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

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(Received 10 July 1996; accepted for publication 22 August 1996)

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 cm²) was also demonstrated. © 1996 American Institute of Physics. [S0003-6951(96)03344-X]

Argon atoms in the energetic metastable 4s(3/2) and 4s(1/2) states, in combination with trimethylpentaphenyltrisiloxane vapors present as dilute contaminants in the vacuum chamber, were used to create ~80-nm features in Si, SiO₂, and Au substrates. The metastable atoms are de-excited 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 Si₃N₄ — 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 cm²) 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. This type of lithography — that is, lithography based on forming an advanititious resist by reaction with contamination vapors — requires high doses (~10⁻¹¹ C/cm²) of electrons. Because this dose requirement is much more severe than the ~10⁻⁴ C/cm² needed to form a resist in PMMA, contamination-based lithography using electron-beams is not presently used for processing. Electron-beam lithography 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: (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, 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); (5) optical de-excitation of metastable atoms can, in principle, be used to form patterns. 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 cm²) 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 SiO₂, 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 ~2x10⁻⁷ 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. These sources also emit ions, electrons, UV photons, and both thermal and energetic neutral atoms. 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 3x10¹¹±15% atoms cm⁻² sec⁻¹. 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 Si₃N₄ membrane. 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

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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. 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 cm²) 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 received a total dose of \( \sim 1.4 \times 10^{16} \) atoms/cm² 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
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 ~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 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.

This work was partially supported by NSF grant PHY 9312572. This work made use of the Harvard MRSEC shared facilities and the MIT Center for Materials Science and Engineering facilities. K. S. Johnson was supported by an AT&T Graduate Fellowship. J. H. Thywissen was supported by the Fannie and John Hertz Foundation. A. P. Chu was supported by an NSF Fellowship. For assistance in sample analysis, we thank Yuan Lu, Mike Frongillo, Libby Shaw, Steve Shepard, and Rich Perilli. We thank S.L. Rolston, James L. Wilbur, Andreas Bard, and Chris Constantine for fruitful discussions.

21. An increase of the silicon signal due to the resist material was not observed when using a silicon dioxide substrate because of the large substrate contribution to the silicon signal.