Resistless high resolution optical lithography on silicon

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In this letter, we report on the high resolution patterning of a silicon surface without using a resist layer. A hydrogen passivated silicon surface is chemically modified by illumination with ultraviolet light (UV, $\lambda=350.7$ nm) in air. Auger electron spectroscopy (AES) revealed that silicon oxide was formed at the illuminated areas. A light interference pattern was made on the silicon surface by two UV laser beams, oxidation occurred only at the maximum intensity, but not at the minimum. In this way oxide lines were fabricated with a width below 200 nm on a 500 nm period. The oxide lines were used as a wet etch mask to etch more than 25 nm into Si(110) without affecting the oxide. The advantage of this technique is that it is a very simple process which allows the high resolution patterning over large areas of silicon without using a resist. © *1995 American Institute of Physics.*

Further downscaling of device dimensions in the IC technology requires new lithographic processes which enable high resolution patterning of silicon surfaces over large areas. A very promising process is the local oxidation of a hydrogen passivated silicon surface. Local oxidation has been induced by using a scanning tunneling microscope (STM)[1–3,7,12] an atomic force microscope (AFM),[4,5] or electron beam lithography.[6,7] The oxide patterns were used as a wet etch mask[5,7] or as a mask for selective metal deposition.[3,6] The local oxidation of a hydrogen passivated silicon surface has received much attention because the passivation layer is only one monolayer thick. This means that a very high lateral resolution can be obtained. This was demonstrated by Lyding *et al.*[2] who fabricated 2 nm narrow oxide lines on H terminated Si(100) using a STM in ultrahigh vacuum (UHV). Unfortunately, STM and AFM, and to a lesser extend *e*-beam lithography, are not very suitable for large area patterning due to the long writing times. In this letter, we report on the UV light induced oxidation of hydrogen terminated silicon. Using two interfering UV laser beams, oxide lines with a width below 200 nm were fabricated over a large area.

Si(100) or Si(110) samples were prepared by cleaning in trichloroethylene, acetone, and ethanol, followed by a 60 s dip in 10% diluted hydrofluoric acid (HF) to passivate the surface with hydrogen. The passivated surface is stable against oxidation in air for 2 h. A Si(100) sample was illuminated in ambient with 350.7 nm light from a krypton laser. The light power was 150 mW, illumination time 15 min and the beam diameter ~0.5 mm. After illumination the sample was investigated with a scanning Auger microscope (Perkin-Elmer PHI 670 Nanoprobe). The time between the HF dip of the sample and introducing the illuminated sample in the UHV system for the Auger analysis was 1 h, keeping the oxidation of the surface due to exposure to air to a minimum.

Figure 1 shows two Auger spectra, one of the illuminated area (labeled illuminated), and the other of an unilluminated area (labeled unilluminated) on the same sample. The illuminated area shows a peak at 92 eV, the pure silicon peak from crystalline silicon, and a peak at 76 eV, the chemically shifted silicon peak from SiO_2. At 500 eV a large oxygen peak is present. On the unilluminated area the pure silicon peak is very large, the shifted silicon peak from SiO_2 is only very small. The oxygen peak at 500 eV is also much smaller, indicating that less oxide is present. The presence of some oxygen on the unilluminated area is presumably caused by the presence of OH groups at the surface.[8] From these spectra it can be concluded that a thin SiO_2 layer is formed when a hydrogen terminated Si surface is illuminated with UV light in air.

To demonstrate that UV light induced oxidation can be used to pattern a Si surface over a large area with high resolution, we illuminated a Si(110) sample by two interfering

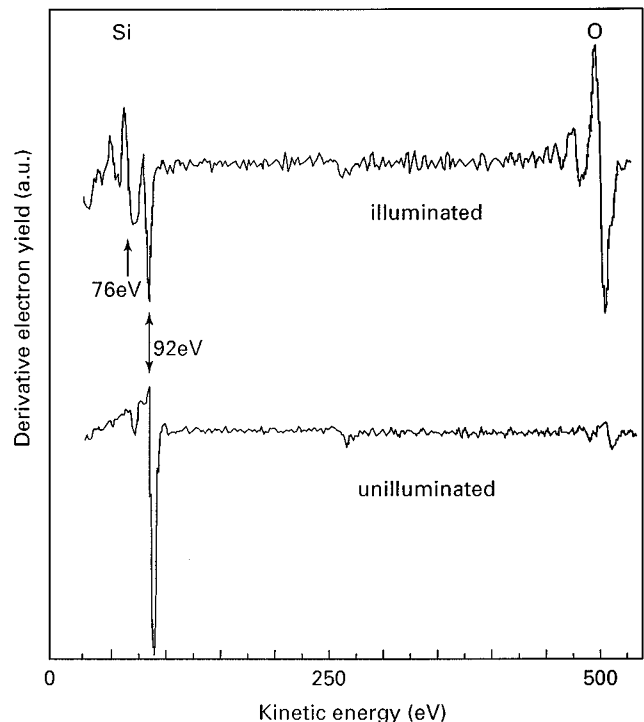

FIG. 1. Auger spectra of an illuminated ($\lambda=350.7$ nm) silicon surface (top spectrum) and an unilluminated silicon surface (bottom spectrum).

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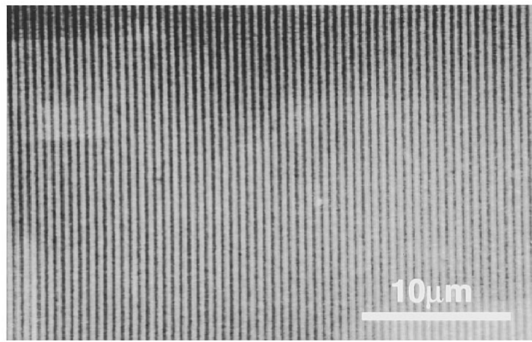

FIG. 2. SEM image of silicon oxide lines on Si(110), which appear bright, made with laser interference after a wet etch with TMAH, the grating spacing is 500 nm.

UV laser beams using a 50/50 UV light beam splitter. The interference fringe spacing, given by $\lambda/(2 \sin \theta)$, where λ is the wavelength of the light (350.7 nm) and θ is the half-angle between the two laser beams, is in our case 500 nm. For a sufficiently long exposure time, oxidation will only occur at the maximum intensity, but not at the minimum, in this way silicon oxide lines can be made on the sample over a large area. After the illumination, the sample was etched in tetramethyl ammonium hydroxide (TMAH, 40% diluted in water, at 75 °C) for 5 s. TMAH is a very selective anisotropic etchant, and the silicon etch rate is much higher than the silicon oxide etch rate.[9] The oxide lines were written along the Si$[1\bar{1}2]$ direction, as the Si etch rate is the lowest in the $[111]$ directions, the sidewalls are perpendicular to the surface.[7,10] Scanning electron microscope (SEM) and AFM images were made after the etching. Figure 2 shows a SEM image of the pattern after etching with TMAH. A perfect regular line pattern can be seen, the distance between the lines is about 500 nm, and the linewidth is about 250 nm. Because the laser beam has a Gaussian shape, the maximum intensity of the interference pattern is not uniform over the whole area. This is clear in the SEM image, the oxide lines near the bottom are wider than the lines near the top of the image, because the maximum intensity is higher there than near the top. The minimal exposure after which line patterns could still be observed was about $10^2 J/cm^2$.

To verify that trenches have been made in the silicon, AFM images were made. Figure 3 shows an AFM image of the oxide lines after the wet etch. The line pattern with a 500 nm period is clearly visible in the topography, thus the oxide is thick enough to act as an etch mask. Figure 4(a) shows an AFM height profile of the lines, demonstrating that at least 25 nm Si was etched. The linewidth is estimated to be 300 nm wide, but this is not very accurate because the height profile is a convolution of the surface topography and the shape of the AFM tip. Figure 4(b) shows a height profile of oxide lines made with a lower maximum intensity. These oxide lines are significantly narrower than the lines in Fig. 4(a), we estimate the width of the lines to be below 200 nm.

The mechanism of the UV light induced oxidation is not clear. At first sight, heating of the surface by the laser beam might be important. However, with a simple calculation we estimate the temperature rise, due to heating by the laser, to be less than 25 °C. This temperature rise is not expected to cause the oxidation in this time period, much higher temperatures are required to get significant oxidation[11] (typically 700 °C or more). In order to investigate the importance of the photon energy, we illuminated a hydrogen passivated silicon surface with laser light which had a longer wavelength (514.5 nm). The exposure was at least 10 times higher than in the UV light experiments, but no oxidation was observed.

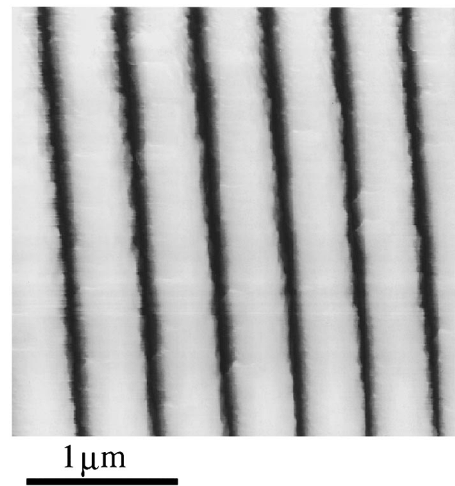

FIG. 3. AFM image of silicon oxide lines on Si(110), made with laser interference after a wet etch with TMAH, the grating spacing is 500 nm.

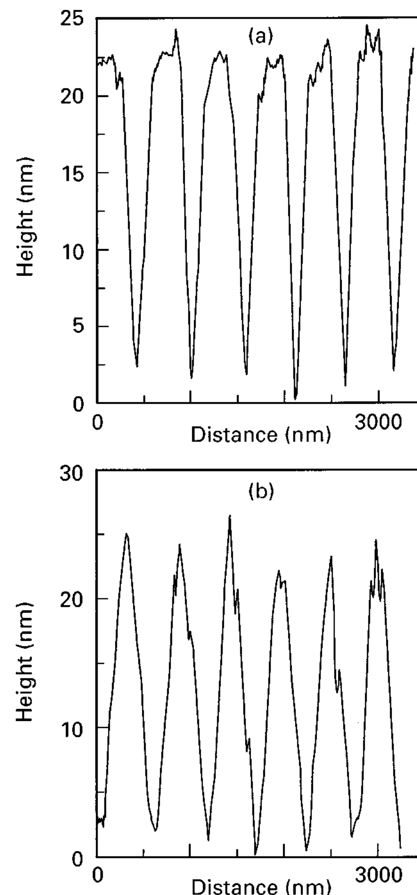

FIG. 4. AFM height profiles of silicon oxide lines on Si(110) made with laser interference after a wet etch with TMAH. The light intensity used to make the lines of profile (a) was higher than for the lines of (b).

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This suggests that the photons must have a sufficiently large energy to induce the oxidation. The Si–H binding energy is ~3 eV and the photon energy of 350.7 nm light is 3.5 eV. The photon energy of 514.5 nm light, which caused no oxidation is 2.4 eV. If the photons have enough energy they can directly break the silicon–hydrogen bonds at the surface, which leads to the oxidation. It is interesting to note that the oxide thickness measured from the Auger spectrum in Fig. 1 (labeled illuminated), using the method described in Ref. 7, is 1.3 nm. This is a typical thickness for a native oxide. Using an illumination time which was 3 times shorter, we found an oxide thickness of 1.1 nm. This suggests that after the hydrogen has been desorbed, a native oxide is formed, and that oxidation is almost not further enhanced by the UV illumination.

In conclusion, we have demonstrated that a hydrogen passivated silicon surface can be oxidized by illumination with UV light in air. An interference pattern was used to make oxide lines on Si, oxidation occurred only at the maximum intensity, not at the minimum. The oxide lines were used as a wet etch mask, the width of the lines which could be made was below 200 nm. Oxide lines cannot only be used to structure a silicon substrate, but could also be used to pattern a thin film of amorphous silicon,[7,12] or the oxide patterns can act as a mask for selective metal deposition.[3,6] The UV light sensitivity of the oxidation is 10^4 times lower than that of conventional organic optical resists, this means that much longer writing times are required. Although this is a disadvantage, this process can still be useful because it is very simple, inexpensive, and allows the large area patterning of silicon surfaces with very high resolution.

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