

Nanostructure fabrication in silicon using cesium to pattern a self-assembled monolayer

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This letter describes the formation of nanometer-scale features in a silicon substrate using a self-assembled monolayer (SAM) of octylsiloxane on silicon dioxide as a resist sensitive to a patterned beam of neutral cesium atoms. The mask that patterned the atomic beam was a silicon nitride membrane perforated with nm and μm scale holes, in contact with the substrate surface. In a two-step wet-chemical etching process, the pattern formed in the SAM was transferred first into the SiO_2 layer and then into an underlying silicon substrate. This process demonstrated the formation of silicon features with diameter ~ 60 nm. © 1997 American Institute of Physics. [S0003-6951(97)00735-3]

In the experiment described here, ~ 60 -nm-wide features in neutral atomic cesium were transferred into a silicon substrate using a self-assembled monolayer (SAM) as a positive resist. The SAM resist of octylsiloxane was formed on a layer of silicon dioxide on a silicon $\langle 100 \rangle$ substrate. The SAM was patterned by exposure to 10–30 atoms of cesium per molecule of SAM, through a mask consisting of a silicon nitride membrane with nm and μm scale holes. The patterned SAM layer acted as a resist against a wet-chemical etch that transferred the pattern into the silicon dioxide layer. In a second etching step, the patterned silicon dioxide layer was used as a mask for an etch into the underlying silicon substrate. This work demonstrates the first use of neutral atoms to form patterns in an alkanesiloxane SAM on amorphous silicon dioxide. Two potential applications of this technique are as a high-resolution detector for atomic cesium and as a component in resist-based neutral atom lithography.

Atomic optics experiments can generate periodic atomic distributions with < 100 nm features.^{1–4} Recent experimental progress, such as the development of new atomic sources⁵ and flexible methods for guiding^{6,7} and patterning⁸ atoms, suggests that future experiments hold promise for creating atomic distributions with more arbitrary patterns or with smaller characteristic length scales. Detection of position distributions of alkali atoms with nm scale resolution is currently a challenging problem. If an alkali atomic pattern is deposited directly on a substrate, the pattern will be destroyed upon exposure to atmosphere, since the alkali atoms react immediately with dioxygen, water, and carbon dioxide. Analysis *in situ*, using scanning tunneling microscopy, can show features with sizes < 20 nm,⁹ but such techniques are experimentally inconvenient. By using a resist/etch system to transfer the pattern formed in cesium into a more durable substrate, such as silicon, we create a copy of the pattern, in a process loosely analogous to the way that photographic

film is used to create a permanent copy of a pattern of light; both processes amplify the initial image-forming events, albeit in different ways. The “atom photograph” can then be imaged outside of vacuum using conventional microscopy techniques to give spatial information about the atomic distribution on the < 100 nm length scale.

Additionally, because neutral atoms have a small de Broglie wavelength, lithography using neutral atoms may prove useful in creating smaller structures than are currently possible with conventional light-based lithography. Beams of neutral atoms are also simple to construct, are insensitive to Coulombic forces, and can be used in patterning a large area ($\sim \text{cm}^2$) in a parallel process. These advantages make transferring nm scale atomic patterns into silicon interesting for applications such as device fabrication.

Previous work has shown that SAMs are sensitive to damage by electrons^{10,11} and by neutral atoms.^{12–16} SAMs are capable of nanometer-scale resolution, and can act as resists to transfer nanometer-scale features into underlying materials. An electron beam has been used to pattern SAMs formed on silicon dioxide, yielding ~ 6 nm features.¹⁷ Nonanethiolate SAMs formed on a gold layer and patterned with neutral atomic Cs have been used as a resist to transfer ~ 70 -nm-wide features into the gold.¹⁴ Our previous efforts to create nanostructures by using cesium to damage SAMs on gold seemed to be limited by the grain size of the underlying gold substrate; by using amorphous silicon dioxide we expect to avoid these limitations.

SAMs offer several potential advantages for use as resist materials that transfer patterns formed in neutral atoms into permanent substrates:

- (1) SAMs are sensitive to several neutral atomic species, e.g., cesium,^{14,15} sodium,¹⁸ metastable argon,^{12,16} and metastable helium.^{13,16}
- (2) Because SAMs are thin (~ 1 nm), they are sensitive to low doses of cesium (~ 10 Cs atoms per molecule of SAM¹⁴) and metastable rare gas atoms.^{12,13,16}

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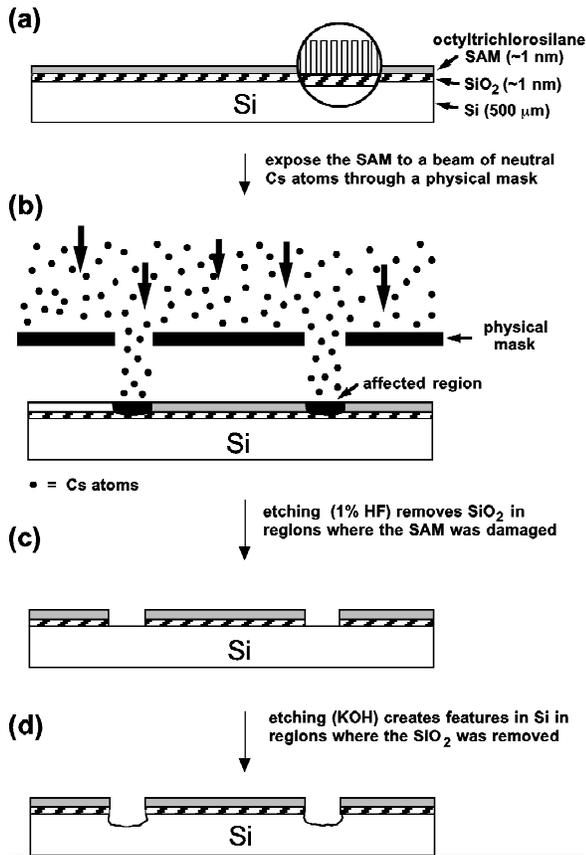


FIG. 1. Schematic diagram of the experimental procedure (not to scale). (a) A SiO₂ substrate was first coated with a SAM of octylsiloxane. (b) The substrate was then exposed to a beam of neutral cesium atoms through a physical mask. (c) In a wet-chemical-etching step, the pattern of damage caused by the cesium was transferred into the SiO₂ layer. (d) Finally, the SiO₂ pattern was used as a mask for etching into the underlying Si substrate.

- (3) The chemistry of SAMs is well understood. They can be made in different lengths and with different end groups. A SAM could perhaps be engineered to make it more sensitive to a particular damaging agent.
- (4) SAMs can be formed on many materials (e.g., conductors such as the coinage metals;¹⁹ GaAs, a semiconductor;^{20,21} and silicon dioxide, an insulator²²), so if the damage mechanism is general, a pattern formed in a SAM could be transferred to many types of substrates.

Transferring a pattern, via a SAM, into silicon dioxide is of particular interest because a pattern in the oxide may be used as a high-resolution mask for a subsequent isotropic or anisotropic etch into the silicon. Anisotropic etches into silicon can yield features with high aspect ratios. This technique may be used to amplify a feature formed with only a few monolayers of cesium into a deeper feature (tens of nm) which may be more easily imaged.

Figure 1 outlines the processing steps taken with the samples of octylsiloxane SAM on SiO₂. The substrate used in these experiments was a silicon wafer with a SiO₂ overlayer that was measured, using ellipsometry, to be ~9 Å thick. The wafer was cleaned by immersion for 30 min in piranha solution, rinsed in distilled water, and dried under filtered nitrogen gas. The SAM was formed by soaking pieces of the cleaned wafer for >12 h in a solution of ~1%

octyltrichlorosilane in toluene at room temperature. A cloudy white precipitate was seen on samples as they were taken out of this solution. This film of excess reactants was removed by rubbing the sample with a cotton swab wet with toluene. The rubbed samples were then rinsed in toluene, and dried under filtered nitrogen. The thickness of a typical SAM was measured using ellipsometry to be 12 ± 2 Å.

The Cs beam incident on the samples was patterned with a physical mask consisting of a perforated 50-nm-thick membrane of silicon nitride that was supported on a silicon wafer.²³ The SAM sample, with the mask clamped in close contact with the sample surface, was exposed to up to 30 atoms of neutral cesium per SAM molecule, from a collimated atomic beam. The atomic beam was created by heating cesium in an oven to ~290 °C and extracting atoms through a 1.6-cm-diam circular aperture in the oven wall. The atoms then passed through a 1.3-cm-diam circular aperture 27.0 cm away from the oven, and the sample was placed 17.0 cm further along the path of the atomic beam. Sample entry was accomplished through a load-lock chamber pumped with a LN₂-cooled sorption pump. Pressures in the main chamber during exposure were typically 5×10^{-8} Torr. The flux in the atomic beam was determined by measuring the optical thickness of the beam for circularly polarized laser light tuned to the $6S_{1/2}F=4$ to $6P_{3/2}F=5$ transition (852 nm) in atomic Cs. This measurement is described in Ref. 14, and was done on an atomic beam collimated to ~3 mRad. This result gives the correct flux at the center of the unapertured beam as well. The typical flux during the exposure of samples was 10 Cs atoms per SAM molecule per hour. The exposure time could be easily reduced by increasing the oven temperature, and thus increasing the flux in the atomic beam.

After exposure, the samples were removed from the vacuum system and etched with a two-step wet-chemical-etching process. The first step consisted of a 20 s dip in 1% HF at 20 °C. This removed the SiO₂ layer in places where the SAM resist had been damaged. After being rinsed with distilled water, the samples were immersed for 4 s in the second etching bath, an alcoholic KOH solution at 70 °C. The patterned SiO₂ layer acted as a mask for this second etching step, so that features were etched into the silicon substrate only in regions where the SiO₂ had been removed. All the sample transfer steps, before and after exposure and etching, were conducted in ambient laboratory conditions. The patterned silicon samples were analyzed using a Park Scientific Autoprobe CP atomic force microscope (AFM).

Figure 2 shows AFM images of features etched into a silicon substrate following exposure to a beam of atomic cesium through a mask that had an array of holes with sizes ~500 and ~60 nm. The ~500-nm-wide features have a depth of 20–40 nm. The AFM tip used in creating these images had a radius of curvature of ~20 nm, which we expect limits the resolution of the image of the ~60-nm-wide features shown. These images were generated from a sample that had been exposed to the atomic beam for 1.5 h, for a total dose of ~15 Cs atoms per SAM molecule. Similar features have also been formed after exposures of the SAM for 1–3 h. In some samples, we do not observe features at every

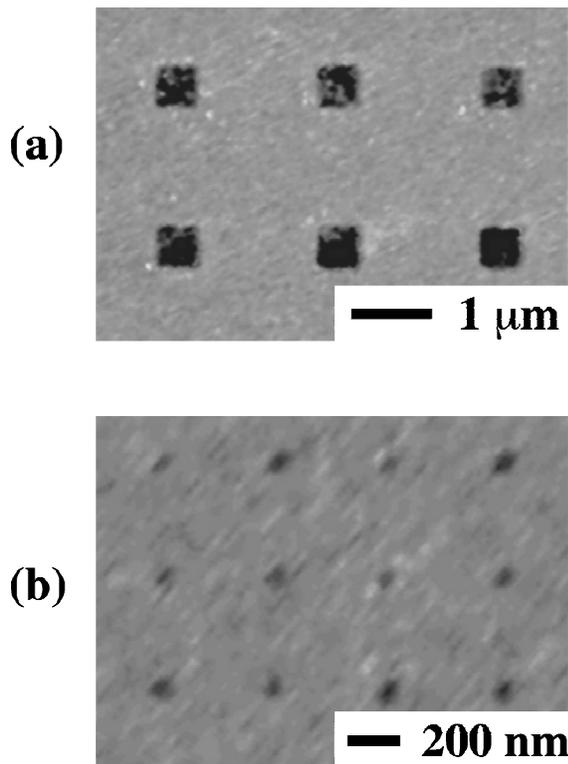


FIG. 2. (a) AFM image of ~ 500 -nm-wide structures etched into silicon after exposure of a sample of octylsiloxane SAM on SiO_2 to a beam of cesium. The sample was first etched for 20 s in an aqueous solution of 1% HF at $\sim 20^\circ\text{C}$, then for 4 s in an alcoholic solution of KOH at $\sim 70^\circ\text{C}$. The features have a depth of 20–40 nm. (b) AFM image of < 100 -nm-wide features etched into the sample.

point where the mask was expected to transmit cesium. This effect is not yet understood.

A mechanism through which neutral cesium in its ground state could damage SAMs has not been established. The precise minimum dose of cesium that is required to pattern the SAM is also not yet established. Future work might investigate these questions, as well as establish a lower limit on the size of features that can be generated with this technique.

In this work, we have demonstrated that nanostructures can be formed in a SAM of octylsiloxane by exposure to neutral atomic cesium. These nm scale features can then be transferred into silicon dioxide and silicon using chemical etching steps. Since the SAM was formed on amorphous silicon dioxide, the feature sizes are not limited by substrate grain sizes, as was the case for alkanethiolate SAMs on gold. Because cesium can pattern SAMs formed on two different substrates (gold^{14,15} and SiO_2), we might expect that the same mechanism would allow patterning of SAMs formed on other substrates, such as GaAs, or the remaining coinage metals. In using cesium to pattern a SAM on silicon dioxide, we present a step towards transferring a pattern formed optically in an alkali atomic beam into silicon dioxide and silicon substrates.²⁴ This technique has great potential for application as a detector for patterns formed with new atomic optics methods, or as a component of a nanolithographic system.

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