

**Demonstration of a Nanolithographic Technique
using a Self-Assembled Monolayer Resist
for Neutral Atomic Cesium**

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Abstract

This experiment demonstrates the formation of nanometer-scale features in a gold substrate using a self-assembled monolayer (SAM) of nonanethiolate as a resist for a patterned beam of neutral cesium atoms. The mask used to pattern the atomic beam was a silicon nitride membrane perforated with nm- and μm -scale holes. A dose of ~ 3 monolayers of cesium damaged the SAM sufficiently to allow penetration of the damaged regions by an aqueous etching solution. Etching transferred the pattern of damage in the SAM layer into the underlying gold substrate. Features of $\sim 70\text{-nm}$ size were etched into the gold substrate. Investigations of the reflectivity of samples exposed to the atomic beam without a mask and subsequently etched revealed that the resist-etch system exhibits a minimum threshold dose of cesium for damage; at doses lower than ~ 3 monolayers, the damage was insufficient to allow penetration of the SAM by the etching solution.

Conventional lithographic processes incorporate three basic elements: 1) a damaging agent (*e.g.* photons, ions, or electrons), 2) a patterning mechanism (*e.g.* a mask or focusing optics), and 3) a resist that is sensitive to the damaging agent (typically a ~ 1 - μm -thick organic layer). The relatively recent development of optics for neutral atomic beams¹ has yielded a patterning mechanism for lithographic techniques that use neutral atoms.²⁻⁴ There is, therefore, interest in new resist systems that are sensitive to exposure to neutral atoms.⁵⁻⁸ The experiment described in this paper demonstrates a new method of making nanostructures that uses a patterned beam of neutral cesium atoms to damage a ~ 1.2 -nm-thick self-assembled monolayer (SAM) resist of alkanethiolates on gold^{9,10} (see Figure 1). The atomic beam was not patterned optically, but with a contact mask consisting of a $40\ \mu\text{m} \times 40\ \mu\text{m}$ silicon nitride (Si_3N_4) membrane perforated with nm- and μm -scale holes. Exposure to the cesium altered the SAM layer sufficiently to allow penetration of a wet-chemical etch, resulting in ~ 70 -nm-wide features etched into a ~ 20 -nm-thick gold layer on a silicon substrate. With an appropriate mask and a broad atomic beam, patterning over larger areas ($\sim \text{cm}^2$) should be possible without increasing exposure times or feature size. The primary application for this technique is the fabrication of nm-scale structures, however, this method might also be used for high-resolution detection of atomic density.

Lithography using neutral atoms has several desirable features: the theoretically achievable image resolution of patterns formed with neutral atoms is limited by the size of the atom ($\sim 0.3\ \text{nm}$),¹¹ and because neutral atoms are not subject to Coulombic forces, this technique avoids some of the instabilities inherent in ion- and electron-beam lithography. Cesium has several attractive features for atomic lithography: 1) Cesium has cycling

atomic resonances with large electronic susceptibilities in regions of the spectrum (852 and 895 nm) that are easily accessible by relatively high powered diode (~ 100 mW) and solid-state (~ 1 W) lasers; it can, therefore, be easily and inexpensively manipulated using laser light. 2) A wide variety of atomic optical elements have already been developed for use in patterning atomic cesium, and in preparing high-quality beams.¹ 3) Thermal effusive sources of cesium are in widespread use; they are relatively inexpensive and simple to fabricate.

Current techniques for neutral atom lithography fall into two classes: 1) an optically patterned atomic beam (*e.g.* sodium,² chromium,³ and aluminum⁴) is deposited directly onto a substrate; or 2) the internal energy stored in excited metastable states of neutral atoms (*e.g.* argon⁵ and helium^{7,8}) is used to damage a SAM. Metastable argon can also be used to create a resist on the substrate using contaminant vapor in the vacuum system.⁶ In patterning a gold substrate by image transfer from a resist of SAM exposed to neutral cesium atoms, we demonstrate a new technique for neutral atom lithography that uses a fundamentally different physical mechanism to pattern a resist. Unlike experiments using the internal energy of metastable atoms (~ 10 eV) to damage the resist, the damage process for cesium is likely to be chemical because the energy stored in the thermally occupied states in the ground state hyperfine manifold (~ 4 μ eV) and the kinetic energy (~ 50 meV) together should be insufficient to effect collisional damage to the chemical bonds in the resist (~ 2 eV).¹²

This resist-based technique potentially incorporates several advantages of resist systems for application to neutral-atom lithography and high-resolution atomic detection:

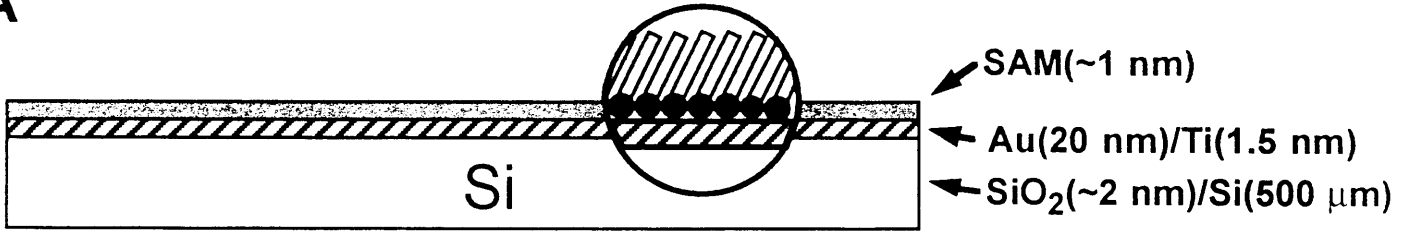
- 1) Unlike direct deposition schemes that build features up one atom at a time, the etching

process used to transfer the pattern from cesium into gold can amplify the depth of the image, so a few monolayers of material can be used to make a taller structure (20 nm) in less time. 2) Conventional resists are thick ($\sim 1 \mu\text{m}$), and therefore would not be chemically sensitive to monolayer-level doses of neutral atoms. Because typical beams of neutral cesium are relatively low in flux (~ 3 min monolayer time), the thinness of SAMs (~ 1.2 nm), and therefore their sensitivity to low doses of cesium, was critical to accomplishing exposures in realistic time scales. 3) If the dose profile of a feature includes some undesired background, resists that exhibit a minimum dose threshold for damage can be used to narrow a feature and improve its contrast after image transfer. We observed evidence of such a threshold at a dose of ~ 3 monolayers for mm-scale features formed in samples exposed to a broad cesium beam without a mask. 4) If the amount of gold remaining after etching depends linearly on dose, and if this linearity is observable at the nm scale, careful exposure of a SAM resist in this dosing regime could detect atomic density with nm-scale resolution: the relatively inert patterns created in the resist or substrate could be imaged outside of vacuum using conventional techniques of high-resolution microscopy. For mm-scale features, there was a region, between ~ 3 and ~ 7 monolayers of cesium, where such a linear response was observed.

Figure 1 shows the processing steps used in this experiment. 20-nm-thick gold films were deposited by electron-beam evaporation onto a Si (100) substrate with a ~ 2 -nm-thick native oxide layer using 1.5 nm of Ti as an adhesion promoter. The SAMs were formed on the gold by overnight immersion in a solution of ~ 1 mM nonanethiol ($\text{CH}_3(\text{CH}_2)_8\text{SH}$) in absolute ethanol (EtOH). After the samples were removed from solution, they were rinsed several times with EtOH, and were subsequently dried using nitrogen gas with particulates

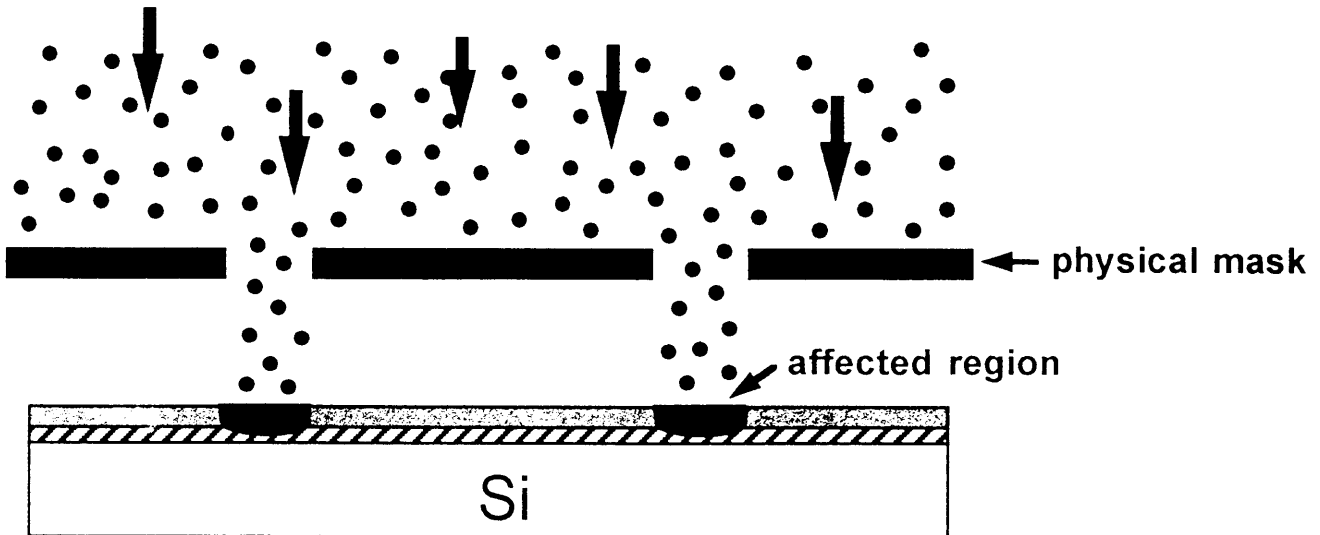
Figure 1 : Schematic diagram of the experimental procedure (not to scale). **A)** A Au/Ti/SiO₂/Si substrate was first coated with a SAM of nonanethiolate. **B)** The substrate was then exposed to a beam of neutral cesium atoms through a mask that was in close contact ($\sim 5 \mu\text{m}$) with the surface. **C)** In a final etching step, the pattern of damage caused by the cesium was transferred into the gold layer.

A



↓ expose the SAM to a beam of neutral Cs atoms through a physical mask

B



• = Cs atoms

C

↓ etching removes gold in regions where the SAM was damaged



larger than $0.2 \mu\text{m}$ removed by filtration. A patterned 50-nm-thick Si_3N_4 membrane¹³ was placed in contact ($\sim 5 \mu\text{m}$ spacing) with the substrate. The mask and substrate were held in place with a steel clip. The samples were then put into the vacuum system and exposed to the beam of cesium for times varying between 5 min and 2 hours. Immediately upon removal from the vacuum system (< 5 min delay) the exposed samples were etched for 7 min in a wet-chemical etch.¹⁴ When outside of vacuum, the samples were exposed to ambient laboratory conditions. The samples were analyzed using either scanning electron microscopy (SEM) or optical reflectometry.

Figure 2 shows a schematic diagram of the atomic beam apparatus used to expose the samples. The atomic beam was created by heating cesium in an oven to $\sim 290^\circ\text{C}$ and extracting atoms through a 1.6-mm-diameter circular aperture in the oven wall. The beam was collimated using a 1.8-mm-diameter circular aperture placed 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 LN_2 -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 in atomic Cs. The typical flux was 20 monolayers per hour, where we define a monolayer to have the surface density of the SAM molecules (4.6×10^{14} atoms/cm²).

Figure 3 shows a SEM of ~ 70 -nm- and ~ 500 -nm-wide features formed in a gold surface by cesium exposure, as well as the masks used to form these features. Typical exposure times were ~ 15 minutes, corresponding to a dose of ~ 5 monolayers. The roughness of the edge of the damaged regions was ~ 20 nm, which was comparable to the

Figure 2 : Schematic diagram of the apparatus used for the exposure of samples of SAMs on a gold surface to a measured dose of cesium from a neutral atomic beam. The sample holder could be removed to allow for the determination of cesium flux by the measurement of absorption of resonant laser light by the atomic beam.

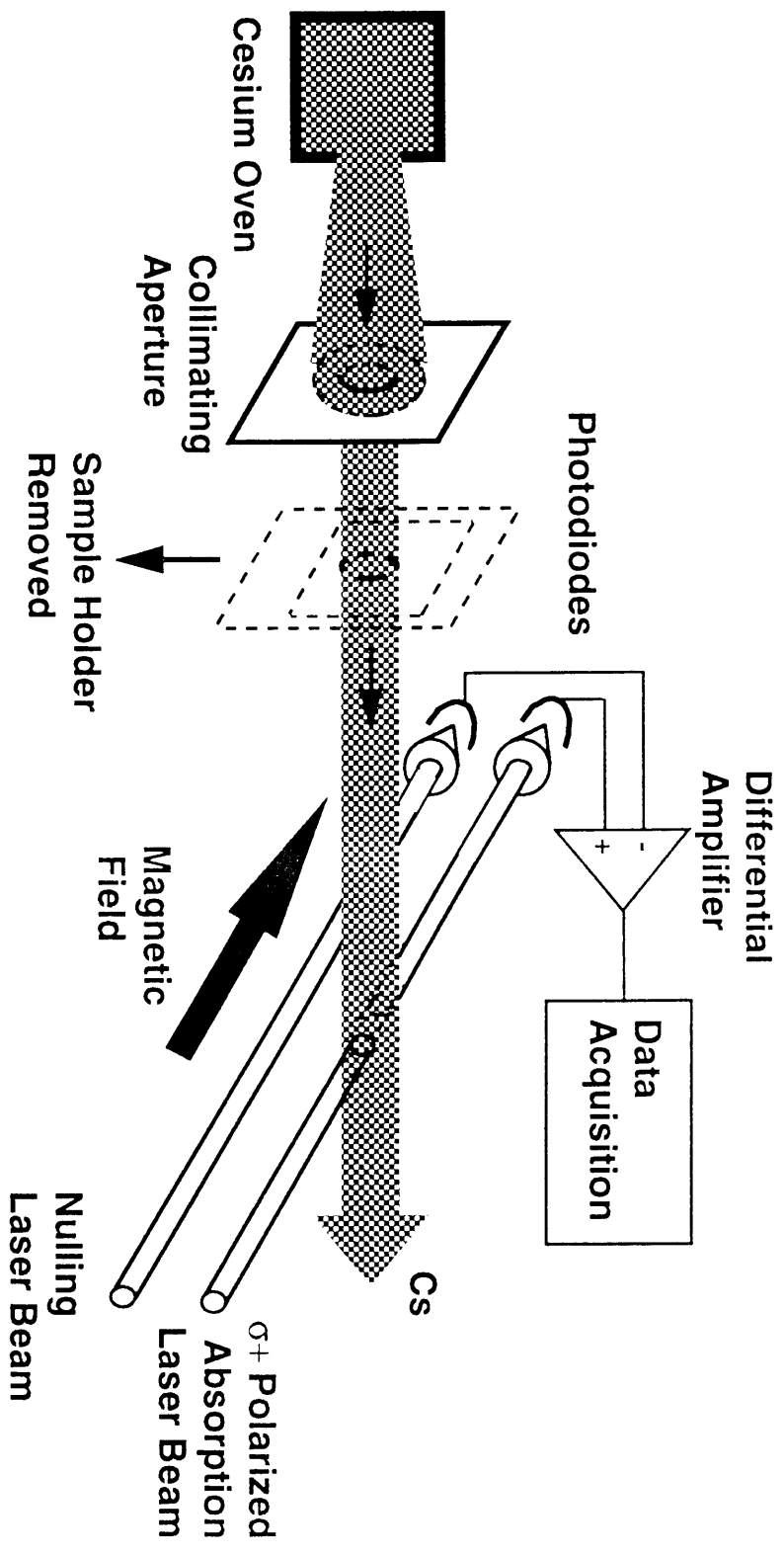
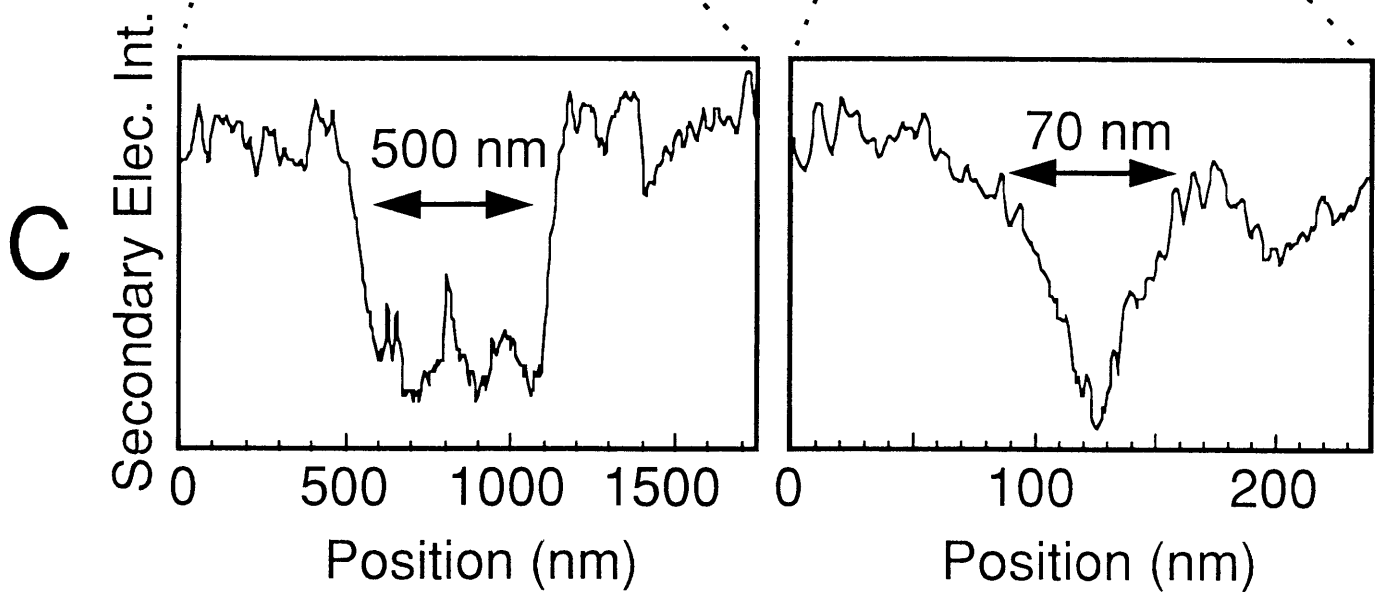
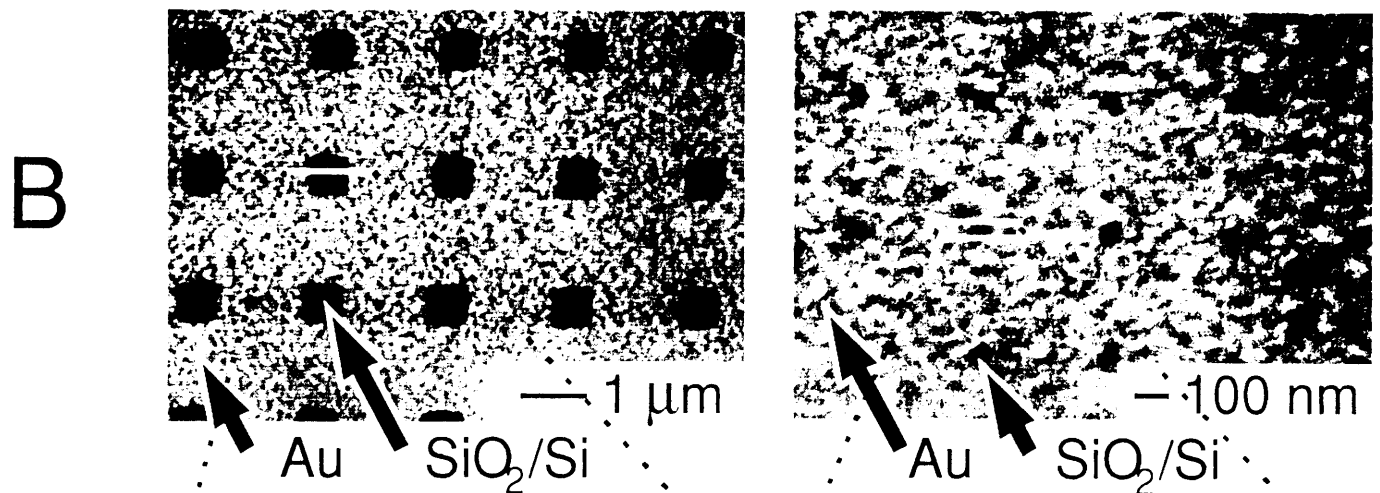
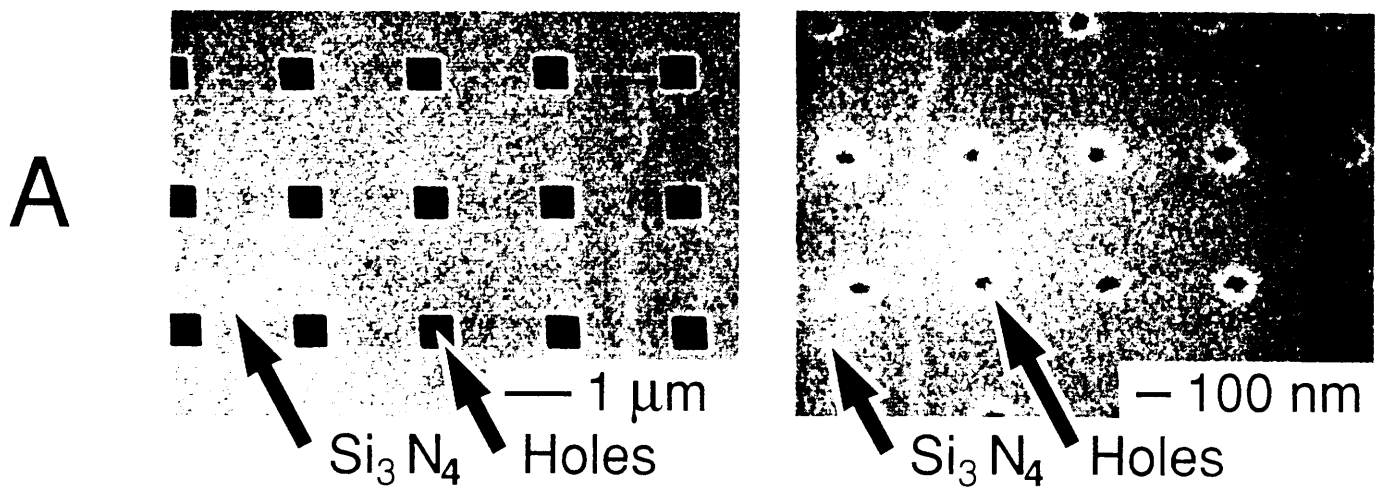


Figure 3 : **A)** SEM image of 500-nm- and 50-nm-scale holes in a Si_3N_4 mask that was used to pattern the atomic beam. The fabrication of the mask is described elsewhere.¹³ **B)** Image of features formed in Au after exposure to a dose of ~ 5 monolayers of monatomic neutral cesium through the mask shown in **A** and subsequent etching. **C)** Cross-section of SEM images shown in **B**. The secondary electron intensity across a typical feature is shown in arbitrary units, averaged over 1 nm in the vertical axis for the 500-nm-wide feature, and 11 nm in the vertical axis for the 70-nm-wide feature.



granularity of the gold surface.

In order to investigate the damage to the surface as a function of dose, samples were also exposed to the atomic beam without using a mask. Using the known flux profile of the atomic beam and the measured reflectivity profile of damaged spots to normally incident light at 632 nm, the damage to the surface was determined as a function of the dose of cesium atoms. The reflectivity of the gold has previously been correlated, using atomic force microscopy, to the amount of gold remaining on the surface.⁷ Figure 4 shows the transfer function from cesium dose into the reflectivity of the etched gold layer. Below ~ 3 monolayers, no visible damage was observable. After ~ 3 monolayers, increased dose resulted in further etching. Above ~ 10 monolayers, increased dose induced protection against etching.

Control experiments demonstrated that damage was caused by atomic cesium and not by some other agent, *e.g.* molecular cesium, other chemical contaminants, or thermal radiation from the oven. Radiation pressure from laser light resonant only with atomic cesium was used to distort the circular profile of the atomic beam.¹ None of the other possible beam constituents would be deflected by the laser light. Figure 5 shows the distorted damaged spot on an etched substrate. Damage observed outside of the original beam spot — where cesium had been pushed by the light — established that the cesium atoms did damage. The lack of damage in regions that originally were in the beam — where cesium had been removed — indicated that cesium atoms were predominantly responsible for the damage seen in these experiments. When longer exposures were used, radiation pressure established that the protection effect that was observed at high doses (> 10 monolayers) was also due to atomic cesium.

Figure 4 : Reflectivity of an etched gold surface whose protective SAM resist had been damaged by a measured dose of cesium atoms from an atomic beam without a mask. The reflectivity was measured with incident laser light at 632 nm. Different symbols refer to data obtained for different exposure times on the same sample. Reflectivities for a range of doses were extracted for each exposure time by examining the reflectivity along the gradient of the dose profile. The inset graph shows that for doses above ~ 10 monolayers, a slow increase in reflectivity was observed with increasing dose. We define a monolayer to have the surface density of the SAM (4.6×10^{14} atoms/cm²).

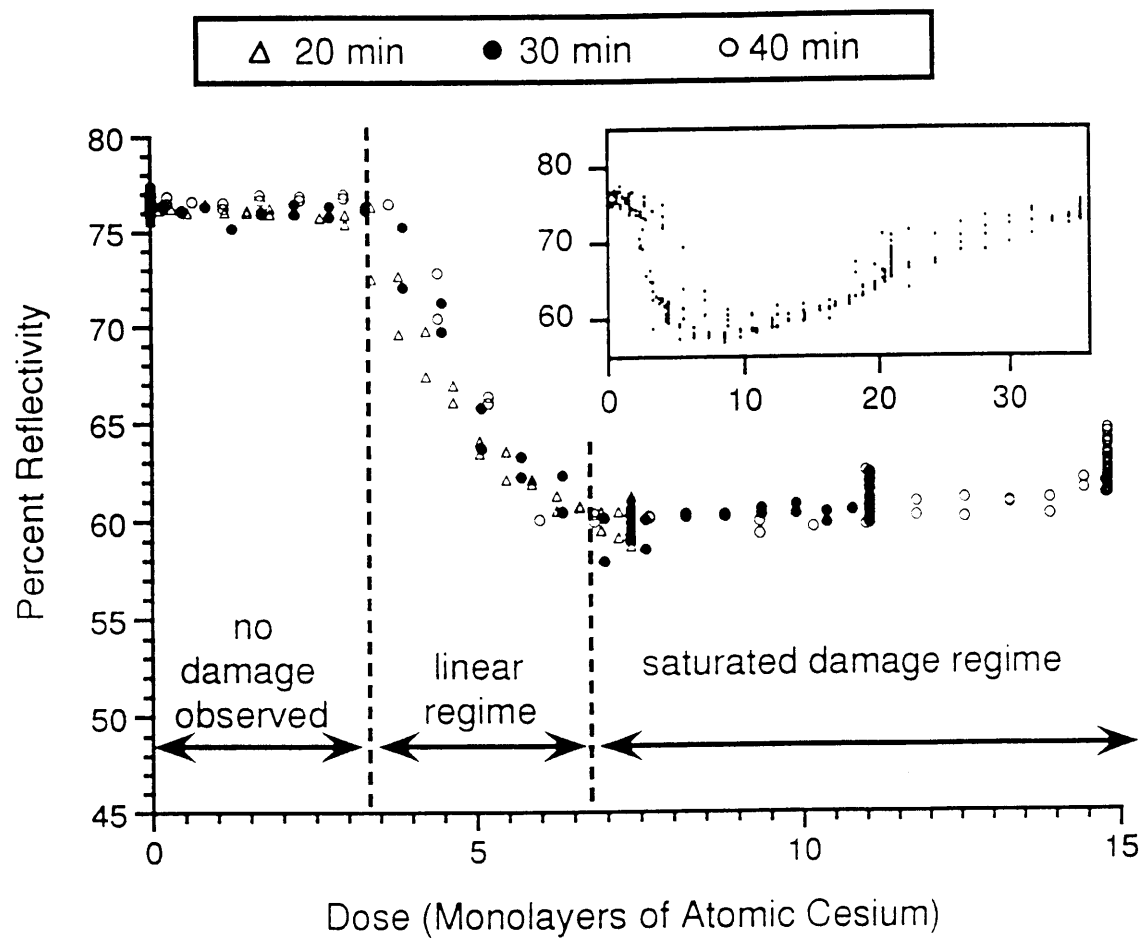
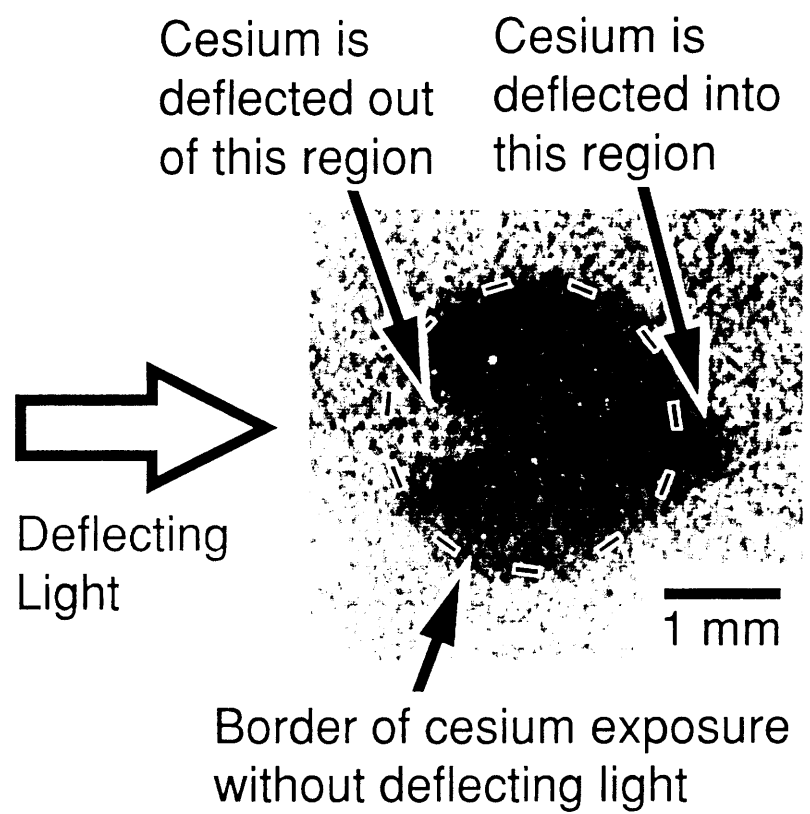


Figure 5: Photograph of an etched sample made in a control experiment where the SAM resist was exposed to an unmasked cesium beam that had been distorted by radiation pressure. For exposures (not shown) without deflecting laser light, the resulting etched spot was circular, as indicated by the dashed lines in the figure. The observed distortion of the damaged region for the sample shown here proved that atomic cesium was responsible for the damage effect seen in this paper.



The central result of this paper is that nm-scale patterns can be fabricated in a gold surface by exposing a nonanethiolate SAM resist to a patterned beam of neutral cesium atoms. Relatively low doses (~ 3 monolayers) of atomic cesium were sufficient to sensitize the SAM surface to penetration by a subsequent wet-chemical etch. When studied using the reflectivity of the gold substrate as an assay, this technique showed a critical thresholding effect. This effect might be used to improve the contrast or narrow features with broad backgrounds.

The damage mechanism of the SAM was not explored in this paper; it is likely that the damage is caused by a chemical interaction of the cesium with some component of the SAM surface or the SAM-Au interface.¹⁵ Because SAMs incorporating a variety of surface chemistries can be formed, this chemical damage mechanism suggests that the technique described in this paper could be exploited either to optimize the exposure time, or increase the range and utility of possible structures created with neutral atoms.

In control experiments that established that only atomic cesium effected the surface damage, the substrate was patterned on the macroscopic length-scale by optical deflection of the cesium beam using radiation pressure forces. In past experiments, light forces from an optical standing-wave have been used to pattern similar materials on the nm length-scale.²⁻⁴ The technique presented here could be used to transfer nm-scale features formed by optical standing-wave focusing into gold features. Because the patterned gold layer can then be used as a mask to etch into the underlying silicon,⁵ the result presented in this paper is a first step toward fabricating nanostructures in silicon using optically patterned neutral atomic beams.

Experimental

The optical thickness of the cesium beam was determined by measuring absorption of 852-nm laser light¹⁶ on resonance. The incident laser was shaped by expanding the laser beam to a ~ 1 -cm-diameter spot, and then aperturing to a diameter of 1.8 mm and $10 \mu\text{W}$ of power. Upon entering the σ^+ -polarized laser beam, the atoms in the $F=4$ ground state were quickly optically pumped into the $m_F = 4$ Zeeman sublevel. A ~ 5 Gauss magnetic field was used to establish the quantization axis for the atoms. Measurements of the absorption were made before and after each exposure and averaged (drifts were typically less than 10% over 1 hour). Analysis of absorption data allowed calculation of flux to a combined systematic and statistical error of ${}^{+30\%}_{-10\%}$. An oven temperature of $\sim 290^\circ\text{C}$ (measured using thermocouples outside the oven) was used to calculate the longitudinal velocity distribution, which was assumed to be thermal. The geometrical factor from the non-uniform radial density profile of the atomic beam was included in the analysis. This profile was verified experimentally by probing the atomic beam with resonant laser light, and re-imaging the fluorescence onto a CCD-array.

The reflectivity of mm-scale regions of damage in the gold surface from the unmasked atomic beam was measured using light from a helium-neon laser at 632 nm. The laser beam was spatially filtered by focusing through a $100\text{-}\mu\text{m}$ pin-hole, and then focused using a 5-cm lens to a $1/e^2$ diameter on the substrate of $20 \mu\text{m}$. A portion of the specularly reflected light was directed into a photodetector (assumed to be linear over the power ranges used — $0.1 - 4 \mu\text{W}$) and compared to the incident laser power. The 100% reflectivity level was calibrated using a high-quality mirror.

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