"Reagentless" Micropatterning of Organics on Silicon Surfaces: Control of Hydrophobic/Hydrophilic Domains[1]

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The covalent attachment of monolayers to semiconductor surfaces is of growing interest for potential applications from surface passivation to the incorporation of chemical/biochemical functionality at interfaces for use in biosensors and biosensor arrays.[2−5] The rapid development and unrealized potential of microarrays on solid supports has stimulated the development of a number of novel methods for the spatially resolved chemical modification on the micron scale.[6−10] One approach to defining and controlling reactive regions on this length scale is to control the surface tension and wetting properties by patterning regions of hydrophilic and hydrophobic character. Such an approach has been developed on thiol[11] and glass surfaces[12,13] for the controlled delivery of DNA.

It has been shown that alkyl monolayers can be formed on the Si(111) surface with a variety of reagents by reaction with the hydrogen-terminated surface, Si(111)−H. Chidsey and co-workers were the first to report the formation of an organic monolayer on Si(111)−H by the radical initiated reaction of alkenes.[14,15] This seminal work has led to a number of thermal, electrochemical, photochemical, and catalytic methods for the covalent modification of Si(111)−H surfaces.[16−22] In most cases, these organic monolayers effectively passivate the surface and provide remarkable chemical stability.

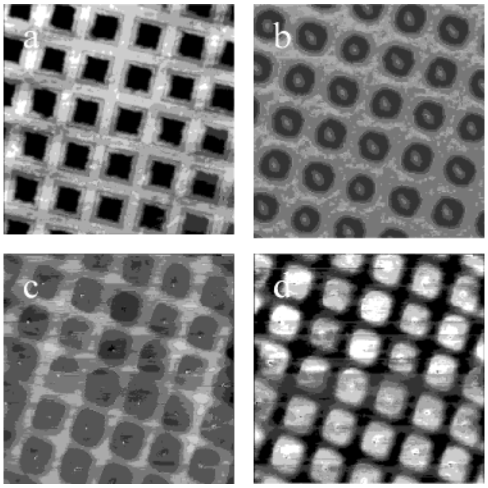

Figure 1. (a) AFM tapping mode image of the gold minigrid mask, (b) CCD optical image of the patterned Si(111) surface after exposure to water vapor, (c) AFM height image of the patterned surface, and (d) AFM frictional force image using an unmodified silicon nitride tip (all images 140 × 140 μm^2).

The ability to photoinitiate the reaction of alkenes with Si(111)−H surfaces opens the possiblilty of direct photopatterning of organics on the surface. Effenberger et al. were the first to adapt photolithographic methods for patterning organic monolayers on Si(111)−H surfaces.[23] In this case, alkenes and aldehydes were deposited as thin films on the Si(111) surface and exposed to UV light (ca. 385 nm) through a mask to write $>$100 μm features. It was further demonstrated that the unexposed areas remained reactive.

The approach developed by Effenberger requires that the volatile organic molecules are present in the patterning step, a practice that is discouraged in many clean room facilities. Furthermore, the organic reagents must be scrupulously free of water, oxygen, and peroxides which are known to react to oxidize the silicon surface on irradiation. Chidsey found that even after distilling alkenes from sodium directly into a reaction vessel, there was significant oxide contamination in the photoreactions.[24] The inability to remove traces of oxygen and peroxides from the organics appears to be a major limitation. However, the fact that the surfaces so easily photooxidize presents a simple alternative.

Herein, we describe the fabrication of Si(111) surfaces patterned with organic monolayers and oxide on the 10 μm scale. We have combined the facile photooxidation of the Si(111)−H surface with the hydrosilylation of a terminal alkene to develop a novel "reagentless" or organic-free approach for the patterning of silicon surfaces. In the first step the surface is irradiated at 254 nm through a mask in air to create a pattern of silicon oxide on an otherwise hydrogen-terminated Si(111) surface. The spatial resolution is simply determined by the quality of the optical system. The unexposed area, which remains hydrogen terminated, may then be reacted with suitable organic molecules in either a photochemical or thermal process. We find by ellipsometry that the photooxidation results in the formation of a ca. 10 Å thick layer of silicon oxide. While the photooxidized regions do not react with alkenes under the condition for reaction with Si(111)−H, they do react readily with octadecyltrichlorosilane suggesting a predominance of Si−OH groups at the surface.

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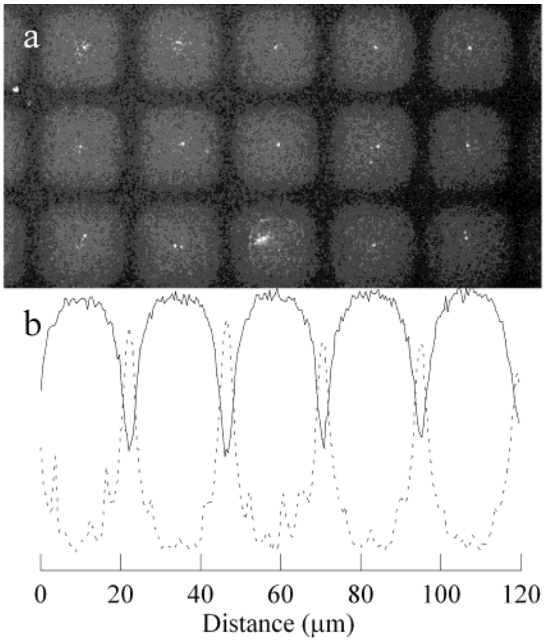

Figure 2. (a) SEM of the patterned surface. (b) SAES line scan of the modified surface depicting the relative abundance of carbon (dashed) and oxygen (solid) as a function of distance.

Typically, n-type Si(111) (ca. 2 ohm·cm) is cleaned with piranha solution (3:1 H_2SO_4:H_2O_2) at 100 °C for 30 min before immersion in a deoxygenated aqueous NH_4F solution for 15 min. The resulting Si(111)H surface is pressed against the mask, a gold grid (Buckbee-Mears) with ca. 10 μm diameter wires with a center-to-center spacing of 25 μm (Figure 1a). The surface is then exposed through the mask by using a pen lamp (254 nm) in ambient air for 30 min. The sample was removed, immersed in deoxygenated 1-decene, and irradiated (300 nm) for 3 h.

This step initiates a hydrosilylation reaction between the hydrogen-terminated surface (the part that was masked to UV light by the gold minigrid) and the 1-decene.[15,23,24] The wafer was then rinsed with THF and 1,1,1-trichloroethane to remove any physisorbed hydrocarbons from the surface.

After the irradiation, an optical image of the surface, after exposure to water vapor, reveals a well-ordered pattern (Figure 1b) with the oxide (squares) being hydrophilic and the 1-decene modified surface (lines) being hydrophobic. The ability to control surface tension with this precision has potential applications in microarray fabrication. Water droplets on the array of silicon oxide pads (about 160 000/cm^2) are self-centering and eliminate errors in placement by mechanical devices. An AFM height image (Figure 1c) of this surface shows an organic surface that is topographically higher than the oxide. The contrast is improved in the frictional force image (Figure 1d) in which the hydrophilic nature of the silicon oxide squares is evident.

The modified surface was further characterized by SEM (Figure 2a) and Scanning Auger Electron Spectroscopy (SAES, Figure 2b). SEM clearly shows the contrast between the oxide and alkyl regions. A SAES line scan across the pattern clearly shows the expected anti-correlated 25 μm periodicity of carbon and oxygen.

There are a number of advantages to this simple and flexible approach to chemically pattern the surface. For some applications it may be convenient to leave the oxide layer intact or to react the oxidized silicon surface with alkyl trialkoxysilanes or alkyl trichlorosilanes to introduce organic function to the oxide itself, e.g. organic functional groups such as amines or aldehydes to serve as attachment sites for DNA and proteins.[25] Furthermore, one may take advantage of the fact that the oxide is easily removed by exposure to aqueous solutions of HF or buffered HF while the alkylated regions are inert.[22] Thus it is possible to convert the previously oxidized surface into a newly hydrogen-terminated surface and fill it in with a different organic molecule.

In conclusion, a simple photolithographic process has been developed for micron scale patterning of organic monolayers on Si(111)−H. It is unique as it does not require the organic molecule for the patterning step. In this simple example we have demonstrated the ability to control the wetting properties of the surface on this length scale. Future work will focus on further elaborating the chemistry at the oxide/monolayer interface for applications in DNA and protein microarrays and for the fabrication of hybrid organic/semiconductor devices.

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