High-dose exposure of silicon in electron beam lithography

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Abstract. Nowadays, features with sizes smaller than 10 nm can be obtained with electron beam lithography. For such small structures, high exposure doses are required to stay away from the shot noise limit. We investigated the effect of high-dose electron exposure of silicon substrates and subsequent dry development by reactive ion etching. We found that silicon can be directly patterned at electron doses ranging from 0.05 to 3.06 C/cm^2. The effect of backscattered electrons is seen as a halo around the patterns. In the given dose range, a gradual transition from positive tone (low-dose) to negative tone (high-dose) behavior is observed. It is demonstrated that the patterning is likely to be caused by structural changes of the silicon substrate, resulting in different etch rates in exposed and unexposed areas. X-ray photoelectron spectroscopy analysis has been applied to determine if the thickness of the native oxide in the irradiated areas is different from the thickness at a reference position (not irradiated). Small but significant differences have been observed, the largest increase being 0.3 nm. [DOI: 10.1117/1.2841716]

Subject terms: electron beam lithography; dry etching; proximity effect; high exposure dose.

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1 Introduction

Among all lithographic techniques, electron beam lithography (EBL) is generally accepted to have the highest practical resolution. EBL studies on polymethylmethacrylate (PMMA)[1,2] and hydrogen silsesquioxane[3] show resolution down into the sub-10-nm range. Ultimate resolution EBL in the nanometer regime poses severe conditions on both the resist and the electron probe. Specific extra requirements to the ultrahigh resolution resist are a molecular size as small as possible and an ultrathin layer thickness, the latter to get rid of electron forward scattering. The electron probe also needs to be as small as possible, but then the shot noise in the electron beam is a point of concern. The shot noise is given by the square root of the number of electrons in the beam. Thus the signal-to-noise ratio (S/N) is also proportional to the square root of the number of electrons in the beam. This can be expressed as $S/N=(D\times A/e)^{1/2}$, where D is the exposure dose (coulombs per square centimeter); A is the area of the beam spot; and e is the elementary charge. So, the S/N ratio decreases with decreasing spot size A. To keep the S/N ratio sufficiently large, e.g., >100, the dose has to be increased correspondingly to compensate for the smaller spot size. Given a specific spot diameter d, this leads to a required minimum dose of $D>4\times 10^4 e/(\pi d^2)$. For example, to expose a pixel of 1-nm diameter, equal to the beam diameter d, the minimum dose required to stay away from the shot noise limit is 0.204 C/cm^2. This dose is two orders of magnitude larger than doses typically used in PMMA-based microfabrication processes.

It is the objective of this paper to investigate the effect of high-dose electron beam (e-beam) exposure of silicon substrates beyond the shot noise limit. This is important to know, especially when nanopatterns in ultrathin resist layers are to be transferred into the underlying substrate by dry etching. If etching properties would be altered by the e-beam exposure, then the pattern transfer would become dependent on the exposure as well, which is highly unwanted.

2 Experiment

For the e-beam exposure experiment, we used (100)-oriented, 20-to-30 Ω cm, p-type silicon wafers. The wafers were cleaned in an ultrasonic bath consecutively for 2 min using acetone and 2 min using isopropanol. The e-beam exposure was done in a Vistec Electron Beam Pattern Generator 5000$^+$ (Best, The Netherlands) at 100-keV beam energy, with an aperture of 400 μm, a beam current of 225 nA, and an estimated spot size of 163 nm. The test pattern consists of a series of 20×50-μm^2 rectangles. Each rectangle was exposed with a different dose. The exposure dose ranges from 0.05 C/cm^2 to 3.06 C/cm^2.

After exposure, the wafers were subjected to a fluorine-based reactive ion etching (RIE) process, resembling a typical pattern transfer after resist exposure. A parallel plate Leybold Z-401S RIE etcher (Alzenau, Germany) was used. The reactive gas was SF_6 at a flow of 12.5 sccm (standard cubic centimeters per minute). The process pressure was set to 50 μbar and a rf power of 40 W was used. Anticipating pattern transfer using ultrathin resist layers, a low bias voltage was chosen. As the bias voltage in the parallel plate configuration cannot be controlled independently of the rf

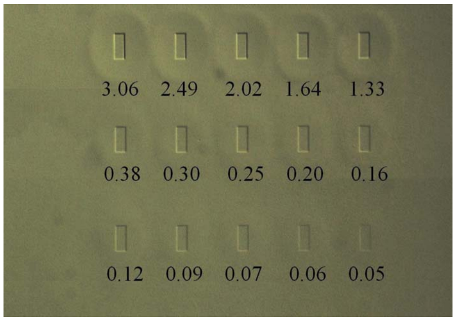

Fig. 1 A series of 20×50-μm^2 rectangles, written directly on silicon. For each rectangle, the electron dose (coulombs per square centimeter) is indicated. The sample was etched in a SF_6 plasma for 70 s.

power, the wafer was placed at an elevated level, inside the plasma, and thus subject to the floating potential of only a few volts. To determine absolute values of the etch rate in the exposed and unexposed area in silicon, an inkmark was placed on the unexposed surface of the sample, prior to the etching process. After etching, the mark was removed with acetone and the etch depth was measured with respect to the original wafer surface, using a Tencor Alpha-step surface profilometer (San Jose, Calif.).

3 Results

In Fig. 1, a top view optical microscope image is shown, in oblique illumination mode, of an exposure dose series of 20×50-μm^2 rectangles after a 70-s dry etch. The exposure dose (in coulombs per square centimeter) corresponding to each of the rectangles is indicated. Most interestingly, the rectangles are visible over the entire chosen dose range of 0.05 to 3.06 C/cm^2. For the higher electron dose, the contrast is enhanced and a second interesting feature is observed: a halo around the rectangles. The halo is slightly ellipsoid along the long axis of the rectangle and its size increases for increasing electron doses. To quantify these observations, Alpha-step measurements were performed across the etched structures. The following parameters are defined (see Fig. 2): d_u is the etch depth in the unexposed area far from the exposed area (under the inkmark), d_e is the etch depth in the exposed area, and $\Delta d = d_u - d_e$ is the height of the resulting structures as seen in Fig. 1. In these measurements, only d_u and Δd are determined; d_e is derived from these. After etching, the sample was cleaned in an ultrasonic bath for 2 min to remove the inkmark. For 70-s etching time, the Alpha-step measurement, taken from the inkmark results in an etch depth, $d_u = 90$ nm.

Figure 3 shows three Alpha-step height profiles of etched rectangles exposed at three different doses: 3.06, 0.38, and 0.05 C/cm^2. The indicated etch depth of 90 nm at the outer ends of each scan is the reference etch depth (d_u) of unexposed silicon. The overall experiment shows areas with etch delay and areas with etch enhancement (all compared to the reference depth of 90 nm). In describing the etch depth behavior as a function of dose, we first consider the primary exposure area and then the surrounding area.

In Fig. 4, the ratio of the etch depths in the primary exposed and nonexposed areas, i.e., d_e/d_u, is plotted versus exposure dose. The ratio is a highly nonlinear function of the dose. For low doses (e.g., 0.05 C/cm^2), the etch depths in the exposed and unexposed areas are almost equal. For higher doses, the exposed area is etched increasingly slower than the unexposed area. The etch depth ratio approaches asymptotically a value of about 0.68.

The etch depth in the unexposed area in the vicinity of the rectangles (the halo regions) is also strongly dependent

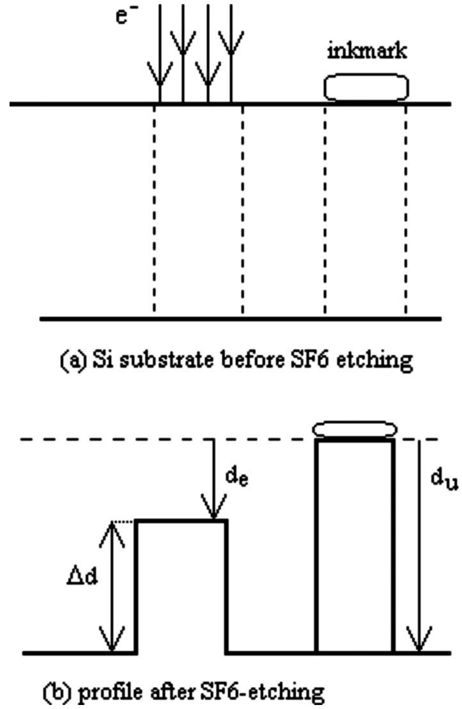

Fig. 2 Schematic overview of the silicon substrate, before (a) and after (b) etching. The etch depths d_u, in the unexposed area; d_e, in the exposed area; and their difference, $\Delta d = d_u - d_e$, are indicated.

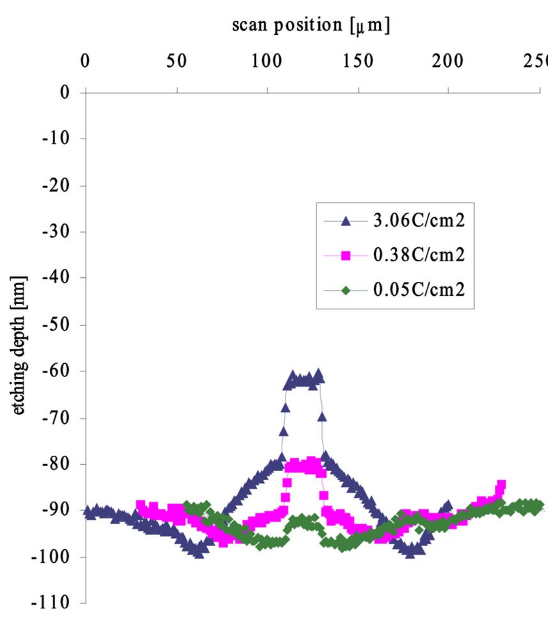

Fig. 3 The etch depth with respect to the original silicon-wafer surface (the zero at the vertical axis) as a function of the profilometer scan position, for three different doses as indicated in the figure.

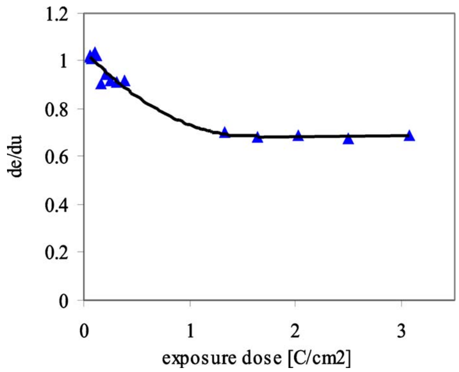

Fig. 4 The ratio of etch depths in the exposed (d_e) and unexposed (d_u) area as a function of the exposure dose. The triangles are the measured data, the solid line is a guide to the eye.

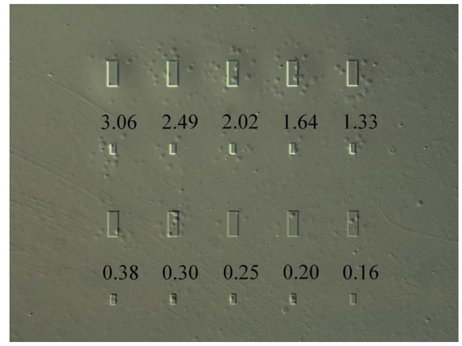

Fig. 5 Pattern of rectangles and surrounding halo after e-beam exposure and dry development. Experimental conditions as in Fig. 1, except that a 20-nm-thick gold layer is applied before exposure and removed before RIE. Each 10×20-μm^2 small rectangle was exposed at the same dose as the large rectangle directly above it. Experiment demonstrates that electron-induced carbon buildup does not contribute to the observed patterning.

on the electron dose. For a high dose (e.g., 3.06 C/cm^2), a broad area of etch delay (compared to unexposed area) near the exposed rectangle is observed, evolving to a narrow band of etch enhancement at the outer distance (see Fig. 3). In this dose range, the shape of the halo is clearly visible (see Fig. 1). Its magnitude corresponds more or less with the proximity range of backscattered electrons. For a lower electron dose, the broad area of etch delay becomes less pronounced, and the outer band of etch enhancement shifts inward. Finally at the lowest dose (0.05 C/cm^2), it all evolves to an area of overall etch depth enhancement. In the low dose range, the halo almost disappears.

To check for possible interference with e-beam–induced carbon deposition from residual carbonaceous contamination in the vacuum, gold-coated (20-nm) silicon substrates were e-beam exposed. When e-beam–induced carbon deposition would play a role, the thickest layer would be in the exposed region and a thinner layer in the backscatter electron regions. In subsequent dry etching, this would result in different etch depths. After exposure, the gold layer was removed (and so any possible carbon deposit) by wet chemical etching, and next the pattern was developed using RIE. However, etch results were similar as without the gold film (see Fig. 5) and possible interference with carbon deposit can be ruled out.

4 Discussion

First, the possible correspondence of the pronounced halo effect around the exposed areas with the proximity range of the backscattered electrons is considered more quantitatively. The interaction volume in which the primary electrons generate the backscattered electrons intersects the substrate surface with a circle of radius r_b. In a modified diffusion model, Kanaya and Okayama[4] obtained the radius r_b, as

$$r_b = \frac{CR\gamma}{1+\gamma},$$

where C is a constant equal to 1.1, γ=0.187$Z^{2/3}$, and R is the range of the primary electron given by

$$R = 5.025 \times 10^{-12} \frac{AE_p^{5/3}}{\rho \lambda_s Z^{8/9}} \quad [R \text{ in cm}].$$

A is the atomic weight (in grams), E_p is the primary electron energy (in electron volts), ρ is the density of the substrate material (in grams per cubic centimeter), Z is the atomic number, and λ_s is a constant equal to 0.182. For 100-keV electrons incident on a silicon substrate, this results in a range R of 69 μm and a value for r_b of 40 μm. For the highest dose (3.06 C/cm^2), the halo extends about 45 μm from the rectangle. This compares rather well to the estimated backscatter electron range.

The question that remains after observing the positive and negative tone resist behavior of the silicon is what causes the enhancement and the reduction in etching speed in these areas. The slight etch enhancement at low doses may be due to defects generated under e-beam exposure. Dangling bonds involved in defects are generally more reactive toward fluorine species than undamaged (unexposed) monocrystalline silicon. Etch delay in silicon etching has often to do with the presence of oxidic species (SiO_x) at the surface, which are removed more difficultly, the more so when ion bombardment is at a low level as in the present experiments. Excessive defect concentration (amorphization) due to e-beam exposure could possibly give enhanced native oxide formation and so induce some etch delay. X-ray photoelectron spectroscopic (XPS) analysis has been applied to determine if the thickness of the native oxide in the irradiated areas is different from the thickness at a reference position (not irradiated). During the measurements, the angle between the axis of the analyzer and the sample surface was 45 deg; the information depth is then about 7 nm. The measurements have been performed using monochromatic AlKα radiation with measuring spots of 10 μm. By means of wide-scan measurements, the elements present at the surface have been identified. The chemical state and the atomic concentrations of the elements present are determined from accurate narrow-scan measurements. Calibrated phosphohexose isomerase–sensitivity factors were used to convert peak areas to atomic concentrations. Local XPS measurements were performed in three regions: in the exposed area (for rectangles with an electron dose of 3.06, 2.49, and 2.02 C/cm^2), in the vicinity of the exposed area and in the area far away from the exposed area (also called the reference position). The results of the XPS analysis reveal that the largest value of SiO_2 layer thickness is found in the rectangles that correspond to an electron dose of 3.06 C/cm^2 (1.52 nm) and 2.49 C/cm^2 (1.51 nm). A slightly thinner layer of SiO_2 (1.47 nm) is found at the rectangle that was exposed with an electron dose of 2.02 C/cm^2. Between the rectangles, the amount of SiO_2 (approximately 1.40 nm) is larger than at the reference positions (approximately 1.33 nm). To obtain insight into the reproducibility, the measurements have been repeated after a few days. Again a spot of 10 μm was applied. The results are very similar with the ones described in the previous experiment. Next to the rectangle that was exposed with 3.06 C/cm^2, the amount of SiO_2 is larger than at the reference positions, but the amount decreases as a function of distance from the rectangle. The accuracy of the XPS measurements was also tested on a bigger structure, a rectangle of $350 \times 500\ \mu m^2$ that was exposed with a dose of 0.3 C/cm^2. The results clearly show that the thickness of SiO_2 is larger at the irradiated area than at the reference positions (0.5 and 10 mm from the exposed area) by approximately 0.3 nm.

To determine the crystallinity of the exposed area, we tried the X-ray diffraction technique. Unfortunately, we were not able to make any local measurements (in the exposed area, next to the exposed area, and far away from the exposed area) because the beam was too large with respect to the exposed patterns.

The most important message from this study is that silicon substrates are sensitive to high-dose exposure with electrons, and exposed patterns can be developed in a dry etching process. This could be a disadvantage when transferring nanopatterns into the underlying substrate using ultrathin resist layers. However, direct patterning of silicon, without the use of a resist layer, would be an interesting future application.

5 Conclusion

Direct patterning of silicon is possible, when using high electron exposure doses and subsequent dry development in fluorine plasma under low energy ion bombardment. Such high doses are required when writing small structures and simultaneously stay above the shot noise limit. Besides the primary exposure pattern, an additional halo-shaped structure is observed due to exposure from backscattered electrons. The size of the halo around the pattern is in agreement with the estimated backscatter electron range. Patterns are a superposition of positive and negative tone effects. We demonstrated experimentally that e-beam–induced carbon deposition from contamination is not an explanation for the observed patterning. It is suggested that the e-beam induces defects, which either enhance the etch rate by improved fluorine attack or reduce etchability by stronger native oxide formation, depending on the defect concentration level. XPS measurements indeed revealed an increase of the SiO_2 layer in the exposed areas.

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Anda E. Grigorescu is a PhD student working in the charged particle optics group at Delft University of Technology, The Netherlands. Her primary area of interest is the study of ultimate resolution that can be achieved when using ultra thin layers of e-beam resist. She developed a Monte Carlo simulation program that calculates not only the trajectories and the energies of the scattered secondary electrons both in the substrate and resist, but also the bond breaking distributions in the resist. The aim of the simulation is to optimize the parameters, such as incident energy, substrate material, resist material to obtain the ultimate resolution.

Marco C. van der Krogt received his BSc in engineering physics (major: applied physics) from the Rijswijk Institute of Technology (RITE), after a graduation period at Leiden University. In 2002, he joined the Nanofacility of the Kavli Institute of Nanoscience at Delft University of Technology. He is a specialist in a wide spectrum of nanodevice fabrication techniques; his main topics are thin film processing and technology development for nanophotonic devices.

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