 4. (a) 1.00-µm² constant-current image of gold ring nanostructures (typical scanning conditions). The gold has collected along a step edge, as well as along three circular etch pit edges. These etch-pit templates are ~750 Å in diameter. (b) 1.00-µm² constant-height image (-0.60 V, 170 pA, 1.22 µm sec⁻¹ scan rate). Gold collection along a terrace edge has been identified with a hand-drawn white line. Many circular etch pits, some of which are merged etch-pit templates, are decorated with gold nanostructures. These images are typical of pre-mesa gold-ring nanostructures.

Figure 5. Constant-current topographic STM images depicting the types of nanostructures formed on etch-pit templates. (a) 0.1-µm² image of a small gold ring structure. Ratio of thickness of gold deposited to pit diameter was 0.02. Etch-pit template is ~550 Å diameter. This image was taken with a –0.99 V sample bias and 75
pA tunneling current. Total z-dimension is atomic in scale. (b) 0.15-µm² area of a large pre-mesa gold-ring structure. The etch-pit template is ~650 Å diameter, and the ratio of gold deposited to pit diameter was 0.03. This image was taken with a sample bias of –0.60 V, tunneling current of 154 pA and scan rate of 1.22 µm sec⁻¹. Z-dimension corresponds to 67 Å maximum (top right structure) and ~3.35 Å minimum (center of etch pit). The outer diameter of this pre-mesa nanostructure is approximately 1100 Å.

(c) Same scanning conditions as in (b), a 0.15-µm² area of two hexagonal gold mesas.

(d) Line scan across the tops of the two mesa structures from left to right. The heights of these two mesas are 44 Å and 38 Å, and they are 363 Å and 500 Å in diameter. The mesas are atomically flat except for some adsorbed gold atoms on the tops of the nanostructures. The ratio of deposited gold thickness to pit diameter was 0.2.

**Figure 6.** Constant-current STM image of gold-mesa structures (typical scanning conditions) formed on a high density (8.2×10⁹ pits cm⁻²) etch-pit template. After gold deposition, the density of the gold nanostructures was found to be 1.04×10¹⁰ pits cm⁻², ~1.3 times that of the etch-pit templates. A high density of mesa structures has collected along a step edge running diagonally through the image, as highlighted by the two arrows outside the image field of view. Notice the formation of numerous triangular gold-mesa structures.

**Figure 7.** XPS survey spectrum of core-level photoelectron emission from HOPG etch pit template coated with 49 Å of gold. Oxygen is incorporated into the graphite surface as part of the etching process and is present in the spectrum without gold (data not shown).
Figure 8. XPS survey spectrum of core-level photoelectron emission from HOPG etch pit template coated with 60 Å of silicon. Oxygen is incorporated into the graphite surface as part of the etching process, as well as due to the formation of a silicon oxide layer either during deposition, or immediately following deposition. Annealing temperature was 450°C.

Figure 9. High-resolution XPS silicon 2p core-level photoelectron spectra of an etch-pit template substrate coated with 60 Å of vacuum-deposited silicon. The solid line is the raw data overlayed with the sum of the fitted peaks. The higher binding energy peak (103.3 eV) corresponds to silicon oxide (2p1/2 and 2p3/2 combined). The peak separation between the metallic Si 2p1/2 and Si 2p3/2 is 0.6 eV. The ratio of metallic silicon to oxidized silicon was 6.3 (the sum of the 2p3/2 and 2p1/2 normalized areas of the metallic silicon peaks and the total normalized area of the silicon oxide peak).

Figure 10. Constant-current image (0.25 µm²) of silicon mesa structures formed on etch-pit templates (120-Å diameter). Individual nanostructures comprised of monolayer and multilayered terraces have been identified. Terraces are, on average, 4.7 ± 0.1 Å high, and range from 170 to 510 Å in diameter.

Figure 11. Histogram plot of height information of the rectangular regions shown in Figure 10 (A-D). These histograms have been analyzed by fitting the data with multiple (two to four) gaussian peaks in order to determine the peak center values and error. Prior to binning, image data were slope corrected by a standard first-order tilt correction algorithm and smoothed with a 9-point Savitsky-Golay smoothing algorithm, to remove noise spikes and increase peak definition. These silicon terraces are, on average, 4.7 ±
0.1 Å high. The number of data points analyzed for each histogram were: 12,065 (a), 5,913 (b), 6,715 (c), and 5,925 (d).

**Figure 12.** Histogram of heights and diameters of pre-mesa gold ring and “final” gold mesa nanostructures. Each pre-mesa ring structure consists of between five and eight individual pre-mesa structures. The heights and diameters of these individual pre-mesa gold nanostructures were compared to the heights and diameters of a separate HOPG template sample containing “final” gold mesa nanostructures. Analysis of these two HOPG template samples resulted in the distributions shown above. Both pre-mesa rings and final gold mesas have approximately the same heights. This indicates that there exists an optimal height of ∼112 ± 31 Å for gold nanostructures. The number of analyzed nanostructures forming pre-mesa gold rings was 476, and the number of final gold mesa structures analyzed was 104.

**Figure 13.** Tip-induced movement of pre-mesa gold ring nanostructures inside monolayer-deep etch-pit templates a) constant-current mode; b) constant-height mode. Two scan cycles have occurred between the image a) and image b). The gold on the lower pit has been pushed to the center of the etch pit, as shown by the bottom arrow. In addition, gold has been moved slightly towards the center of the top etch pit as shown by the top arrow. Image c) depicts the beginning of atomically flat pre-mesa gold ring structures as seen in “Line A” from image a). Part d) depicts a typical monolayer-deep etch-pit template with a diameter of 1009 Å “Line B” in image a).
Growth of HOPG Etch Pits at 650°C

Monolayer Pit Etch Rate
= 30.8 ± 2.7 Å min⁻¹
Histogram of Pit Diameters for HOPG Templates

- $t_{etch} = 20$ min.
- $T_{etch} = 650 \, ^\circ C$
- Mean Diameter $607 \, \text{Å} \pm 9\%$
Monolayer-Deep Etch Pits on HOPG Prior to Gold Deposition
Decoration of Etch-Pit Edges with Gold Nanostructures

Figure 4.doc
Gold Rings, Disks, and Mesas on HOPG Molecule Corrals

Figure 5.doc
Line Scan of Gold Mesas Formed on HOPG

Atomically Flat Gold (111)
Gold Mesas Produced on a High-Pit-Density HOPG Template
XPS of Gold Vapor Deposited onto HOPG Molecule Corrals

<table>
<thead>
<tr>
<th>Peak</th>
<th>Center (eV)</th>
<th>FWHM (eV)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1s</td>
<td>531.9</td>
<td>2.37</td>
<td>2.0</td>
</tr>
<tr>
<td>C1s</td>
<td>284.6</td>
<td>0.55</td>
<td>87.9</td>
</tr>
<tr>
<td>Au 4f(_{5/2})</td>
<td>87.8</td>
<td>0.66</td>
<td>---</td>
</tr>
<tr>
<td>Au 4f(_{7/2})</td>
<td>84.2</td>
<td>0.68</td>
<td>10.1</td>
</tr>
</tbody>
</table>
XPS of Silicon Vapor Deposited onto HOPG Molecule Corrals

<table>
<thead>
<tr>
<th>Peak</th>
<th>Center (eV)</th>
<th>FWHM (eV)</th>
<th>Atomic %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1s</td>
<td>532.5</td>
<td>1.71</td>
<td>6.7</td>
</tr>
<tr>
<td>C1s</td>
<td>284.6</td>
<td>0.56</td>
<td>83.7</td>
</tr>
<tr>
<td>SiOx</td>
<td>103.2</td>
<td>1.80</td>
<td>3.0</td>
</tr>
<tr>
<td>Si 2p₁/₂</td>
<td>100.1</td>
<td>0.75</td>
<td>---</td>
</tr>
<tr>
<td>Si 2p₃/₂</td>
<td>99.5</td>
<td>0.66</td>
<td>6.6</td>
</tr>
</tbody>
</table>
High-Resolution XPS of Silicon Vapor Deposited onto HOPG Molecule Corrals

\[
\text{Si}^\circ : \text{SiO}_x = 6.3
\]
Silicon Nanostructures Formed by Vacuum Evaporation onto HOPG Molecule Corrals
Histograms of Silicon Nanostructure Heights

a) Mean Height = 4.4 ± 0.1 Å
   Mean Height = 4.4 ± 0.2 Å
   Mean Height = 5.1 ± 0.3 Å

b) Mean Height = 5.0 ± 0.1 Å

c) Mean Height = 4.9 ± 0.1 Å
   Mean Height = 4.6 ± 0.1 Å

d) Mean Height = 4.8 ± 0.1 Å
Comparison of Ring and Mesa Nanostructure Heights and Diameters

Pre-Mesa Ring Height: 111 ± 30 Å

Pre-Mesa Ring Diameter: 329 ± 78 Å

Final Mesa Height: 116 ± 35 Å

Final Mesa Diameter: 429 ± 73 Å
Tip-Induced Movement of Gold Nanostructures

---

**Figure 13.doc**

- **a)**
  - Image showing two line segments labeled as Line A and Line B with a distance marker of 1000 Å.
  - Color-coded structure with arrows indicating movement.

- **b)**
  - Similar image to (a) but with a different color scheme and additional arrows.

- **c)**
  - Graph showing line profile labeled Line A with height values ranging from 0 Å to 80 Å on the y-axis and distance (Å) on the x-axis.
  - Marked area showing a monolayer-deep etch-pit.

- **d)**
  - Graph showing line profile labeled Line B with height values ranging from 0 Å to 5 Å on the y-axis and distance (Å) on the x-axis.
  - Measured distance: 3.4 Å.