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Lithography can be performed with beams of neutral atoms in metastable excited states to pattern self-assembled monolayers (SAMs) of alkanethiolates on gold. An estimated exposure of a SAM of dodecanethiolate (DDT) to 15 to 20 metastable argon atoms per DDT molecule damaged the SAM sufficiently to allow penetration of an aqueous solution of ferricyanide to the surface of the gold. This solution etched the gold and transformed the patterns in the SAMs into structures of gold; these structures had edge resolution of less than 100 nanometers. Regions of SAMs as large as 2 square centimeters were patterned by exposure to a beam of metastable argon atoms. These observations suggest that this system may be useful in new forms of micro- and nanolithography.

A new method of microlithography has been developed that uses a beam of neutral inert gas atoms in metastable excited states to pattern self-assembled monolayers (SAMs) of alkanethiolates on gold (*1*–*3*). Lithography with neutral metastable atoms has several advantages. Unlike techniques that use beams of electrons or ions, there are no electrostatic interactions within a neutral beam that limit focusing or flux density, either in a single beam or in a parallel array of beams. Because of their short (<0.01 nm) deBroglie wavelength, thermal beams of neutral atoms can in principle be focused (*4*) to a spot that is limited by the size of the atom. In contrast to photolithography, where practical problems with optics and diffraction limit the resolution to ~100 nm, it is possible to create and manipulate (*4*) beams of neutral atoms with de Broglie wavelengths <0.01 nm. For these beams, the effects of diffraction will be very small, even for lithography through masks with 10-nm scale features.

SAMs on gold and silicon have been used as resists in a number of types of lithography (*5*, *6*). Their thinness (typically <2 nm) is essential for metastable atom lithography: interactions between a metastable atom and a substrate are limited to a surface layer that is probably ≤0.5 nm thick (*7*), and fluxes of metastable atoms from present sources (*8*, *9*) are low (~1×10^{14} atoms s^{-1} sr^{-1}). For exposure of a resist to take place in a practical period of time, it must therefore be complete after contact with a few monolayers of metastable atoms with the surface.

The ability to damage SAMs with metastable inert gas atoms and to transform this damage into permanent structures of gold or other materials such as silicon (*10*) may be useful in both lithography and atom optics. For lithography, light forces could be used to focus (*11*) metastable atoms onto a SAM resist and make possible lithography without a physical mask. In atom optics (*4*), damaging SAMs with neutral atoms may be useful in high-resolution detectors of atomic center-of-mass wave functions. In both applications, the use of atoms to expose SAMs is conceptually similar to the use of photons to expose a photographic emulsion, in that both use chemical development to achieve amplification of a sensitizing event.

Figure 1 outlines our experimental procedure. The substrate was a thin film of gold supported on a titanium-primed silicon wafer (*12*); this substrate supported a 1.5-nm-thick SAM (*2*) of dodecanethiolate [DDT, $CH_3(CH_2)_{11}SH$]. The substrate was exposed (*13*) to a beam of Ar atoms in which less than 1 in 10^4 were in either the 4s $^3P_2$ (80%, 11.5 eV) or 4s $^3P_0$ (20%, 11.7 eV) metastable states (*8*). This beam was mechanically collimated to ~1 mrad and shaped spatially by a triangular aperture to a ~3 mm^2 area (larger areas of exposure were possible). The time of exposure was typically 1 to 4 hours, although we explored exposure times ranging from 15 min to 36 hours (see below). After exposure, the pattern of damage in the SAM was developed into a pattern of gold with a ferricyanide etch (*14*).

A diagram of the apparatus used in these experiments is shown in Fig. 2. The flux of metastable inert gas atoms was generated with a dc discharge similar to one described in detail elsewhere (*8*). The experiments used a nominal pressure of 2×10^{-6} Pa; with the discharge on, the pressure rose to roughly 3×10^{-3} Pa. The collimated metastable beam was directed toward a stainless steel plate detector. Because of collision-induced electron emission (*15*), the metastable flux could be measured by recording the current on the detector (*16*), or on the sample itself, with a picoammeter. The measured current was typically 1.7 nA; this value corresponds to an electron emission rate of ~3×10^{11} events per second per square centimeter.

We exposed a SAM/gold substrate to the beam of metastable Ar by using a transmission electron microscopy (TEM) grid (~10 μm thick; 5-μm-wide lines, Fig. 3, A and B)

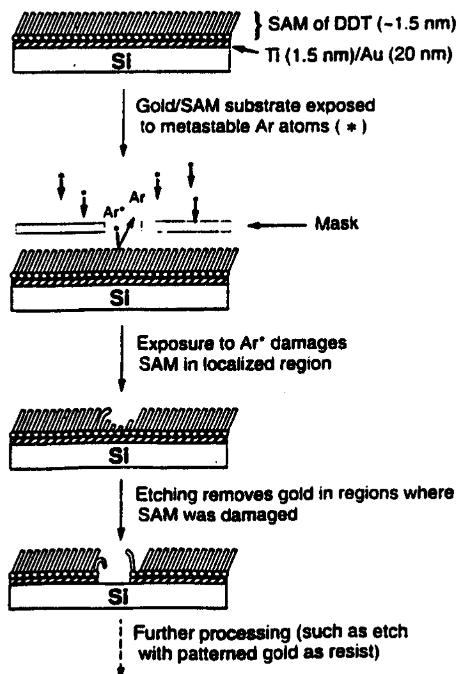

Fig. 1. Schematic of the experimental procedure. Dimensions are not to scale. The structure of the SAM when damaged and at the border of the etch pit is unknown but is probably disordered.

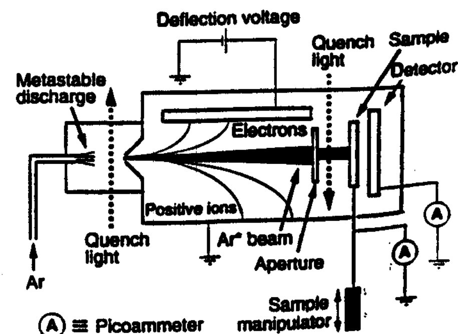

Fig. 2. Schematic of the experimental apparatus. See text for details.

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as a mask; etching formed gold structures in the pattern of the grid (Fig. 3, C to E). The edge resolution (~100 nm, Fig. 3E) of the gold structures was comparable to that of the TEM grid (Fig. 3B). This result demonstrates that SAMs patterned by Ar* can be used for lithography. It also establishes the upper bound for the resolution in our experiments. Gold structures fabricated in this manner could be used further as resists for anisotropic etching (*5*, *10*, *17*) of silicon (Fig. 3F).

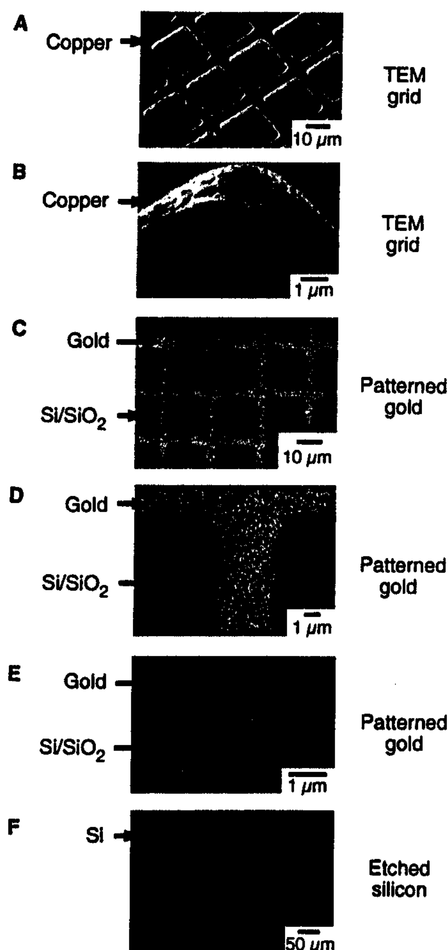

Fig. 3. Exposing SAMs of dodecanethiol on gold to a beam of metastable Ar, followed by wet-chemical etching, produced structures of gold and silicon with features ranging from 5 μm to several millimeters. (**A** and **B**) Scanning electron microscopy (SEM) images of a Cu TEM grid used as a mask (in contact with the surface of the substrate) to form the features in (**C**) to (**E**). The image in (B) shows a smaller region of the TEM grid in (A) at higher magnification: the sample was tilted to help visualize the edge resolution of the grid. (C to E) SEM images of patterned gold structures fabricated with the TEM grid shown in (A) and (B) as a mask. (**F**) An SEM image of a fracture profile of silicon structures fabricated by anistropic etching using gold microstructures as resists. These gold microstructures (not shown) were prepared by using a larger wire grid (~25-μm-wide lines, not shown) than the grid shown in (A) and (B). The edge resolution of the silicon structures was comparable to the edge resolution of the wire grid.

Control experiments that deexcited the metastable atoms ($4s\ ^3P_2$ state) in the beam established that the damage to the SAM was due only to metastable atoms (*18*). Irradiation at 764 nm (*19*) excited Ar atoms from the $4s\ ^3P_2$ state to the $4p\ ^1D_2$ state, which decayed in a rapid cascade to the ground state of the atom; the $4s\ ^3P_2$ atoms (~80% of the metastable atoms) were thus quenched. Exposure of a SAM/gold substrate to an unquenched beam (integrated flux equivalent to 1.3×10^{16} metastable atoms per square centimeter, or ~28 monolayers) caused sufficient damage so that etching was complete in the exposed region after 40 min in the etching solution. Exposure to a quenched beam for the same time (integrated flux equivalent to 2.6×10^{15} metastable atoms per square centimeter, or ~6 monolayers reduced damage to a level at which the substrate did not show pitting (above the level expected for unexposed DDT SAMs) after a 60-min exposure to the etching solution. These experime show that the metastables were the cause damage to the SAM in the unquench beam (*20*).

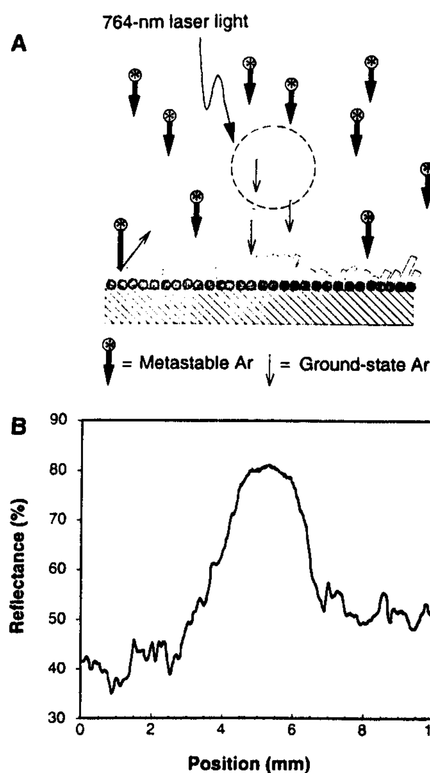

Fig. 4. (**A**) A beam of 764-nm light (dotted circle in diagram) quenched Ar* to Ar where it intersected the beam of metastables. Exposing a SAM/gold substrate to a "spatially quenched" metastable beam produced a pattern of damage that reflected the distribution of the flux of Ar* in the modified beam. (**B**) A plot of optical reflectance, (measured at normal incidence, linearly polarized light at 632.8 nm) versus position on a sample prepared with a "spatially quenched" metastable beam and etching. Higher reflectance corresponded to regions of gold not removed by the etch (that is, where exposure to the quenched beam did not damage the SAM).

In a different control experiment, beam of light with a spatial intensity dist bution ($1/e^2$ width ≈2 mm) narrower th the spatial distribution of the metastab (~3 cm) was directed transversely throu the beam of metastables a few millimet from the substrate (Fig. 4A); the Ar* w quenched only in the region of intersecti Exposing a SAM/gold substrate to this p tially quenched beam resulted in a pattern damage that reflected the spatial distributi of Ar* in the modified beam (Fig. 4B). T experiment confirmed that Ar* was the sp cies in the metastable beam that damag the SAMs. It also showed (at the millime scale) that beams of Ar* that have be patterned spatially by optical quenching c be used to pattern SAMs (*21*).

To correlate the dose (D_{Ar^*}) of metast ble Ar delivered to the SAM resist with t damage to the SAM that resulted from t exposure, the SAM/gold substrates were e posed to Ar* through a triangular apertu and etched (*14*). The time (t_{etch}) requir to form the pattern in the gold (*22*) d creased with increasing dose (Fig. 5); integrated flux equivalent to ~100 mon layers of Ar* produced saturating levels damage.

In summary, exposure of SAMs of DD on gold to metastable Ar atoms sensitiz them to etching by an aqueous ferricyani solution. This method of patterning SAM suggests a new approach to lithography b using neutral metastable atoms as energ carriers. Because there is ample precede that light forces can direct the deposition neutral atoms spatially on a surface (*11*

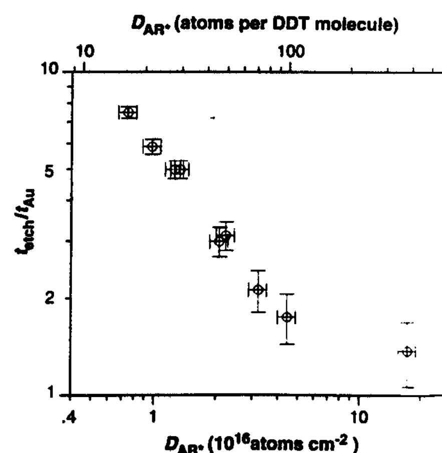

Fig. 5. The time required to form a triangular patter in the gold by etching (t_{etch}), normalized to the tim required to etch unprotected gold (t_{Au}, 9 min), versu the dose of metastable Ar (D_{Ar^*}, expressed in atom per square centimeter and as atoms per DDT mole cules, or monolayers). See text for details.

and because this work demonstrates quenching of metastable neutral atoms by optical pumping in selected regions of space (Fig. 4), what we describe here is, in principle, an "all-optical" method of forming nanometer-scale patterns.

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12. Gold films were formed by electron-beam evaporation of ~1.5 nm of Ti (adhesion promoter) and ~20 nm of gold (99.999%) onto a silicon wafer.
13. Several mechanisms for deexcitation of Ar^* by the surface are possible. We do not know which mechanism results in damage to the SAM. See F. Bozco, J. T. Yates Jr., J. Arias, H. Metiu, R. M. Martin, *J. Chem. Phys.* **78**, 4256 (1983).
14. We used an aqueous ferricyanide etch [0.001 M $K_3Fe(CN)_6$, 0.01 M $K_4Fe(CN)_6$, 0.1 M $K_2S_2O_3$, and 1 M KOH]; Y. Xia; M. Zhao, G. M. Whitesides, unpublished results.
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16. These detectors typically operate with efficiencies of between 4 and 22% for Ar^*. See F. B. Dunning and A. C. H. Smith, *J. Phys.* **B4**, 1696 (1971). If we assume a detector efficiency of 13%, we can estimated the flux of metastable atoms to be 2.6×10^{12} atoms per second per square centimeter. We refer to the dose of metastables in "atoms per DDT molecule" (or just "monolayers") which corresponds to 4.6×10^{14} atoms per square centimeter.
17. J. L. Wilbur, E. Kim, Y. Xia, G. M. Whitesides, *Adv. Mater.*, in press. We used 1% NH_4F (~1 min) to remove the native SiO_2 and an alcoholic solution of potassium hydroxide (4 M KOH, 15% isopropyl alcohol, 60°C, 15 min) to etch silicon. See (*10*) for details.
18. The source produced electrons and positive ions that were deflected away from the sample by a stainless steel rod maintained at ~1700 V. Higher voltages did not further reduce the detector current. It also generated photons (visible to vacuum ultraviolet) and neutrals with high kinetic energies.
19. The light intersected the atomic beam just before the beam left the discharge area (before the collimating aperture). See Fig. 2.
20. This observation also confirmed that metastable atoms were the major component of the signal on the detector (or sample).
21. We have used a standing wave of 764-nm light as an optical mask to fabricate arrays of lines with micrometer-scale features. J. L. Wilbur, K. K. Berggren, A. Bard, S. L. Rolston, J. D. Gillaspy, M. Prentiss, G. M. Whitesides, unpublished results.
22. The transition from a pattern that was marginally visible by eye to a pattern that was distinctly visible occurred in <5 min. The estimated error in t_{etch} is therefore ± 2.5 min.

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