Using neutral metastable argon atoms and contamination lithography to form nanostructures in silicon, silicon dioxide, and gold

K. S. Johnson,[a),c)] K. K. Berggren,[a)] A. Black,[b)] C. T. Black,[a)] A. P. Chu,[a)] N. H. Dekker,[a)] D. C. Ralph,[a)] J. H. Thywissen,[a)] R. Younkin,[a)] M. Tinkham,[a)] M. Prentiss,[a)] and G. M. Whitesides[b)]
Harvard University, Cambridge, Massachusetts 02138

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This letter describes the fabrication of ~80 nm structures in silicon, silicon dioxide, and gold substrates by exposing the substrates to a beam of metastable argon atoms in the presence of dilute vapors of trimethylpentaphenyltrisiloxane, the dominant constituent of diffusion pump oil used in these experiments. The atoms release their internal energy upon contacting the siloxanes physisorbed on the surface of the substrate, and this release causes the formation of a carbon-based resist. The atomic beam was patterned by a silicon nitride membrane, and the pattern formed in the resist material was transferred to the substrates by chemical etching. Simultaneous exposure of large areas (44 cm^2) was also demonstrated. © *1996 American Institute of Physics.* [S0003-6951(96)03344-X]

Argon atoms in the energetic metastable $4s[\frac{3}{2}]_2$ and $4s[\frac{1}{2}]_0$ states, in combination with trimethylpentaphenyltrisiloxane vapors present as dilute contaminants in the vacuum chamber, were used to create ~80-nm features in Si, SiO_2, and Au substrates. The metastable atoms are deexcited to their ground state upon contacting molecules adsorbed on the substrate, and release their internal energy (~12 eV); this release resulted in the formation of a carbon-containing resist layer on the surface. Passing the beam of atoms through a physical mask — a perforated membrane of Si_3N_4 — resulted in a patterned resist on the substrate. This pattern was transferred into the underlying substrate by wet-chemical etching. The atomic beam, with an appropriate mask, could be used to pattern large areas (44 cm^2) in a single exposure. Current fluxes of metastable beams and the efficiency of the resist formation process require long exposure times (~15 hours) to form a layer that is sufficiently impermeable to act as an effective resist.

Beams of electrons have been used in conjunction with similar contaminants present in a vacuum system to produce ~8-nm features.[1–3] This type of lithography — that is, lithography based on forming an advantitious resist by reaction with contamination vapors — requires high doses ($\sim 10^{-1}$ C/cm^2) of electrons. Because this dose requirement is much more severe than the $\sim 10^{-4}$ C/cm^2 needed to form a resist in PMMA, contamination-based lithography using electron-beams is not presently used for processing. Electron-beam lithography[1,4] is also a serial process with resolution limited by scattering and secondary electrons; low beam currents are required to limit Coulombic instabilities in the beam.

Several characteristics of metastable atoms make them interesting for lithography:[5] (1) the deBroglie wavelength for atoms is short (~0.01 nm in this work) and should not limit the resolution; (2) beams of metastable atoms can be generated with large cross-sections, and these beams can be used to pattern wafer-sized areas in a single exposure; (3) the process by which the energetic metastable atoms transfer energy to the surface is localized at the surface layer,[6] so the resolution should not be decreased significantly by electron scattering; (4) optical fields can be used to focus atoms to form small features (~ 25 nm);[7] (5) optical de-excitation of metastable atoms can, in principle, be used to form patterns.[5,8] This letter demonstrates that contamination lithography using metastable atoms can be used to generate structures ~ 80 nm in size. Simultaneous exposure of a full wafer also demonstrates patterning over large area (44 cm^2) in a single exposure.

Figure 1 shows the process used to generate nanostructures in three different material substrates: (i) Si ⟨110⟩ wafers with native (~2 nm) oxide layer, (ii) Si ⟨100⟩ wafers with a 300-nm-thick overlayer of thermally grown SiO_2, and (iii) substrates formed by electron-beam evaporation of 20 nm of Au onto a Si substrate with a 2-nm-thick Ti adhesion layer.

The substrates were exposed to a beam of metastable argon inside an oil diffusion pumped vacuum system with a base pressure of $\sim 2\times 10^{-7}$ Torr. The diffusion pump oil used (DC705) consisted of trimethylpentaphenyltrisiloxane (90%) and poly(phenylmethylsiloxane) (10%). A direct current discharge source was used to produce the beam of metastable atoms.[9] These sources also emit ions, electrons, UV photons, and both thermal and energetic neutral atoms.[9] High voltage electrostatic deflection plates were used to prevent the charged particles from reaching the substrates. The flux of metastables hitting the substrate surface was estimated, using a steel plate detector, to be $3 \times 10^{11} \pm 15\%$ atoms cm^{-2} sec^{-1}.[10] The detector and substrates were placed 50 cm away from the source of the atomic beam.

The substrates were exposed to the beam through two different physical masks. Nm-scale features were created by exposure through a patterned 50-nm-thick Si_3N_4 membrane.[11] A stainless steel mesh was used as the mask in a demonstration of exposure of a large area. A combination of machined aluminum mounting clamps and conductive carbon tape was used to hold the masks and substrates in the vacuum system.

The patterns of protective resist were transferred to the

[a)]Department of Physics.
[b)]Department of Chemistry.
[c)]Electronic mail: kent@atomsun.harvard.edu

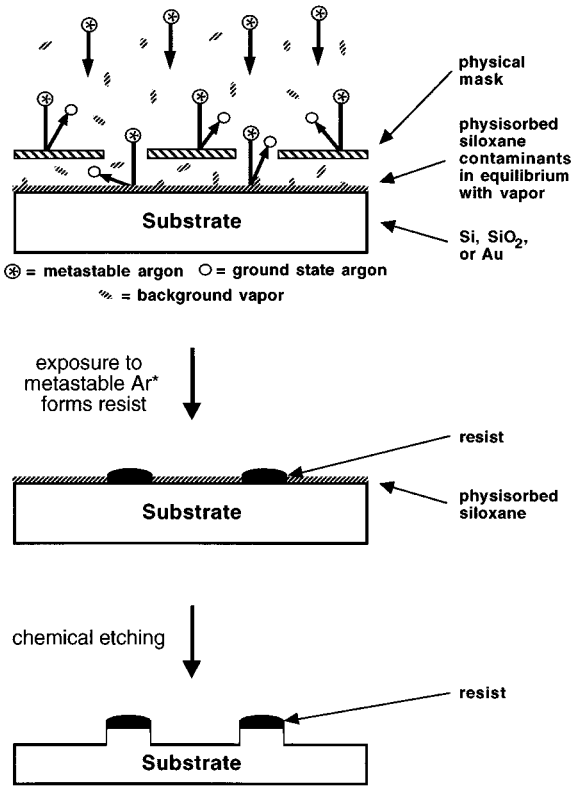

FIG. 1. Schematic representation of the process used to create nanostructures. Samples were exposed to a beam of neutral metastable argon atoms that had been passed through a physical mask; the environment was vacuum (base pressure $\sim 10^{-7}$ Torr) containing an adventitious vapor of diffusion pump oil. A carbon-containing resist was formed in regions exposed to these atoms, and the pattern was transferred to the underlying substrate by wet chemical etching. Silicon dioxide, silicon, and gold substrates were etched in 1% aqueous HF solution, 40% aqueous KOH solution, and aqueous ferricyanide solution, respectively.

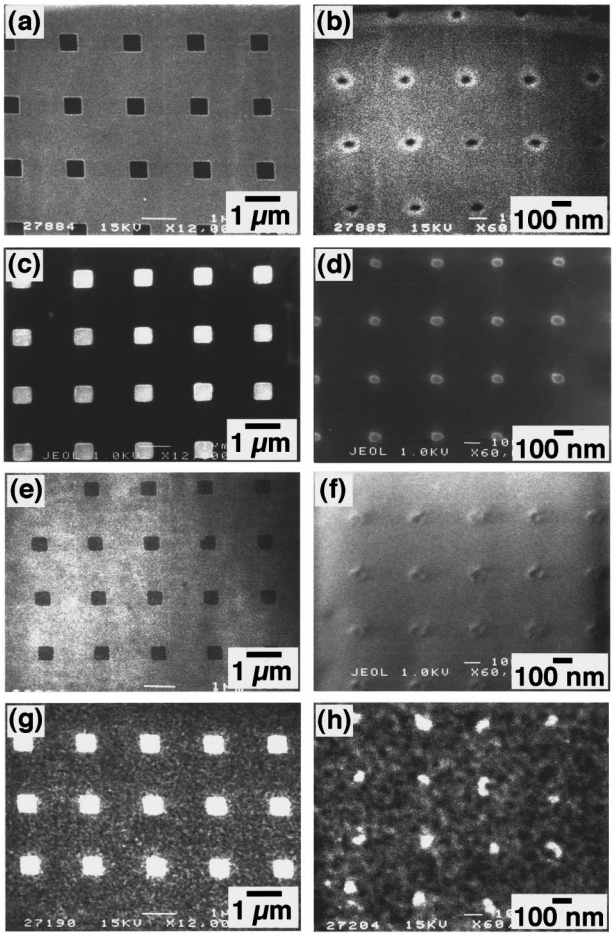

FIG. 2. SEM images of the masks used and of the nanostructures created using the process shown in Fig. 1. **(a) and (b)** Two regions of the silicon nitride mask (50-nm-thick membrane) used to pattern the atomic beam: regions of 500 nm square holes (a) and ~50 nm round holes (b). **(c) and (d)** Si ⟨110⟩ with a ~2-nm native oxide layer exposed for 16 hr through the mask shown in (a) and (b) and etched first in 1% aqueous HF to remove the oxide, then in 40% aqueous KOH to etch the silicon. **(e) and (f)** SiO_2 exposed for 15 hr through the mask in (a) and (b) and etched for 180 sec in 1% aqueous HF. **(g) and (h)** Au film exposed through (a) and (b) for 18 hr and etched for 8 min in aqueous ferricyanide solution.

underlying substrate by wet chemical etching. The silicon oxide layer was removed by treatment with 1% aqueous HF solution for 15 sec (native oxide) or 2–4 min (thermal oxide), and the silicon etched with 40% aqueous KOH solution at 70 °C for 1–4 sec. The Au samples were etched in an aqueous ferricyanide solution for 7–10 min.[12] Samples were transferred in ambient laboratory conditions both before and after exposure. Etched substrates were imaged by a scanning electron microscope (SEM). X-ray photoelectron spectroscopy (XPS) and Auger spectroscopy (AES) helped characterize the composition of the organic material present on the substrate surface before etching. Reactive ion etching (RIE) was used to characterize further the resist material that formed.

Figure 2 shows structures formed in silicon, silicon dioxide, and gold substrates using the procedure outlined in Fig. 1. The smallest features formed are less than 80 nm. Combined with the controls described below, these images show that contamination based resists formed by interaction of metastable argon with adsorbed pump oil support a resolution of at least 80 nm, and that this resolution can be achieved in insulating, semiconducting, and metal substrates with appropriate wet chemical etching procedures. This feature resolution is limited by the size of the physical mask and our ability to place the mask close to the surface, by the resolution of the etching procedure used to transfer the pattern to the substrate, and by the resolution of our imaging system. In the case of gold, the resolution is also limited by the grain size of the gold films, as is apparent in Fig. 2(h).

Figure 3 shows a full 3-in wafer (44 cm^2) patterned with a single exposure. The Si ⟨100⟩ substrate with a 300-nm thermal oxide layer was exposed through a stainless steel mesh of 1.4 mm periodicity (0.98-mm holes) held approximately 0.1 cm above the substrate surface. The sample shown received a total dose of $\sim 1.4 \times 10^{16}$ atoms/cm^2 during a 22 hour exposure and was etched in 1% aqueous HF solution for 140 sec. This high dose was used to maximize the contrast and uniformity of the resulting image.

Analysis of XPS spectra from silicon dioxide surfaces with varying exposures to the atomic beam revealed that increasing exposure time resulted in the intensity of the carbon ($1s$) signal increasing relative to the principal substrate constituents (silicon and oxygen). A silicon dioxide substrate exposed to the atomic beam for 21 hours exhibits a carbon ($1s$) peak that is 2.6 ± 0.3 times more intense in the exposed regions than in the unexposed regions. The increase in the carbon signal was accompanied by similarly significant

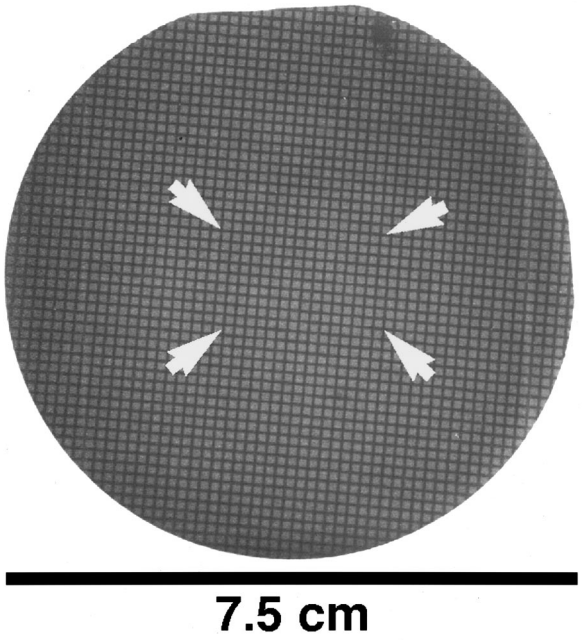

FIG. 3. Photograph of a patterned 3-in. wafer (44 cm^2 area). A 300-nm thermal oxide layer on Si ⟨100⟩ was exposed to a beam of metastable argon atoms (total dose $\sim 1.6\times 10^{16}$ atoms/cm^2) and then etched for 140 sec in aqueous HF solution. The atomic beam was patterned by a stainless steel mesh. The arrows indicate the approximate positions in the atomic beam at which substrates (Figure 2(c)-(h)) were exposed to create nanostructures.

decreases in the intensity of the oxygen $(1s)$ and silicon $(2p)$ peaks. Additionally, Auger electron spectra of exposed gold substrates indicated that both the carbon $(1s)$ and silicon $(2p)$ peaks were more intense in the exposed regions than in the unexposed areas.[13] Since carbon and silicon are both atomic constituents of the diffusion pump oil, the XPS and AES spectra of the resist material are consistent with the pump oil being the source of the resist material.

Silicon ⟨100⟩ samples exposed to the atomic beam for 24 hours through a stainless steel mesh (see Fig. 3) were used to characterize the effect of RIE on the resist material. The pattern of resist material was removed after two minutes of oxygen RIE. (SEM imaging and the observed hydrophilicity were used to establish the complete removal of the carbon pattern.) The macroscopic pattern formed in the resist material was also transferred into the silicon substrate using a $SiCl_4$ RIE.

Control experiments verified that metastable atoms, rather than other constituents in the beam, were the dominant contributor to resist formation.[5] The metastable atoms can be induced to release their internal energy before hitting the substrate by resonant optical excitation using laser light; in order to excite atoms in both the $4s[\frac{3}{2}]_2$ and the $4s[\frac{1}{2}]_0$ states, we use light with $\lambda\sim$ 801.5 nm and $\lambda\sim$ 794.8 nm, respectively. In this optical pumping process, light excites metastable atoms to an excited state that rapidly decays to the ground state of the atom, dissipating the internal energy as a UV photon.

Beams ($\sim$1 mm $1/e^2$ radius) of laser light were passed through the atomic beam $\sim$ 1 cm before the atoms hit the substrate. For all three types of substrate, a robust protective resist did not form in the regions where the atoms traveled through the laser light. The light acted as a ''virtual mask'' for the metastable atoms, returning them to their ground state before they reached the surface. This result indicated that, for the exposure times investigated, metastable argon atoms, not any other beam constituent, were central in the formation of the resist.

Coating the substrates with $\sim$1 nm of DC705 diffusion pump oil prior to exposure to the atomic beam reduced the exposure time required to form an effective resist to approximately 1 hour. This observation is further evidence that the adsorbed pump fluid is involved in the formation of the resist and that the rate of resist formation is limited, in part, by the availability of material at surface during exposure.

This work demonstrates that a resist can be formed on a substrate by exposure to a beam of metastable argon atoms[14] in the presence of a siloxane vapor. This patterned protective layer can be transferred to a variety of substrates by wet chemical etching. With an appropriate mask, the resolution is better than 80 nm. The exposure times demonstrated in this work are quite long–further improvements in throughput are required if this technique is to be used for practical applications. We do not completely understand the process that forms the resist at the molecular level.

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[12] 0.001 M $K_4Fe(CN)_6$, 0.01 M $K_3Fe(CN)_6$, 0.1 M $K_2S_2O_3$, and 1 M KOH; see Y. Xia, X.-M. Zhao, E. Kim, G. M. Whitesides, Chem. Mater. **7**, 2332 (1995).
[13] An increase of the silicon signal due to the resist material was not observable when using a silicon dioxide substrate because of the large substrate contribution to the silicon signal.
[14] Some other energetic metastables might be used in this process: He* ($\sim$20 eV), Ne* ($\sim$16 eV), Kr* ($\sim$10 eV), Xe* ($\sim$10 eV), and H_2* ($\sim$10 eV).