Letter

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Au “Ink” for AFM “Dip-Pen” Nanolithography

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Scanning probe lithography is a rapidly growing research field, in which atomic force microscope based “dip-pen” nanolithography (DPN) is a simple new technique for creating chemically distinct nanostructures on surfaces in a “direct-write” fashion. Previous works demonstrate the transport of alkanethiol to a gold substrate, resulting in the formation of patterned self-assembled monolayers. Here, we show that surface-induced reduction of metal ions combined with DPN can be used to create metallic nanostructures on Si surfaces. Au nanostructures with sub-100-nm resolution can be created routinely, showing that the DPN technique is a general method for nanofabrication.

In recent years, scanning probe lithography (SPL) has attracted great attention. Many SPL techniques have been developed in the past decade based on various chemical, physical, and electrical modifications of surfaces, including mechanical scratching,5 electrochemical anodization of Si surfaces,6,7 decomposition of self-assembled monolayers,8,9 electric field induced chemical reactions,10,11 electrochemical reactions in solution using electrochemical scanning tunneling microscope tips,12,13 and so forth. Several comprehensive reviews of scanning probe microscope related lithography can be found in the literature.14–18 More recently, a new SPL technique, “dip-pen” nanolithography (DPN),19,20 has demonstrated the ability to pattern monolayer films of thiolated organic molecules with sub-100-nm resolution on gold substrates. The technology uses the spontaneous condensation between the atomic force microscope (AFM) tip and substrate to transport organic molecules from the AFM tip to the surface in the area specifically defined by the tip/surface interaction. To draw a familiar analogy, the AFM tip acts as a “pen”, the organic molecules act as “ink”, and the surface acts as “paper” for nanostructures to be “drawn” on. It has also been demonstrated for direct patterning of nanoscale structures in both a serial and parallel fashion.21 This technique provides a potentially more accessible, cheaper, and versatile alternative to conventional high-resolution lithographic methods such as e-beam lithography.

Previous demonstrations of DPN have patterned long-chain alkanethiol molecules onto gold surfaces. However, there is no reason other molecules that have a certain affinity for a specific surface could not be used for DPN. We have recently discovered that metal ions can be electrochemically reduced and deposited on surfaces to form metallic nanostructures using a modified electrochemical DPN technique.22 Here, we report that Au(III) complexes can be used directly (without applied voltages as in the electrochemical DPN method) as “ink” for DPN on Si “paper”. This is the first demonstration of an ionic substance being transported from the AFM tip and chemically reacting with the surface to form metallic nanostructures. It further demonstrates that DPN is a versatile technique that can be used to create various nanostructures in a “direct-write” fashion. We believe that the underlying mechanism for the deposition of Au onto the silicon surface is the surface-induced reduction of the Au(III) precursor to insoluble Au(0).

The experiments were performed on a Digital Instruments NanoScope IIIa controller with a MultiModeAFM. To precoat the AFM tip with the gold precursor, a contact mode AFM cantilever (Digital Instruments, NP-20) was dipped into a 1% w/w HAuCl4 aqueous solution (Alfa Aesar) for 30–60 s and dried with compressed air. Silicon surfaces were prepared by soaking n-doped silicon (100) wafers (Monoto Silicon Technologies) in 2:1 H2SO4/H2O2 solution for 2 h. The SiO2 surface oxide layer was then removed by 5% aqueous HF treatment. Normally, the wafer was used for lithography within 1 h of oxidation removal. To deposit

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nanostructures, the precoated contact mode AFM tip was translated across the silicon surface at a rate of 0.005–0.02 μm/s. The relative humidity was maintained between 40% and 50% using a commercial humidifier and dehumidifier. After lithography, the modified areas were located again with the help of preformed landmarks and imaged in tapping mode AFM, again using the Nanoscope IIIa and MultiMode microscope with clean silicon tapping mode tips (Silicon-MDT).

Like other DPN techniques, the AFM tip specifically defines the area of deposition. The spontaneously condensed water droplet between the tip and surface is used as a nanosize reaction vessel. The process is outlined as follows (Figure 1): when the precoated AFM tip comes in contact with the silicon surface, a nanosize water "meniscus" spontaneously forms between the tip and the surface because of the capillary effect. This meniscus serves as the nanometer scale reaction vessel that limits the area where deposition can occur. Metal ions are dissolved in the reactor, reduced to metal atoms, and deposited on the substrate through a reaction mechanism discussed below.

As shown in Figure 2, Au nanostructures with sub-100-nm resolution can be created routinely using this DPN technique. As with any scanning probe technique, the geometry is defined by the translation of the AFM tip, so this technique offers broad flexibility in the kind of patterns that can be fabricated, including (but not limited to) lines, geometric shapes, and even letters. The letters "DU" in Figure 2 demonstrate that the morphology of the features can be easily controlled by directing the movement of the AFM tip.

The nanostructure morphology strongly depends on the scanning speed, the humidity of the ambient environment, and the geometry of the AFM tip. Faster tip translation speeds result in less deposition because fewer Au(III) complexes have time to diffuse away from the tip and deposit onto the surface. At slower tip translation speeds, the deposited Au features are higher and more continuous (more deposition) than they are at faster speeds (less deposition). This is consistent with the idea that the lithographic process is controlled by Au(III) complex diffusion from the tip to the surface. The ambient humidity affects the size of the deposited features because the humidity directly affects the size of the condensed meniscus between the tip and the surface. Therefore, higher humidity increases the width of the deposited gold features. The dimensions of the created structure also depend on the geometry of the AFM tips used in the experiments. Control of the tip geometry, the translation speed, and the ambient humidity should allow one to deposit nanostructures with a specified length, width, and height within certain limits.

Certain characteristics of the deposited features indicate that they are Au(0) nanostructures, as opposed to Au(III) complexes, surface silicon oxide, or other contaminants.

Figure 1. Schematic diagram of the experimental setup.

Figure 2. Tapping mode image of the letters “DU” drawn at 10 nm/s at 40% relative humidity.
First, the lines are very stable; they survive repeated washings in aqueous and nonaqueous solvents and reimaging without much noticeable change in height or width, indicating that they are not composed of soluble Au complexes. Second, upon heating to 300 °C in air, there is no change in the lines, indicating that they are not made of organic material. Upon further heating to 500 °C in an inert atmosphere, the lines aggregate into a series of dots, indicating that the gold features undergo a phase transition and reaggregate in lower energy spherical shapes due to surface tension. Finally, the Au structures are more resistant to HF etching than larger silicon oxide features. Figure 3 shows an Au line alongside SiO2 features created by electrochemical anodization of the Si surface before and after etching with 0.4% HF solution. Note that the silicon oxide dots, which are significantly higher than the deposited Au line, are etched away whereas the Au feature shows little change in morphology.

To understand the formation mechanism of the Au nanostructures on the surface, we have performed the experiment on fully oxidized Si wafers. The experiments showed that no deposition was formed on such surfaces under the same experimental conditions. This observation indicates that the observed Au nanostructures on Si surfaces are probably generated through reactions of the metal ions with the Si surface. It is known that many noble metals in high oxidation states, such as Au(III) or Pd(II), undergo a surface-induced oxidation/reduction or decomposition reaction when they adsorb onto appropriate surfaces.27,28 The resulting adsorbate is in the elemental oxidation state (0) instead of the initial highly oxidized form. This phenomenon has been used to create nanoparticles in porous silicon27 and microscale patterns using microcontact printing.28

The reductive deposition of Au onto silicon substrates has been confirmed by X-ray photoelectron spectroscopy (XPS). Two silicon wafers were cleaned as described above. One wafer was heated to 1000 °C in air for 6 h to form a 80–100 nm thick thermal oxide layer. The surface turned blue after heating. The second wafer was etched in 4% HF for 10–20 s to produce a H-terminated silicon surface. Both the oxide-coated and H-terminated Si wafers were immersed in a 2 × 10^{-4} M aqueous solution of HAuCl4 for 9 h and then removed and washed with ethanol. Figure 4 shows the XPS spectra of the silicon and silicon oxide wafers. Note that the Si surface shows the significant peaks corresponding to Au(0), whereas the SiO2 surface shows no evidence of Au(0) formation. This is consistent with the hypothesis that silicon mediates the reduction of Au(III) to Au(0), but silicon oxide, which is already fully oxidized, cannot facilitate Au deposition. This experiment also corroborates that Au(0) deposits because of its insolubility in aqueous solution, whereas the Au(III) complex is soluble and can be washed away from the surface. Otherwise, the XPS spectra would show Au(III) peaks as well as Au(0) peaks on Si surfaces reacted with Au(III). These observations account for the fact that lithography is observed on Si surfaces but is not observed on SiO2. The presence of both silicon and silicon oxide peaks on the silicon sample indicates that only a thin layer of oxide has formed on the silicon wafer in air after HAuCl4 treatment. This oxide layer could be due to surface oxidation by Au(III) or by native oxide formation. In either
case, however, the reductive deposition of Au on silicon substrates is evident. The Au film is stable against repeated washing with various aqueous and organic solvents. Similar results were observed by Suzer and Dag.29

The height of the deposited nanostructures is typically 4–10 Å. A Au–Au bond length is approximately 2.8 Å, meaning that 1–3 layers of gold atoms are deposited. This level of deposition is consistent with the process being a surface-mediated reaction.

Though this technique has been demonstrated to deposit Au nanostructures on Si surfaces, the approach can be more general. In principle, if one can design a system with one reactant immobilized on the surface and the other delivered by the AFM tip to a specific location to perform chemical reactions, nanometer scale structures can be created as long as the reaction product is insoluble in water. One could envision using this technique to create nanostructures of other materials, modify existing nanostructures, or measure the local chemical properties of the surface. More work in these areas is currently underway.

In summary, we have demonstrated that DPN can be used to deposit Au nanostructures on Si surfaces. The mechanism for nanostructure deposition is the surface-induced reduction of a soluble Au(III) precursor into insoluble metallic Au(0). We believe that this can be a general approach: by carefully choosing an appropriate precursor/surface system, it should be possible to create chemically diverse nanostructures on various surfaces.

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