Patterning of octadecylsiloxane self-assembled monolayers on Si(100) using Ar($^3P_{0,2}$) atoms

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We report the use of metastable Ar($^3P_{0,2}$) atoms and a physical mask to pattern octadecylsiloxane self-assembled monolayers grown directly on silicon surfaces. The damage to the monolayer is confirmed using lateral force microscopy, changes in hydrophilicity, and x-ray photoelectron spectroscopy analysis. Metastable atom exposures sufficient to uniformly damage the monolayer should allow pattern transfer to the underlying Si(100) substrate following chemical and plasma etching. With optical manipulation of the incident metastable atoms, this technique could provide the basis for massively parallel nanoscale fabrication on silicon. © *1999 American Vacuum Society.* [S0734-211X(99)04903-3]

The majority of nanolithography techniques in use today utilize a beam of energetic particles or photons to locally alter a surface resist layer such that subsequent chemical or plasma etching will transfer the pattern to the Si substrate. The use of metastable atom beams to pattern silicon surfaces has also been demonstrated[1–5] and promises very high resolution that is not limited by the scattering of electrons within the resist layer as in electron beam lithography[6–8] or by the diffraction effects of optical lithography.[9–11] Furthermore, metastable atoms can be manipulated in optical fields to restrict metastable atom impact on the surface to a series of well defined lines or points obviating the need for a mask and offering the potential for massively parallel fabrication.[12–14] Because they are so thin (1–2 nm), self-assembled monolayers (SAMs) have considerable potential as resists for high resolution lithography. Earlier work using a dodecanethiol SAM deposited on a gold substrate has shown that such films can be damaged by metastable atom impact and used as a resist to transfer patterns to the underlying gold with edge resolutions as low as 30 nm.[1,3] Octylsiloxane SAMs grown on SiO_2 have also been patterned with sub-100 nm resolution using ground state Cs atoms.[15] Here we demonstrate that an octadecylsiloxane (ODS) SAM grown on a SiO_2 substrate is damaged by incident Ar($^3P_{0,2}$) atoms and that this provides the basis of a technique for nanolithography on silicon.

The ODS SAMs are grown on the native oxide layer of Si(100) wafers by immersion in an octadecyltrichlorosilane solution.[16] (Use of ODS SAMs does not require the initial deposition of adhesion and Au layers as in earlier work.[1,3]) Following a final cleaning in methylene chloride, the samples were placed in an unbaked UHV chamber [base pressure $\sim 5\times10^{-6}$ Pa (4×10^{-8} Torr)] and exposed to a beam of Ar($^3P_{0,2}$) atoms through a Ni mesh that served as a mask.

The Ar($^3P_{0,2}$) atoms are created in a dc discharge by electron impact excitation of argon contained in a supersonic expansion.[5,17] Electron impact also leads to the formation of ions, photons, and long lived Rydberg states. Ions and Rydberg atoms are removed from the beam by application of a transverse electric field. To examine possible effects due to the UV photons also contained in the beam, a gas cell was included in the beam line. Introduction of $\sim 7\times10^{-2}$ Pa (5×10^{-4} Torr) of NO into the gas cell deexcites essentially all the metastable atoms in the beam while allowing the photons to continue through largely unattenuated. The flux of metastable atoms at the target surface was estimated by measuring the current of secondary electrons ejected from a chemically cleaned stainless steel surface. Assuming a secondary electron ejection coefficient of 0.1,[18] these measurements suggest that the source can provide a flux of $\sim 2\times10^{15}$ Ar($^3P_{0,2}$) $m^{-2} s^{-1}$ at the target location $\sim$0.7 m from the source. Tests using the gas cell demonstrated that only $\sim$10% of the current leaving the surface was associated with photon impact.

The damage to the SAM resulting from metastable atom impact was examined using a number of different techniques. Lateral force microscopy (LFM) was used to measure the change in surface friction of the SAM, which is expected to increase when damaged.[19,20] Figure 1 shows a typical LFM image obtained following an exposure of 1×10^{20} Ar($^3P_{0,2}$) m^{-2}, the maximum that could be reasonably achieved using the present apparatus. The damage induced by metastable atom impact has clearly transferred the

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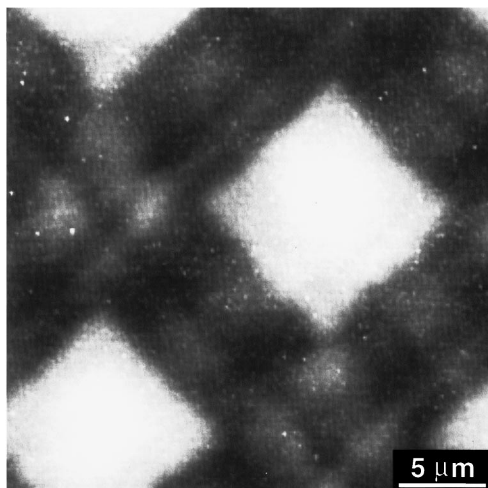

FIG. 1. Lateral force microscopy image of octadecylsiloxane SAM damaged by $Ar(^3P_{0,2})$ impact, showing increased surface friction in the areas damaged by the metastable atoms. The atom beam is patterned before striking the surface by passing through a square Ni mesh with 12.7 μm pitch (5.1 μm wires and 7.6 μm spaces).

image of the mask to the SAM. Damage also increases the hydrophilicity of the exposed areas and can therefore be examined by condensing water on the surface. Figure 2 shows an optical-microscopy image of water droplets formed on the exposed surface. An ordered array of droplets condensed on the damaged SAM areas is observed providing further evidence of patterning. The metastable atom induced damage to the SAMs was also studied using x-ray photoelectron spectroscopy (XPS). (No mask was used in these experiments.) These measurements showed that in areas shielded from metastable atom impact the XPS spectrum was dominated by a single $C(1s)$ peak associated with the $CH_3(CH_2)_{17}$ chain

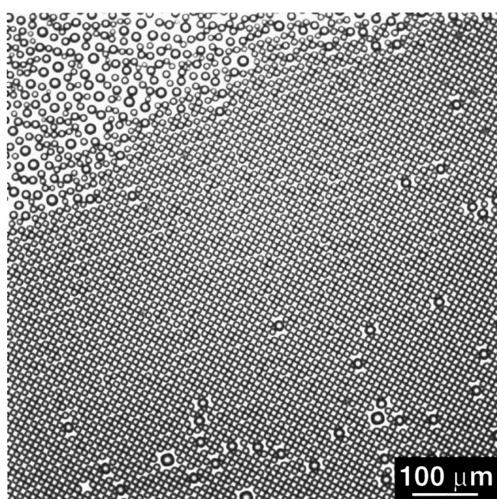

FIG. 2. Optical-microscopy image showing condensation of water on the SAM following exposure to the $Ar(^3P_{0,2})$ beam through the Ni mesh mask. The areas damaged by metastable atom impact become hydrophilic, producing an array of water droplets with the same periodicity as the mask. A small region of unexposed area with a random coverage of droplets is visible in the upper left corner of the image.

portion of the intact ODS monolayer.[21] In regions exposed to metastable atom impact, this peak was decreased by ~20%, and several other peaks were detected at energies 1.2, 2.7, and 4.2 eV above the main peak. These peaks are attributed to C–O, C=O, and CO_2 groups, respectively, and presumably result from reactions between damaged, unsaturated hydrocarbons and atmospheric oxygen and water during transfer to the XPS apparatus. The relatively small decrease in the $C(1s)$ XPS peak, however, suggests that the exposure levels attainable using the present apparatus [1×10^{20} $Ar(^3P_{0,2})$ m^{-2}] are less than the optimal doses required to sufficiently reduce the etch resistance of the SAM to obtain optimum feature contrast. This is consistent with earlier measurements which demonstrated that a minimum $Ar(^3P_{0,2})$ exposure of $\sim2.5\times10^{20}$ $Ar(^3P_{0,2})$ m^{-2} is required to allow uniform and complete etching of a (shorter) dodecanethiol SAM grown on gold.[2]

To check that the observed damage to the SAM was not due to photon impact, tests were undertaken in which the metastable atoms in the beam were quenched using the gas cell, thereby allowing only photons produced in the source to strike the surface. No pattern transfer was detectable using either LFM or condensation methods following exposure times equal to those used for Figs. 1 and 2. Also, no discernible decrease in the C XPS signal was evident. In addition, ancillary studies using Auger analysis showed that extended exposure of hydrogen-passivated Si(100) surfaces to metastable atom impact in the same apparatus[5] did not lead to the build up of carbonaceous deposits which could result in a false indication of patterned damage to the SAM.

The present work shows that metastable atom impact can damage an ODS SAM grown directly on the native oxide of a silicon substrate. Earlier work using an incident electron beam has shown that such damage can form the first step in patterning the underlying silicon.[20,22] To accomplish this, the damaged SAM material is first removed by UV/ozone exposure. The exposed SiO_2 is then removed by selective (isotropic) HF etching followed by anisotropic electron cyclotron resonance reactive ion etching (ECR RIE) of the silicon. Feature depths of ~90 nm have been obtained in this manner. Application of these techniques to the ODS SAMs damaged by metastable atom impact in the present work resulted in pattern transfer, but the feature depths that could be achieved were only a few nm and were apparently limited by the damage level that could be attained using the present apparatus. However, the available data suggest that with the use of higher incident metastable atom fluxes and/or longer exposure times, good pattern transfer with large feature depths and edge resolutions ≲100 nm should be realizable, resulting in a simple technique for direct nanoscale lithography on silicon.

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