Exposure of self-assembled monolayers to highly charged ions and metastable atoms

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The doses of neutral metastable argon atoms (Ar*) and highly charged xenon ions (HCIs) required to damage self-assembled monolayers (SAMs) of alkanethiolates on gold are compared in a set of experiments carried out concurrently. The extent of damage to the SAM is determined by developing the samples in a gold etching solution, then measuring the decrease in reflectivity of the gold; $\approx 10^5$ Ar* are required to cause the same amount of damage as 1 HCI, as measured by this assay. We have also demonstrated HCI micropatterning of a surface using a physical mask, suggesting the application of this system in lithography. © *1999 American Institute of Physics.* [S0003-6951(99)03330-6]

Efforts to improve the techniques of micropatterning surfaces have involved the use of alternative resists or unconventional exposure methods. In this letter we do both simultaneously, using a beam of highly charged ions (HCIs) and a beam of neutral metastable atoms to expose an ultra-thin self-assembled monolayer (SAM) resist. Besides providing one of the first demonstrations of lithographic patterning using HCIs, the results allow us to compare and contrast the relative efficiencies of ion and atom exposure quantitatively.

The internal energy (defined as the energy released in bringing an atom or ion to its neutral ground state) of metastable helium and argon atoms has been used previously to damage SAMs of dodecanethiol (DDT) on gold.[1–3] By using a mask to pattern the exposure, followed by etching, one can form patterns in gold and then in silicon.

The highly charged ions used in this work, Xe^{44+}, have a much greater potential energy (51.3 keV) than the atoms used previously, but they also have greater kinetic energy (350 keV for ions vs <0.1 eV for atoms). The ions neutralize rapidly (typically in less than ≈ 20 fs[4]), however, depositing the potential energy into a small volume localized in the first few nanometers of the surface.[4–6] Because the kinetic energy is deposited in the solid over a region hundreds of nanometers deep, the energy *density* deposited on the surface is dominated by the contribution from the potential energy. Previous studies on mica have confirmed that the amount of damage to the surface caused by ions correlates with changes in internal potential energy (related to the charge of the ion) and not kinetic energy.[7,8]

Figure 1 summarizes the process used to expose SAMs to the beams. The procedure for exposing the substrates to the beam of Ar* is described in detail elsewhere.[2] The flux of Ar* was 1.7×10^4 μm^{-2} s^{-1} in a collimated beam ≈ 7.5 mm in diameter. The ion beam was a continuous stream of $\approx 11.0 \times 10^6$ Xe^{44+} ions/s from an electron beam ion trap

(EBIT),[9] the ion beam was passed through an aperture 3 mm in diameter, 5 mm above the sample.

Gold (40 nm thick) was evaporated onto silicon wafers using titanium (2 nm thick) as an adhesion promoter. The wafers, coated with gold, were stored under ambient conditions prior to the formation of SAMs. SAMs were prepared by immersing the gold films into a solution of dodecanethiol (DDT) in absolute ethanol (0.01 mol) for at least 16 h. Samples were then rinsed with ethanol, and blown dry in a stream of nitrogen gas before being loaded into the vacuum system.

In order to compare directly the doses of atoms and ions required to damage SAMs, we exposed samples to each of the two beams, concurrently, keeping the samples in each chamber under vacuum for the same total time. The pressure in the chamber in the case of the atom exposure experiment was approximately 1 mPa ($\approx 10^{-5}$ Torr) while in the case of the ion exposure the pressure was approximately 1 μPa ($\approx 10^{-8}$ Torr). We performed 12 exposures of HCIs of ≈ 90 min each on 6 separate samples of SAMs of DDT (Table I). The dose given in Table I is calculated from the average of
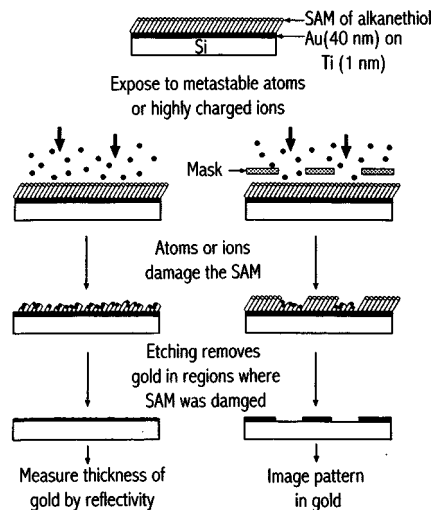

FIG. 1. Schematic of the experimental procedure.

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TABLE I. Exposure time, dose, and loss of reflectance measured when SAMs of DDT are exposed to HCIs and etched.

Time (s)	Dose ($\times 10^{11}$ cm^{-2})	Loss of Reflectance	Time (sec)	Dose ($\times 10^{11}$ cm^{-2})	Loss of reflectance
5400	1.35	22%	5100	1.35	48%
5400	1.24	12%	5040	1.30	41%
4380	1.33	8%	4980	1.39	42%
4380	1.29	7%	4800	1.36	41%
4500	1.34	16%	4620	1.29	41%
4620	1.34	14%	4860	1.27	35%
Average				1.32(04)	27(15)%

FIG. 2. Reflectance of gold vs dose for exposures of SAMs of DDT to Ar*.

the flux before and after the exposure (the flux of ions can vary by up to 10% during the exposure). We determine the flux of ions with an electron multiplier in pulse counting mode; the ion detection efficiency is 0.50 with an uncertainty of less than 0.25.[9]

After exposure to the ion or atom beam, the samples were removed from the vacuum chamber and immediately etched in an aqueous ferricyanide solution (1 mol/ℓ potassium hydroxide (KOH), 0.1 mol/ℓ potassium thiosulfate (K$_2$SO$_4$), 0.01 mol/ℓ potassium ferricyanide [K$_3$Fe(CN)$_6$], and 0.001 mol/ℓ potassium ferrocyanide [K$_4$Fe(CN)$_6$] for ≈20 min). After etching, the samples were rinsed with distilled water and blown dry. The exposed regions were visible as darker areas corresponding in size to the widths of the beams.

The degree of etching of the exposed regions relative to the unexposed regions was quantified as a decrease in reflectivity of the surface.[2] A HeNe laser (λ=632 nm) was focused onto the sample at normal incidence and the reflected beam was separated from the incident beam with a polarizing beam splitter cube. The beam waist was calculated to be ≈15 μm, but the resolution was limited by the point spacing in our scans to 70 μm. The intensity of the reflected beam was monitored with a photodiode as the sample was stepped through the laser beam. The reflectivity was measured at points along several horizontal scans across the surface, each scan separated vertically by ≈0.5 mm, and then averaged. The fractional loss in reflectivity is defined as the unexposed value (average signal outside of the exposed region for that particular sample) minus the average signal from the exposed region divided by the unexposed value.

In the case of HCI exposure through a mask, some of the parameters discussed above were changed slightly. Chromium rather than titanium were used as an adhesion layer, and SAMs of hexadecanethiol (HDT) rather than DDT were used.

After etching, the regions of the surfaces that were exposed to HCIs show a decrease in reflectivity relative to that of unexposed gold. The maximum possible decrease in reflectivity gives a value that corresponds to that of bare silicon; none of the samples showed this maximum. By averaging the reflectivity across the exposed region for each sample, the analysis accounts for the fact that the distribution of ions across the beam (unlike the beam of atoms) is nonuniform. The average loss in reflectivity is 0.27(15) caused by an average dose of ions of 1.32(4)$\times 10^{11}$ ions/cm^2. The uncertainty that we quote is the standard deviation of the 12
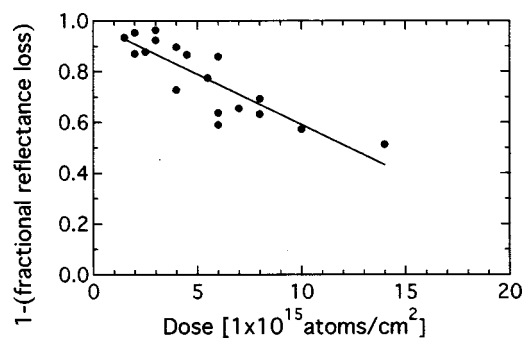
individual data points. Since there may be a systematic component this deviation, we have used this conservative estimate of the uncertainty and not reduced it by the square root of the number of data points. Given that there are 4×10^{14} alkanethiol molecules/cm^2, we infer that each ion—and the subsequent etching process—generates a crater in the gold approximately 35 nm in diameter and encompassing ≈3000 alkanethiol molecules in the SAM. This is in reasonable agreement with the directly imaged results for randomly dispersed single ion impact craters obtained subsequent to our work by the Livermore group (50–63 nm diameter),[10] given the fact that the SAMs used were different, and that the direct images do not appear to be corrected for imaging probing tip effects (tip radii approximately 70 nm). These craters are comparable in size to those formed in a more standard resist, poly (methylmethacrylate), which was exposed to Xe^{44} [after etching, single ion impact craters 25 nm in diameter were observed with atomic force microscopy (AFM)].[11]

In order to compare exposure with HCIs to that with Ar*, we chose various doses of Ar* to bracket the exposure obtained with HCIs and interpolated to the dose which gives an equivalent exposure as measured by the reflectivity. The results of our reflectivity measurements for exposures of SAMs of DDT to metastable argon atoms is plotted in Fig. 2. The slope of the solid line is 4.1(12)$\times 10^{-17}$ cm^2/atom, in reasonable agreement (<2σ) of the previously determined value.[2] The statistical contribution to the overall (combined standard) uncertainty of the present result is 0.6 $\times 10^{-17}$ cm^2/atom. The overall uncertainty is limited by the detection efficiency (ϵ) of the metastable atoms, as described previously.[2]

A loss of reflectivity of 27% (the average loss obtained with HCIs) thus corresponds to a dose of 6.6 $\times 10^{15}$ atoms/cm^2. This value implies that multiple impacts (~16) of Ar* are required to damage a point on the surface such that etching will remove the underlying gold. Therefore, ~10^{15} Ar* are required to cause (after etching) the same amount of damage as one Xe^{44+} ion, as compared to the ratio of potential energy, 4400. That is, the HCI is much more efficient at converting its potential energy to surface damage than is the metastable atom. This nonlinear energy dependence is not surprising because a similar effect has been seen in a comparison of damage to SAMs using Ar* (P.E.=12 eV) and He* (P.E.=21 eV) projectiles.[2] In that case, an increase in the potential energy per atom of less than a factor of 2 resulted in a decrease in the required dose of
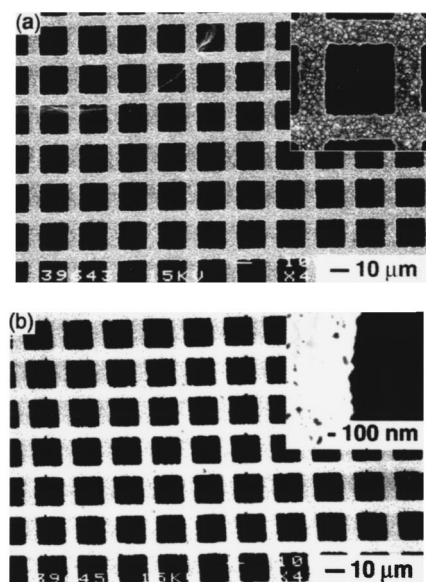
FIG. 3. SEM of (a) the TEM grid and (b) the gold patterns made by exposing SAMs of HDT to HCIs. The insets show that the edge roughness of the features in gold is comparable to that of the TEM grid.

more than an order of magnitude. It was speculated that the damage was caused by secondary electrons, and comparison of the metastable atom dose (assuming one secondary electron per Ar*) with the dose used in experiments where electron beams were used to expose SAMs, gave reasonable agreement. Perhaps the increased efficiency of the He* comes from the decrease in inelastic mean free path[12] as the electron energy goes from 12 to 20 eV, which allows the electron to undergo a higher density of collisions within the SAM. The mean free path increases above 20 eV, but this increase might not be relevant as the damage mechanisms might be quite different for the two projectiles as their potential energies differ by over three orders of magnitude. Because the HCI deposits a large parcel of potential energy into a small volume of the surface in a short time, the excitation is concentrated and collective effects might be important. Two models predict cratering of surfaces due to the large energy density deposited by a single HCI. One model asserts that the HCI will extract many electrons from the surface leading to a charge buildup which will Coulomb explode,[13] ejecting ions from the surface and causing a shock wave that ejects neutral material as well.[14] A second model predicts that the HCI impact excites many surface electrons from bonding states to antibonding states, rendering the material structurally unstable.[15] The result is the displacement of a large number of surface atoms.

In order to demonstrate the ability of HCIs to pattern SAMs, we exposed SAMs of HDT to the ion beam through a physical mask—a nickel transmission electron microscopy (TEM) grid (Fig. 1). Figure 3 shows SEM images of gold patterned by exposing SAMs on gold to a beam of HCIs through a mask for ≈2 h: the flux was measured prior to exposing the samples, and the dose calculated to give a 50% loss in reflectivity of the gold after etching. Samples were etched in an aqueous ferricyanide solution to reveal the pattern in gold. The edge roughness of the features in gold (≈100 nm) is comparable to that of the TEM grid (Fig. 3 inserts).

In summary, we have demonstrated that Xe^{44+} damages SAMs in doses five orders of magnitude lower than doses of Ar*. Using currently available high flux sources of HCIs,[9,16–18] the overall exposure time can be shorter than that used in previous studies involving metastable atoms. Furthermore, since the production of HCI beams is an area of research still in its infancy and appears to be progressing rapidly, there is much room for future improvements. The next generation of EBIT devices, for example, will have a greatly increased intensity and brightness; the brightness, a figure of merit that combines intensity and emittance (ability to focus to a small spot), is expected to be improved by four orders of magnitude.[18]

We have also used HCIs to pattern gold films by exposing SAMs of HDT on gold to ions through a stencil mask, and then etching the gold from the exposed regions. Because this process is significantly more efficient than patterning with metastable atoms, it may be suited to lithography. Furthermore, because of the high energy density the HCIs deposit on the surface, thicker SAMs can be used, leading to a more robust process with greater contrast.

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