

High reaction selectivity on UV-laser-induced desorption from chlorinated Si(111) 7*7 studied by scanning tunnelling microscopy

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 6607

(<http://iopscience.iop.org/0953-8984/5/36/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 14:23

Please note that [terms and conditions apply](#).

High reaction selectivity on UV-laser-induced desorption from chlorinated Si(111) 7×7 studied by scanning tunnelling microscopy

Manabu Suguri, Ken-ichi Shudo, Fumio Komori and Yoshitada Murata

Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

Received 4 December 1992, in final form 19 May 1993

Abstract. Chlorinated Si(111) 7×7 surfaces were examined with scanning tunnelling microscope images after pulsed laser irradiation at 266 and 355 nm with low laser fluence, where the thermal effect can be ignored. From the surface irradiated by the 266 nm laser, dichloride and trichloride species are desorbed, while monochloride species remain on the surface. This desorption selectivity was not observed at 355 nm. These results give useful information to elucidate the formation mechanism of a stripe pattern observed after 266 nm laser irradiation on a Cl-saturated Si(111) 7×7 surface.

1. Introduction

Ultraviolet (UV)-laser-induced desorption from a chlorinated silicon surface is applied for useful etching processes in the semiconductor technology, such as monatomic layer etching and preferred etching. The origin of the remarkable reaction selectivity shown in these photochemical processes at the surfaces, however, has not been elucidated because the technological processes are usually performed in ambient reactive gas with high fluence of pump laser light. In this case, both electronic excitation of the free reactive gas molecule and thermal excitation on the surface are induced by laser light in addition to electronic excitation at the surface.

In order to clarify the phenomena caused only by electronic excitation at the surface, we have studied the UV-laser-induced etching of chlorinated Si surfaces with low enough laser fluence to avoid the thermal excitation process in an ultra-high vacuum (UHV) environment. Under such a severe condition, we should use highly sensitive methods to detect the desorption products or the surface changes. Thus, we have measured the change in the surface structure with a scanning tunnelling microscope (STM) before and after UV-laser irradiation. The structure of chlorinated Si surfaces can be observed with atomic resolution in the STM image [1].

In a previous paper [2], we reported a remarkable change in the STM images on a Cl-saturated Si(111) surface in a UHV chamber after 266 nm laser irradiation. After only 600 shots of pulsed laser irradiation with a fluence of 0.7 mJ cm^{-2} , in which the laser frequency was 10 Hz and the pulse duration 6 ns, a periodic stripe pattern was formed. The troughs run along the $(1\bar{1}0)$ direction, and the widths of the terrace and of the trough are about 6 nm and 1 nm, respectively. On the terrace area, both the rest-atom-like layer and the ordered Cl atoms sitting on the adatom sites of Si(111) 7×7 were seen in the STM image. This pattern is obviously different from the thermally desorbed surface, of which the topmost

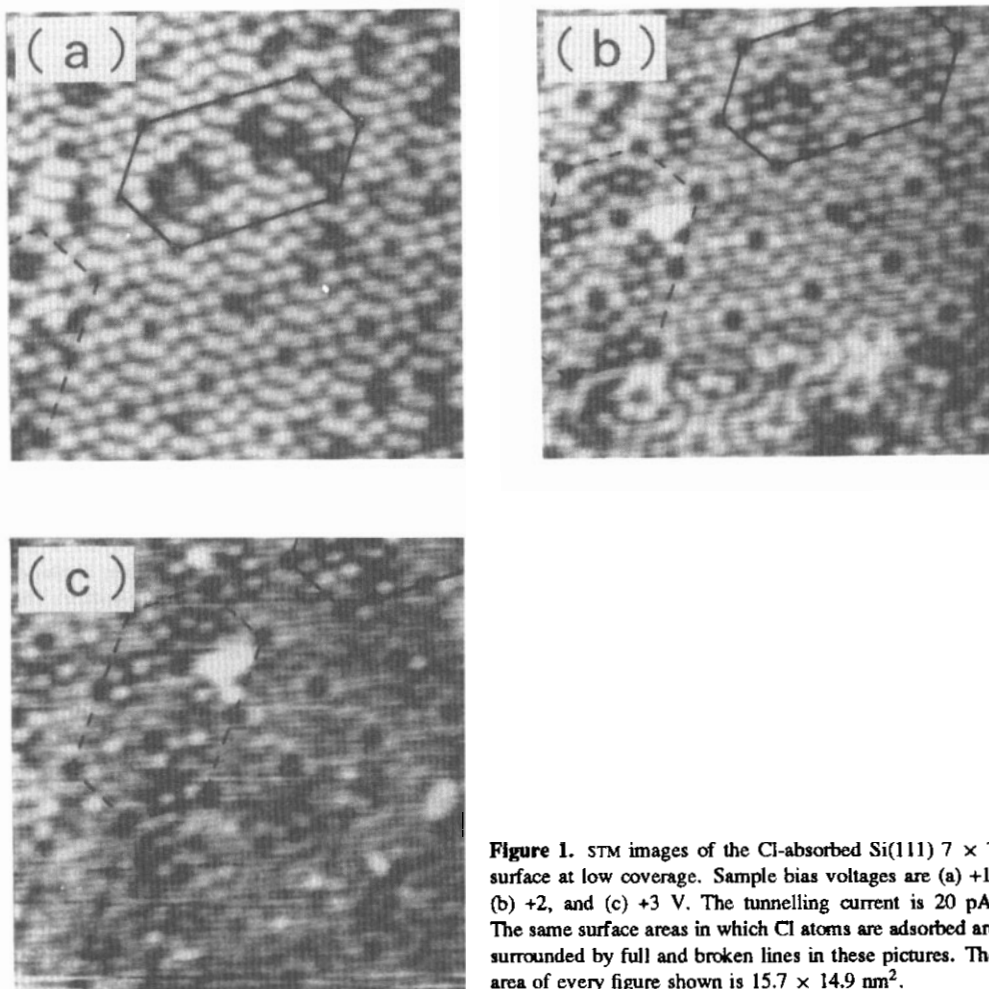


Figure 1. STM images of the Cl-adsorbed Si(111) 7×7 surface at low coverage. Sample bias voltages are (a) +1, (b) +2, and (c) +3 V. The tunnelling current is 20 pA. The same surface areas in which Cl atoms are adsorbed are surrounded by full and broken lines in these pictures. The area of every figure shown is $15.7 \times 14.9 \text{ nm}^2$.

layer is flat and consists of only the rest-atom layer [1, 2]. In contrast, we have not observed the stripe pattern after 355 nm laser irradiation.

In the present paper, we will show first the experimental results of the surface structure change observed by STM before and after laser irradiation with a small Cl coverage. Then, we will discuss the selectivity of the photodesorbed chloride species and the formation mechanism of the stripe pattern caused by 266 nm laser irradiation of the Cl-saturated surfaces.

2. Experimental results

The sample was n-type Si(111) cut from a wafer ($\sim 1\text{--}2 \Omega \text{ cm}$). The surface was cleaned by direct heating at $1200 \text{ }^\circ\text{C}$ for a few seconds in the UHV chamber with a base pressure of 5×10^{-11} Torr. The STM images were observed by a field ion STM [3]. A tungsten single-crystal tip oriented in the $\langle 111 \rangle$ direction was used. The clean 7×7 surface was observed by an STM topograph, and was exposed with Cl atoms and/or molecules generated from a silver chloride electrochemical cell [4] in the UHV chamber. The pressure rise during the Cl dose was lower than 2×10^{-8} Torr.

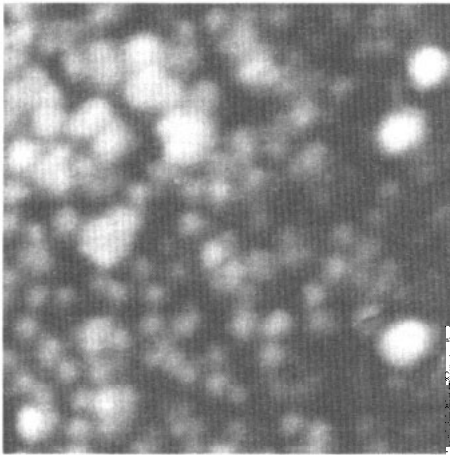


Figure 2. STM image of the chlorinated Si(111) 7×7 surface at a sample bias of +3 V. The adsorbed Cl density is nearly equal to the adatom density of Si(111) 7×7 . The area shown is $9.6 \times 10.7 \text{ nm}^2$.

At low exposure, every Cl atom sits at the on-top site of an adatom of the Si(111) 7×7 surface and can be clearly observed at a sample bias of $\sim +2.5\text{--}3 \text{ V}$, as shown in figure 1(b) and (c). In this figure, the Cl coverage is $\sim 20\%$ of the surface adatom density. On the other hand, the partially defected image of the Si(111) 7×7 surface was obtained at a sample bias of +1.0 V, as shown in figure 1(a). We can identify the defect sites observed at +1.0 V bias voltage as the Cl atom position at +3.0 V bias voltage because the full and broken lines surround the same region in these pictures. Similar results were reported by Boland and Villarrubia [1]. The image corresponding to an empty state of the Si–Cl bond is observed at $\sim +2.5\text{--}3 \text{ V}$ bias voltage. This means that Cl atoms bonded to the Si atoms can be clearly distinguished from the bare Si atoms at the surface in the STM image.

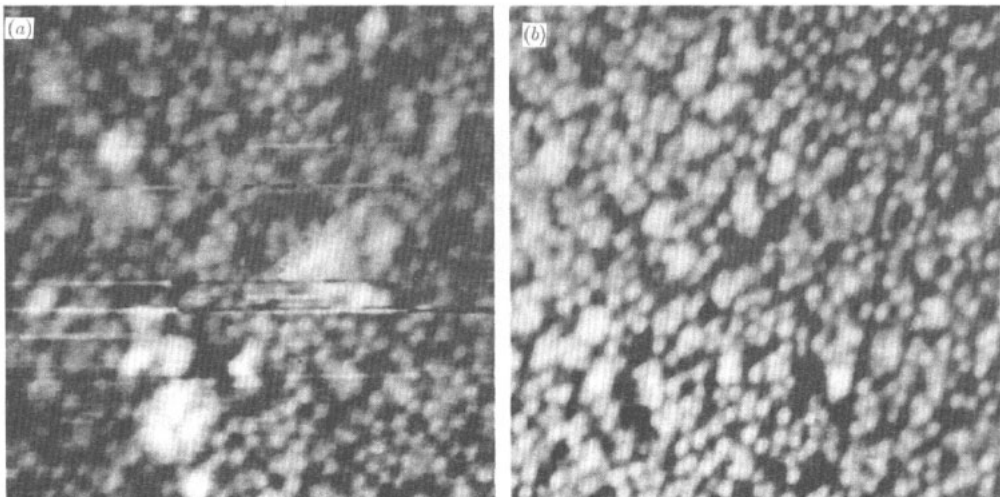


Figure 3. STM images of the chlorinated Si(111) 7×7 surface after irradiation (a) by 266 nm laser light with 3000 shots (laser fluence, 0.7 mJ cm^{-2}) and (b) by 355 nm laser light with 18 000 shots (laser fluence, 0.14 mJ cm^{-2}). Sample bias voltages are (a) +2.5 V and (b) +3.0 V. The areas shown are (a) $17.3 \times 17.4 \text{ nm}^2$ and (b) $19.4 \times 17.4 \text{ nm}^2$.

The Si(111) 7×7 surface was then exposed to an amount of Cl 10 times as high as

the exposure in figure 1. Note that the exposure at this time was about a tenth of that required to make the Cl-saturated surface on which the stripe pattern was observed after 266 nm laser irradiation. The surface was irradiated by UV-laser light of wavelengths 355 and 266 nm, which are third and fourth harmonics of a Nd:YAG laser (Spectra Physics, GCR-11), respectively. The laser pulse duration was 6 ns and the frequency was 10 Hz. The s-polarized Gaussian-shaped laser beam, 10 mm in diameter, was directed through a quartz window onto the sample surface. The incidence angle was 60° from the surface normal. Laser influence was kept low enough that the thermal effect could be ignored.

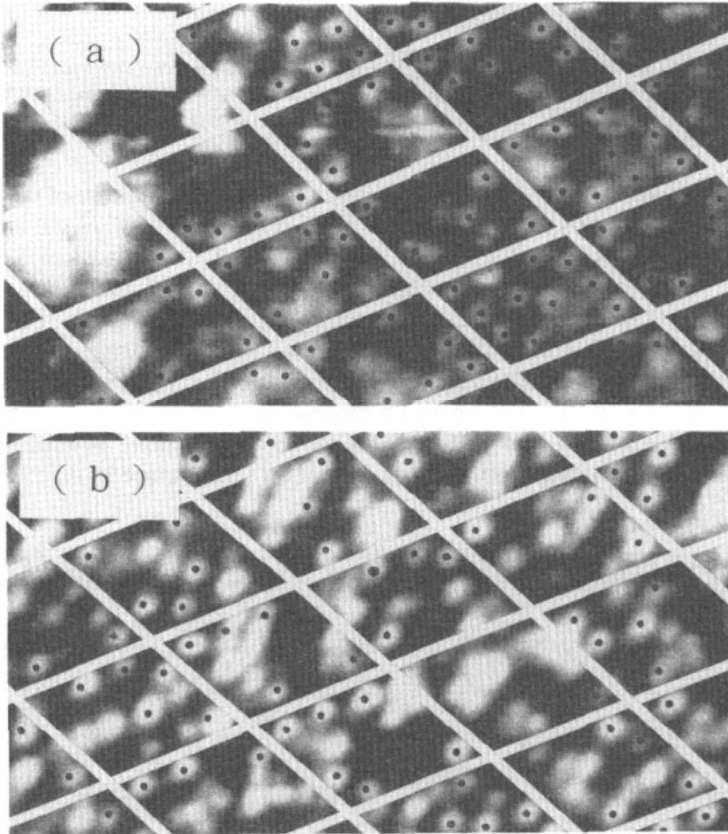


Figure 4. Extended STM images of the same surface as shown in figure 3. The areas shown are (a) $17.4 \times 7.2 \text{ nm}^2$ and (b) $14.1 \times 7.2 \text{ nm}^2$. Dotted bright circles indicate the chloride species registered on the on-top site of adatoms.

Figure 2 shows an STM image of the chlorinated Si(111) surface before laser irradiation. The sample bias voltage was +3.0 V and the area size depicted is $9.6 \times 10.7 \text{ nm}^2$. In this figure, not every bright circle is registered on the adatom site of Si(111) 7×7 , in contrast with the lower-Cl-coverage case shown in figure 1. Figure 3(a) shows an STM image after laser irradiation of 3000 shots at 266 nm with a fluence of 0.7 mJ cm^{-2} . The bias voltage applied to the sample was +2.5 V. Figure 3(b) shows an STM image after 18000 shots at 355 nm with a fluence of 0.14 mJ cm^{-2} . The sample bias was +3.0 V. Figure 4(a) and (b) shows extended pictures corresponding to figure 3(a) and (b), respectively. The full lines in both pictures of figure 4 are marked to indicate the Si(111) 7×7 unit mesh. In these

pictures, a dot is marked at the centre of the bright spots that were identified as sitting on an adatom of Si(111) 7×7 .

3. Discussion

There are three types of reaction product of Cl atoms with the adatom layer of the Si(111) 7×7 surface assigned to SiCl, SiCl₂, and SiCl₃, which were identified using STM by Boland and Villarrubia [5]. Dichloride and trichloride are produced by breaking the Si-Si bond(s) between the adatom and rest-atom layers. These products are registered at different positions from the monochloride, which is located just upon an adatom. The dichloride sits on the bridge site of two adjacent rest atoms, and the trichloride is located on a rest atom, as illustrated in figure 5.

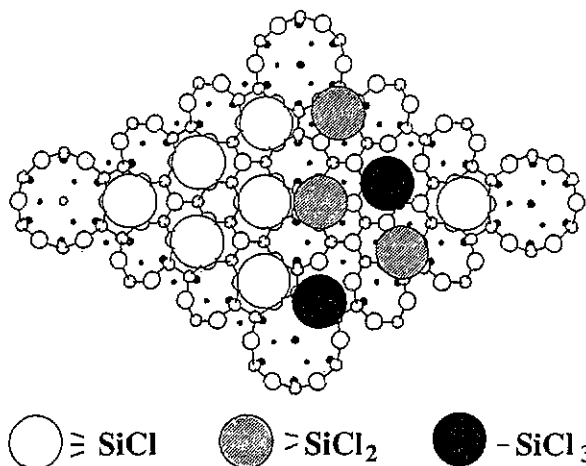


Figure 5. Schematic drawing of an ordered (left) and disordered (right) chlorinated Si(111) 7×7 surface. Only monochloride is shown in the left side. The right side illustrates three kinds of reaction product of Cl atoms with the adatom layer. Large filled, hatched, and open circles are SiCl₃, SiCl₂, and SiCl, respectively.

The bright position in the STM image at a sample bias of $\sim +2.5$ – 3.0 V corresponds to the average position of Si-Cl bonds. Therefore, the randomly distributed chloride picture seen in figure 2 indicates that the chlorinated surface consists of monochloride, dichloride and trichloride, as illustrated in the right half of figure 5.

As indicated by dots in figure 4(a), most of the bright circles appearing on the surface irradiated by 266 nm laser light are ordered and located on the adatom sites. The surface resembles the left half of figure 5 except for some defects observed. These features imply that laser irradiation at 266 nm induces desorption of dichloride and trichloride, and that it leaves monochloride on the surface. A defect appearing in figure 4(a) is a missing adatom created while SiCl₂ and SiCl₃ were desorbed. Contrarily, more than half of the bright circles on the surface irradiated by 355 nm laser light are not registered on the adatom sites and are randomly distributed. All the chloride species remain on the surface after laser irradiation at 355 nm, as seen from figure 4(b). The reaction selectivity in laser-induced desorption at 266 nm is clearly shown in these pictures.

This reaction selectivity in laser-induced desorption is consistent with mass-spectroscopic measurements by Baller *et al* [6]. They studied an etching of Si with Cl₂, where Si exposed to Cl₂ was irradiated with 308 and 248 nm light from an excimer laser at high fluences as high as about 0.4 and 1.0 J cm⁻². A mass spectrometer detected the particles desorbed from a chlorinated Si surface during excimer-laser irradiation, and velocity distributions were measured from time-of-flight spectra. In the 308 nm case only small amounts of chloride species were detected except for SiCl. The 248 nm light resulted

in higher ratios of Si and of SiCl_2 to SiCl than 308 nm light. That is, dichloride species were selectively desorbed at 248 nm, although the thermal process partially contributed to the desorption with a definite activation energy of 0.94 eV.

The difference in the activity of the laser-induced etching between the laser wavelengths 266 and 355 nm is related to the energy loss observed by low-energy electron energy-loss spectroscopy [7]. An energy loss appeared at ~ 4.0 eV after 100 L Cl_2 exposure on $\text{Si}(111) 7 \times 7$. This energy is higher than that of 355 nm light (3.5 eV) and lower than that of 266 nm light (4.6 eV).

We note in figure 4 that the number of dot-marked bright spots at the corner adatom sites is larger than that at the centre adatom sites. The small number of monochlorides on the top of centre adatom in figure 4(b) suggests a tendency for a dichloride or trichloride to form on a centre adatom. This is consistent with the observation in figure 4(a) that most of the defects formed after desorption of the polychlorides are located on the centre adatom sites.

Because UV-laser irradiation at 266 nm induces photodesorption with high reaction selectivity, the following is suggested as a formation process of the stripe pattern presented in the previous paper [2]. Desorption of dichloride or trichloride is induced by laser irradiation at 266 nm, and a vacancy is formed. Then excess Cl atoms or molecules existing on the Cl-saturated surface migrate, and some of them are trapped in the vacancy. These Cl atoms (or molecules) make a dichloride (or a trichloride) with an Si atom adjacent to the vacancy by breaking the Si-Si backbond(s). This process is induced successively by subsequent laser shots. Consequently, troughs would grow and the surface would become striped. A trough is directed along the $[1\bar{1}0]$ direction forming the (113) and $(11\bar{3})$ facets. It is known that the $\{311\}$ face is stable in the Si crystal [8]. On the terrace area, the rest-atom layer or monochloride layer appears after removing SiCl_2 and SiCl_3 . The sequence of the stripe pattern may depend on the surface temperature under laser irradiation, since thermal migration of chlorine atoms or molecules plays an important role in the above formation model.

Acknowledgment

This work was supported by a Grant-in-Aid on Priority Area Research on photo-etched processes from the Ministry of Education, Science and Culture, Japan.

References

- [1] Boland J J and Villarrubia J S 1990 *Phys. Rev. B* **41** 9865
- [2] Suguri M, Hashizume T, Hasegawa Y, Sakurai T and Murata Y 1992 *J. Phys.: Condens. Matter* **4** 8435
- [3] Hashizume T, Hasegawa Y, Kamiya I, Ide T, Sumita I, Hyodo S, Sakurai T, Tochiwara H, Kubota M and Murata Y 1990 *J. Vac. Sci. Technol. A* **8** 233
- [4] Spencer N D, Goddard P J, Davies P W, Kitson M and Lambert R M 1983 *J. Vac. Sci. Technol. A* **1** 1554
- [5] Boland J J and Villarrubia J S 1990 *Science* **248** 838
- [6] Baller T, Oostra D J and de Vries A E 1986 *J. Appl. Phys.* **60** 2321
- [7] Aoto N, Ikawa E and Kurogi Y 1988 *Surf. Sci.* **199** 4080
- [8] Ranke W 1990 *Phys. Rev. B* **41** 5243