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Communication

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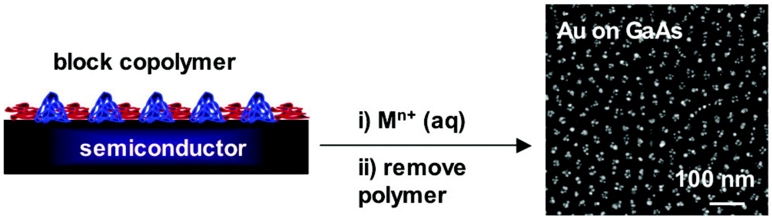

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# Block Copolymer-Templated Chemistry on Si, Ge, InP, and GaAs Surfaces

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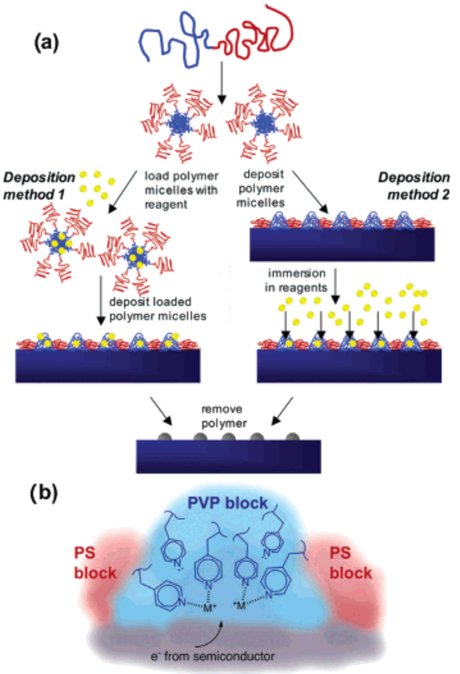
Patterning of surfaces on the nanometer scale is an area of growing interest because of the potential for use in applications as broad as cellular recognition, molecular electronics, genomics, and catalysis. Methods such as Dip Pen Nanolithography (DPN) and other AFM- and STM-mediated processes,[1] $\mu$-contact printing,[2] and related techniques are under intense development worldwide, but the allure of self-assembly to pattern large areas via entirely wet chemical processes is growing.[3] Block copolymers, in particular, that self-assemble into nanoscale structures have been known for quite some time,[4] but recent utilization by workers at IBM, demonstrating their compatibility with existing silicon-based fabrication processes, has focused attention on these materials.[5] Block copolymers are extremely versatile and have been used as nanoreactors to prepare isolated nanostructures, as reactive ion etch masks, as a patterned hydrophobic/hydrophilic organic interface on which polymerization and sol−gel chemistry have been carried out, and others.[6]

In this communication, we describe block copolymer templating of semiconductor surface chemistry, using the block copolymer to direct chemical reactions with the surface in a spatially defined manner. Two approaches are described here, termed deposition methods 1 and 2 (Scheme 1a). Deposition method 1 involves loading the block copolymer micelle with reagent, and then depositing the nanostructures onto the semiconductor surface, at which point the desired reaction takes place as the reagents contact the surface. In deposition method 2, a semiconductor chip coated with a nanostructured monolayer of a self-assembled block copolymer is immersed into the reactive reagent; with the latter method, the quantity of reagent is essentially unlimited and not restricted by the capacity of the block copolymer micelle cores in solution, as is the case with deposition method 1.

The specific class of reactions investigated here is galvanic displacement, the spontaneous reduction of sufficiently oxidizing metal ions to particles, films, and other structures on semiconductor surfaces.[7] The potential for chemical bonding between nanoparticles formed via this method and Ge, GaAs, InP, and perhaps Si is particularly attractive for nanoelectronics and catalysis applications.[6g,7b,e] The diblock copolymer chosen was PS−P4VP, with polystyrene (PS) and poly-4-vinylpyridine (P4VP) blocks, since the pyridines of the P4VP block are well established to associate with metal ions or complexes (Scheme 1b) via direct coordination to metals (e.g., $Ag^+$) or protonation by $HAuCl_4$, for instance.[6h] Since the P4VP pyridine groups make up the core of the micelles under these conditions, the metal complexes are directed into close proximity with the surface, whereupon they undergo a rapid (seconds) reduction to metal nanoparticles. Subsequent removal of the block copolymer template results in a semiconductor interface patterned with metal nanoparticles.

Nanoscale patterning of the spontaneous reduction of $Ag^+$ ions on Ge(100) is shown in Figure 1, via deposition method 1 (Scheme 1a). Three block copolymers of different molecular weights and

***Scheme 1*** [a]



[a] (a) Outline of the block copolymer templated mediated delivery of reagents to semiconductor surfaces (deposition methods 1 and 2). The block copolymer micelles are shown in red (corona) and blue (core). (b) The pyridine groups in the PS−4PVP group associate with metal ions in the core, which are then reduced by electrons from the semiconductor substrate via a galvanic displacement reaction.

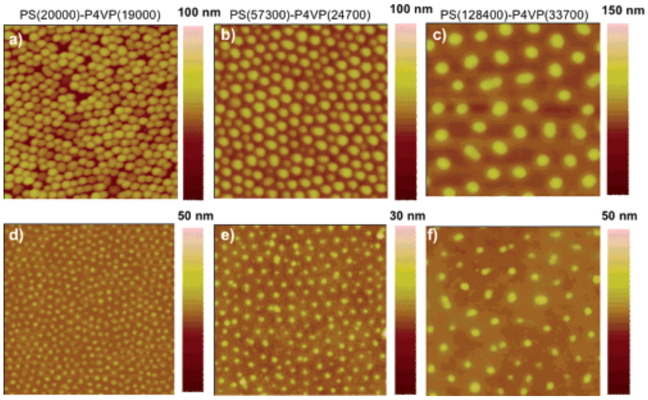


***Figure 1.*** All AFM images 1 $\mu m^2$. (a−c) Block copolymers of different molecular weights spin-coated onto Ge(100) with its native oxide. (d−f) Ag nanoparticles formed from the parent block copolymer on Ge(100).

spacings were loaded with 0.3 equiv of $AgNO_3$ per pyridine (in the P4VP block) in 0.5% (w/w) toluene solutions and were spin-coated onto the native oxide of germanium from toluene. After 10 min, the polymer was removed with ultrasonication (5 min) in

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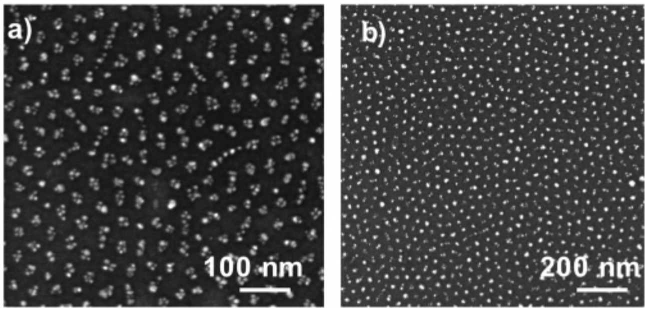

***Figure 2.*** SEM images of Au nanoparticles on GaAs(100) (a) and Si(100) (b) formed from $HAuCl_4$ and HF (aq) with PS−P4VP ($M_w$ = 20 000−19 000).

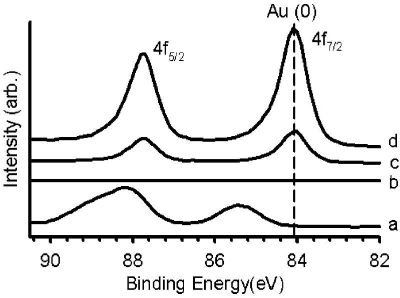

***Figure 3.*** XPS of $HAuCl_4$ deposition on Si(100), native oxide-capped. (a) $HAuCl_4$ dissolved within PS−P4VP ($M_w$ = 20 000−19 000, ratio Au/py = 0.3) in toluene and spin-coated onto Si(100). (b) Rinsing of (a) with toluene results in removal of all Au. (c) Same conditions as (a), except system immersed for 1 min in 0.25% HF; reduction of gold observed. (d) Removal of polymer with ultrasonication in toluene results in strengthening of Au signals due to exposure of Au nanoparticles.

toluene. The resulting Ag(0) nanoparticles adhere strongly to the Ge and have the same pseudohexagonal packing as that of the parent block copolymer, with spacings of 50, 75, and 120 nm and diameters of 10, 10, and 20 nm, respectively. XPS indicates that the $Ag^+$ is rapidly and quantitatively reduced to Ag(0). High-resolution SEM images (Supporting Information) reveal that some of the silver nanoparticle deposition occurs in pairs or small groups. Without block copolymer, $Ag^+$ deposition on Ge produces 80−100 nm nanoparticles and, eventually, microns-long hexagonal stacks of silver disks called nano-inukshuks.[7c] The block copolymer is also exercising a degree of control over nanoparticle size, as well.

As a demonstration of deposition method 2, a 0.5% (w/w) toluene solution of PS−P4VP ($M_w$ = 20 000−19 000) was spin-coated onto the native oxide of Si(100) and GaAs(100) wafer shards to produce a ∼30 nm thick monolayer (ellipsometry) of hexagonal close-packed block copolymer micelles. These substrates were then immersed in a 1 mM $HAuCl_4$ (aq) solution in the presence of dilute HF [GaAs(100) for 5 min, 1% HF; Si(100) for 1 min, 0.25% HF)], followed by removal of the polymer with brief ultrasonication in toluene. As shown in Figure 2, the resulting metal deposition appears as small bundles of close-packed nanoparticles in a shallow etch pit. XPS of $HAuCl_4$ deposition on Si(100) is shown in Figure 3 and reveals that HF is required to facilitate reduction to Au(0) by etching the insulating native oxide and exposing the underlying silicon.[7a] Figure 3a indicates that $HAuCl_4$ on native oxide-coated Si(100) remains as Au(III) and is removed with the polymer (Figure 3b) upon toluene rinsing; no gold remains. In the presence of HF, however, rapid and quantitative reduction to Au(0) occurs (Figure 3c), and the metal nanoparticles adhere to the Si(100) surface when the parent block copolymer is removed with ultrasonication in toluene (Figure 3d).

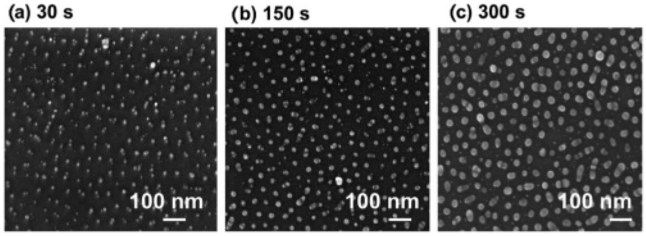

***Figure 4.*** SEM images of Au nanoparticles of increasing size on InP(100) by lengthening the immersion time in 1 mM $AgNO_3$/1% HF (aq).

Control can be exercised over the average nanoparticle diameter, as shown in Figure 4, for silver nanoparticles on InP(100). Utilizing deposition method 2, an InP(100) wafer shard coated with a 30 nm monolayer of PS−P4VP ($M_w$ = 20 000−19 000) was immersed in 1 mM $AgNO_3$/1% HF (aq). Increasing the immersion time yielded an increase in particle size from 10 to 20 to ∼30 nm (30, 150, 300 s contact). Similar results are observed with other metal/semiconductor pairs.

To summarize, electroless deposition chemistry of metal ions can be spatially defined by block copolymers to produce patterned metal nanoparticles on Ge, Si, InP, and GaAs. The electronic characteristics of these interfaces are under investigation. More generally, the application of nanostructured block copolymers to template surface chemistry is expected to be very wide ranging, with potential for inorganic *and* organic surface reactivity on semiconductors, metals, and organic monolayers.

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**Supporting Information Available:** Detailed experimental procedures, XPS for all surfaces, and additional SEM and AFM data. This material is available free of charge via the Internet at http://pubs.acs.org.

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