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Laser etching on the Cl-saturated Si(111) 7 × 7 surface at 266 nm studied by scanning tunnelling microscopy

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Abstract. *Using scanning tunnelling microscopy, we have observed structural* modifications of the chlorinated Si(111) 7 × 7 surface induced by 266 nm laser irradiation. At a very low laser fluence of 0.7 mJ cm^{-2}, at which thermal desorption can be ignored, a periodic striped pattern along the ⟨110⟩ direction of the Si(111) surface is imaged. This pattern consists of flat terraces and narrow grooves of ~60 and ~10 Å in width, respectvely.

1. Introduction

Laser etching on silicon with chlorine has attracted the interest of many researchers and has been studied extensively from both scientific and technological standpoints, since the photochemical reaction frequently shows a remarkable reaction selectivity. The reaction selectivity is important not only for fundamental science but also for technological problems such as monatomic layer etching, reactive ion etching under laser irradiation, and the semiconductor processing in very-large-scale integrated-circuit (VLSI) fabrication. In the laser-induced etching on chlorinated Si surfaces, significant differences between results obtained for 248 and 308 nm radiation have been observed: photo-desorption of surface atoms and molecules gave a higher etch rate at 248 nm than at 308 nm on the reaction of the Si(001) surface with Cl_2 [1], and the $SiCl_2$ yield in a mass spectrum for etch products on a rough Si(111) surface was enhanced at 248 nm as compared with that at 308 nm [2]. These results show that different desorption processes occur for 248 and 308 nm irradiations, and there is the possibility of desorption induced by valence electron excitation at a photon energy of 248 nm. However, the detailed mechanism of desorption has not been elucidated, since dissociation of chlorine molecules occurs in the ambient gas and the thermal effects are dominant under high-power laser irradiation.

In the present paper, we report studies of ultraviolet (UV) laser-induced etching on the Si(111) 7 × 7 surface saturated with chlorine by using scanning tunnelling microscopy (STM) for the surface structure observation. STM images were observed

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after irradiation with very low laser fluence in ultra-high vacuum (UHV), in order to eliminate both the ambient gas effect and the thermal processes. The structure was clearly different before and after only 600 shots of irradiation at 266 nm with a laser fluence of ~0.7 mJ cm^{-2}. The chlorinated Si surface was etched into a surface with parallel grooves at nearly equal distances of ~60 Å.

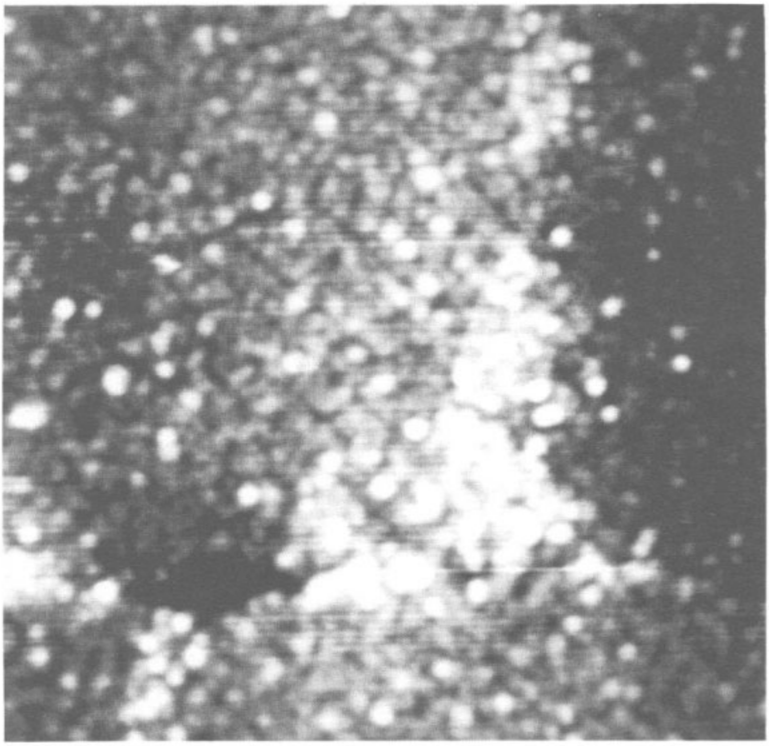

Figure 1. STM image of the Cl-saturated Si(111) 7 × 7 surface at a sample bias of +3 V. The area shown is 450 × 450 $Å^2$.

2. Experiment

The sample was an n-type Si(111) wafer (1 ~ 2Ω cm). The clean surface was obtained after heating the sample to 1300 °C by passing a DC current through it in a UHV chamber with a base pressure of about 1×10^{-10} Torr. The clean 7 × 7 surface was verified from an STM topograph. The surface defect density was a few per cent or less of the adatom density. The surface was exposed to chlorine generated from a solid-state AgCl electrochemical cell [3], until an STM topograph showed no further change. The laser beam at 266 nm was generated by the fourth harmonic of a Nd:YAG laser with a pulse width of ~5 ns and a repetition rate of 10 pulses s^{-1}. The s-polarized Gaussian-shaped laser beam of diameter 10 mm was irradiated through a quartz window onto the specimen surface at an incidence angle of 60 ° to the surface normal. The laser fluence measured at the sample position was ~0.7 mJ cm^{-2}.

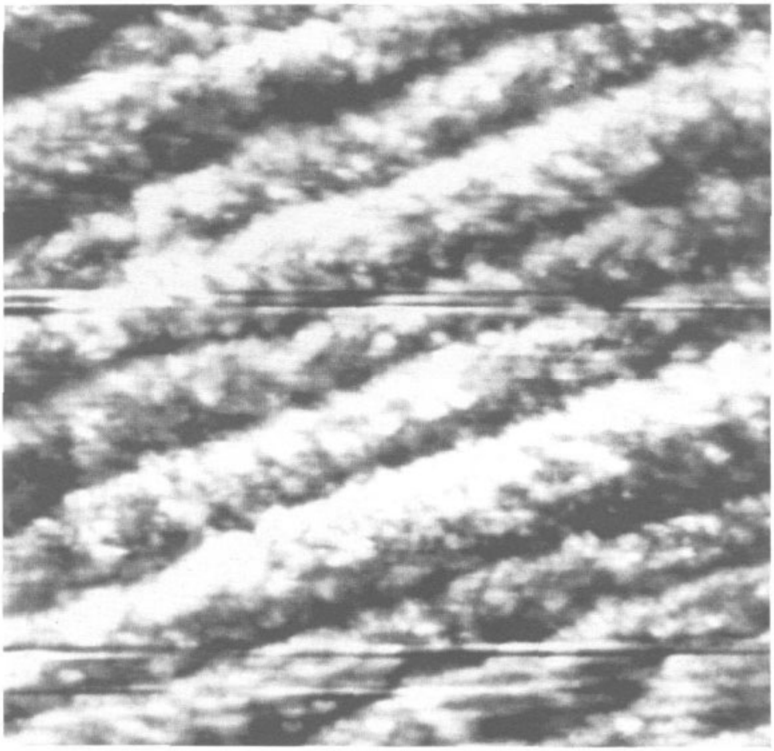

Figure 2. STM image of the Cl-saturated Si(111) 7 × 7 surface following 266 nm laser etching with 600 shots. Laser fluence is 0.7 mJ cm^{-2}. The image is recorded at a sample bias of +3 V and the area shown is 450x450 Å^2.

The surface structures were observed by a field-ion scanning tunnelling microscope [4]. The STM topographs were taken in the constant-current mode by using a ⟨*111*⟩-oriented W single-crystal tip and the tunnelling bias referred to the sample voltage.

3. Results and discussion

Figure 1 shows an STM topograph of the chlorinated surface at saturation coverage before laser irradiation at a sample bias of +3 V (empty state). Troughs based on the dimer rows described in the dimer adatom stacking fault (DAS) model [5] are clearly seen in the figure. The formation of $SiCl_2$ and $SiCl_3$ species for higher coverage has already been suggested by STM measurements, since some of the Cl atoms are arranged out of registry with the 'on-top' site of the adatoms [6,7]. Moreover, after saturated room temperature adsorption, the formation of SiCl, $SiCl_2$ and $SiCl_3$ was observed with surface-sensitive core-level shifts of Si 2p photoelectron spectra using synchrotron radiation with a photon energy of 120 eV [8]. Figure 2 shows an STM topograph at a sample bias of +3 V after laser irradiation. The scan size is the same as that in figure 1. The surface structure is obviously changed by laser irradiation and a periodic striped pattern is found. Parallel grooves ~10 Å in width run across the surface at nearly equal distances of ~60 Å along the ⟨110⟩ direction of the Si(111) surface. The pattern is a single domain in spite of the three fold symmetry of the

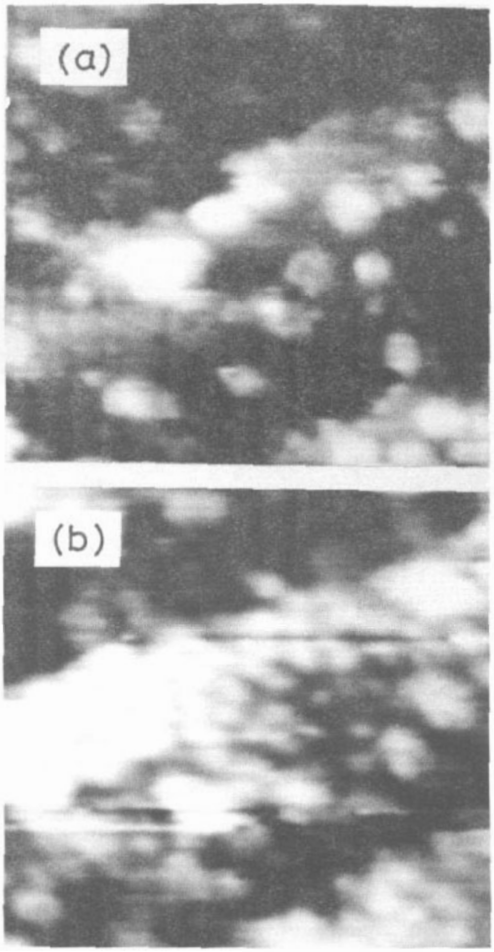

Figure 3. Extended STM images of the same surface as that shown in figure 2 at a sample bias of +3 V. The area shown is 180 × 180 Å^2. The rest-atom-like layer is shown in (a) and the Cl-adsorbed adatom layer on the 'on-top' site is shown in (b).

Si(111) 7 × 7 surface geometry. The direction of the polarity of the s-polarized laser on the surface was perpendicular to the grooves.

Figure 3 shows extended STM images which correspond to figure 2 but show the flat areas in more detail. At a terrace, shown in the lower left-hand corner of figure 3(a), a rest-atom-like layer can be seen, although the atomic resolution topograph imaged was ambiguous because of a sample bias of +3 V. Figure 4 shows an STM topograph at a sample bias of +1 V on the Si(111) surface, which was obtained by annealing the chlorine-saturated Si(111) 7 × 7 surface at 400 °C for 5 min. An atomic resolution topograph shows the flat rest-atom layer with 42 surface atoms in the 7 × 7 unit mesh, which is consistent with the second layer of the DAS model. The troughs based on the dimer rows are clearly seen and the corner holes have a smaller diameter than those in the clean 7 × 7 surface. The surface modification with 470 °C annealing has already been demonstrated by Villarrubia and Boland [6],

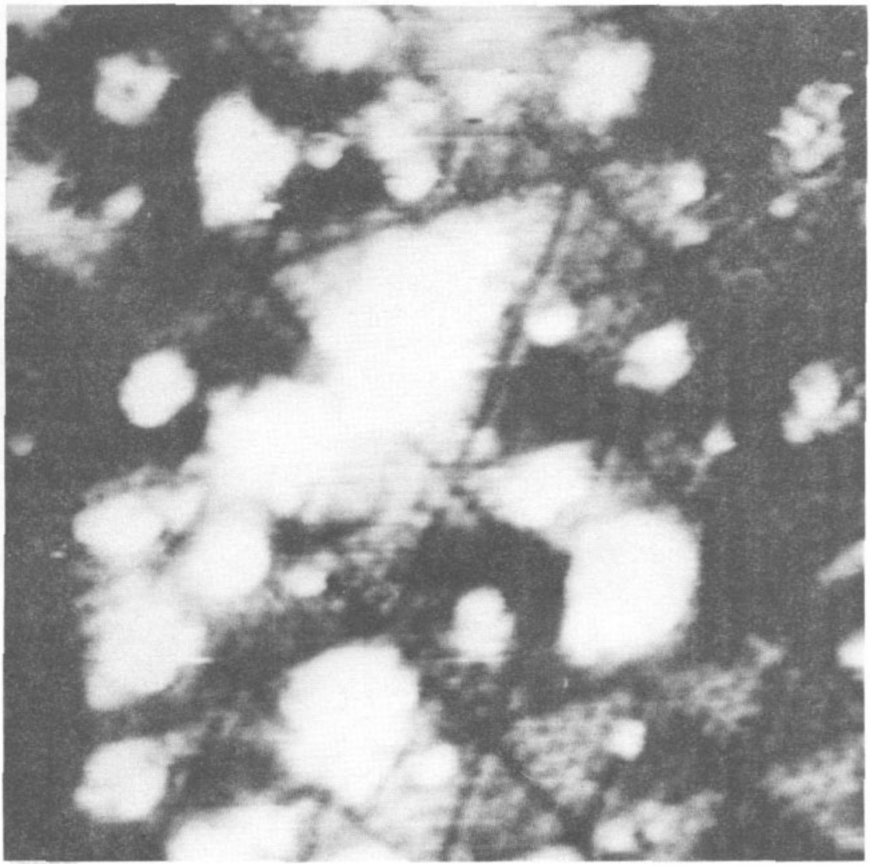

Figure 4. STM image of the Cl-saturated Si(111) 7 × 7 surface following an annealing at 400 °C for 5 min. The image is recorded at a sample bias of +1 V and the area shown is 135 × 135 Å^2.

but we performed similar experiments for comparison with the present experimental results. On the other hand, in the terrace area shown in the centre of figure 3(b), the adatom layer, which is covered with Cl atoms on the 'on-top' site, can be seen. This surface was clearly imaged after the UV laser etching for the chlorinated Si(111) 7 × 7 surface at lower coverage.

Since the laser fluence was ~0.7 mJ cm^{-2}, the estimated rise in surface temperature under laser irradiation is less than 10 K [9]. That is, the surface temperature was below 35 °C, and thermal desorption does not occur below 35 °C [10]. On the other hand, the thermally modified surface shown in figure 4 is isotropic and clearly different from the UV laser etching surface shown in figure 2. It was therefore concluded that the surface modification with the striped pattern is caused by photo-etching due to a non-thermal process.

After 600 shots of laser irradiation, the rest-atom-like layer appeared in a region of the terrace area, while, in some other region of the terrace area, the Cl-covered adatom layer remained unchanged. At the same time, parallel grooves were built up on the surface. The etching mechanism for these surface modifications may be so complex that we cannot elucidate the formation mechanism at the present stage. It is considered, however, that surface diffusion of chlorine atoms plays an important role in the groove formation. The following model can be speculatively proposed: desorption of only the $SiCl_2$ and/or $SiCl_3$ species is induced by valence electron excitation due to UV laser irradiation, as indicated by the mass-spectroscopic result reported by Baller *et al* [2] for laser-induced etching. The rest-atom layer is formed in the region where the backbond breaking has occurred, and the chlorinated adatom layer remains in a terrace area at which Cl atoms are adsorbed on the 'on-top' site of the adatoms. The preferred photo-etching occurs at defect sites such as a terminal point of the grooves after the diffusion of Cl atoms there, since the $SiCl_2$ species are easily formed due to the backbond breaking at defect sites and desorbed by the photo-chemical process. Then, the striped pattern is built up in UV laser etching induced by valence electron excitation.

On the other hand, all of the SiCl, $SiCl_2$ and $SiCl_3$ species must be desorbed by thermal heating at 400 °C for 5 min, although the temperature-programmed desorption spectra show that only a proportion of the β_2-state species are thermally desorbed at 400 °C [10]. Then, the adatom layer is stripped away and the flat rest-atom layer is formed at the surface due to the thermal annealing.

Acknowledgments

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