Surface modification of Cl-adsorbed Si(111)-7x7 by the irradiation of infrared pulsed laser

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Abstract

As the first step to modify a semiconductor surface with light, we have studied the effect of infrared (IR) pulsed laser irradiation on Cl-saturated Si(111)-7×7 surface. After the surface was irradiated by a femto-second IR pulsed laser, we measured temperature programmed desorption (TPD) to observe the change of surface chemical component. Thermal desorption of SiCl₂ molecules was reduced and that of SiCl₄ molecules was enhanced by the IR irradiation. This result can be interpreted that polychloride radicals made of silicon adatoms are removed from the rest atom and form silicon polychloride clusters on the surface. The change was found to occur in the time scale less than 1 s, so that it may be via an electronic excitation process. Desorption of chlorides under the IR irradiation was detected at room temperature, but not detected at low temperature (150 K). The desorption at room temperature increased during the first 60 s of the IR irradiation, which implies that the desorption is due to a temperature rise of the substrate. It is concluded that the IR irradiation effect on the surface is classified into two processes dominated by the electronic excitation and the thermal effect.

1. INTRODUCTION

The kinetics of surface species, e.g. surface diffusion and step movement, should be understood to control a solid surface in atomic scale. Therefore, it is necessary to clarify the reactivity and the reaction process of surface species. Such studies are attractive from the industrial viewpoint and scientific viewpoint. For a decade, photo-stimulated etching of a semiconductor surface has been investigated as one of new techniques to modify the surface. If desorption could occur from a specific surface site as a result of stimulation of the site with photons, selective modification of the surface would be possible. One thereby has to reveal the processes of photon-stimulated desorption in detail. It has been already confirmed that surface adsorbates are desorbed by the excitation of surface electronic states with an ultraviolet or a visible laser. On Si(111)- 7×7 surface, for example, silicon adatoms irradiated by these lasers are desorbed via the excited surface states [1]. However, when photons come into a solid surface, they are absorbed not only by surface but mostly by the bulk, that is, many excited electrons are generated behind the surface. It is not demonstrated sufficiently how the surface species is affected by the electrons excited in the bulk, although this is very important to reveal the processes of photon-stimulated desorption. Accordingly, we have studied the effect of infrared (IR) light irradiation. IR light is not absorbed on the surface but absorbed only in the bulk [14], so that the kinetics of surface species under the excitation of bulk states can be identified. We have observed the change of surface chemical component after IR pulsed laser irradiation to chlorine- (Cl-) adsorbed Si(111)- 7×7 surface. Since a pulsed laser hardly raises a surface temperature, it is expected to observe the effect of electronic excitation, excluding a thermal effect.

Halogen (chlorine, bromine and etc...) adsorption on a silicon surface has been frequently studied as a typical system to modify a semiconductor surface in atomic scale. Since halogen atoms can strip away the first atomic layer of the silicon surface [5], an application to layer-by-layer etching has been expected. Many researchers have been therefore concerned with desorption from the halogen-adsorbed silicon surface. Desorption from the Si(111)- 7×7 surface attracts particular attention because the dimer - adatom - stacking fault (DAS) structure has a variety of sites with different chemical reactivity. For the Cl-adsorbed Si(111)- 7×7 surface, XPS studies showed the

adsorption states corresponding to the bonding of one, two and three Cl atoms to a silicon adatom [2, 3]. The di- and tri- chloride adatoms increase with Cl coverage [3].

During annealing at about 600 K, the adatoms combined with Cl atoms (hereafter, referred to polychloride radicals) diffuse on the surface and Cl-covered rest atom layer appears [2, 4, 5]. Furthermore, under annealing at 743 K, the 7×7 structure gradually transforms into the Cl-covered 1×1 rest atom layer structure without the dimer and the stacking fault [4]. When the surface is heated above 900 K, all the chlorides are desorbed and the Si(111)- 7×7 DAS structure is restored [3, 6, 7].

In this study, we used temperature programmed desorption (TPD) to observe the surface chemical component. Fundamentally, TPD is the method to reveal desorption process of a surface adsorbates, and the desorption process has been gradually detailed from recent researches. We can therefore get information about the surface component from the features of TPD spectra and estimate how the surface component changes.

2. EXPERIMENTAL

Measurements were performed in an ultrahigh vacuum chamber at a base pressure of 2×10^{-8} Pa. A plate ($7 \times 20 \times 0.38$ mm³) of boron-doped p-type ($10 \text{ } \Omega\text{cm}$) Si(111) wafer was used as a specimen. Si(111) surface was cleaned by Ar⁺ sputtering and ohmic heating up to 1420 K, and the 7×7 structure of the clean surface was confirmed by low energy electron diffraction (LEED). The surface was exposed to a Cl gas from an electrolysis cell of AgCl pellet. All the TPD measurements were performed on the Cl-saturated surface. A mode-locked Ti:sapphire laser was used as an IR pulsed laser. Specifications of the laser were as follows: wavelength = 800 nm, fluence = 93 nJ/cm^2 , pulse duration = 80 fs, repetition rate = 80 MHz. The incident laser beam was directed at 45 degree to the surface normal. In TPD, desorption yield was measured with a quadrupole mass spectrometer (QMS) with respect to the surface temperature controlled by ohmic heating. The temperature monitored with a radiative thermometer was increased from 500 K to 1300 K at a rate of 2 K/s, and the desorption yield of four types of mass, corresponding to SiCl⁺, SiCl₂⁺, SiCl₃⁺ and SiCl₄⁺, was successively detected every 0.2 s. We introduced a pulse-counting system to realize

highly sensitive measurement in which the detected signal from QMS was amplified, shaped into pulses and counted [8].

3. RESULTS and DISCUSSION

Solid lines in Fig.1 show TPD spectra of the Cl-saturated Si(111)- 7×7 surface. There are obviously three peaks named A, B and C in the SiCl^+ and SiCl_2^+ spectra. These two TPD spectra are quite similar, which indicates that the desorption signals originate from the same species. It is ascribed to SiCl_2 molecule, and the SiCl^+ signal is produced by an electron impact fragmentation of the SiCl_2 molecule [7].

Peak C appears approximately at 600 K. Polychloride radicals diffuse on the surface and most of them form silicon chloride clusters in this temperature range [4]. Nevertheless, some of the adatoms are desorbed as SiCl_2 molecules as reflected in peak C [7,10]. In the temperature range of peak B, the structure of the Cl-adsorbed Si(111) surface transforms from 7×7 into 1×1 . Isothermal desorption studies on Br-adsorbed Si(111) surface demonstrated that the bromide desorptions from the 7×7 region and the 1×1 region coexisted for peak B [9]. The desorption for peak B therefore occurs along with the surface reconstruction. There is a large desorption for peak A around 907 K. All the chlorides on the 1×1 surface are desorbed in this temperature range and the Si(111)- 7×7 DAS structure is restored. Isothermal desorption studies with QMS revealed that the desorption for peak A follows second order kinetics which suggests a recombinative desorption mechanism involving $\text{SiCl} + \text{Cl} \rightarrow \text{SiCl}_2$ [7, 9, 10]. On the other hand, isothermal desorption studies by means of SDR [6], UPS [11] and SHG [12] resulted in first order kinetics. This contradiction was explained that the second order kinetics would be observed by QMS due to the coexistence of the desorption from the surface defects (steps and pits) [13], which follows first order kinetics, and the desorption from the silicon chloride clusters, which lasts longer [6].

Dashed lines in Fig.1 show TPD spectra after the IR pulsed laser irradiation for 500 s. Comparing the dashed lines with the solid lines, one notes that the desorption of SiCl_2 molecules, appearing in the SiCl^+ and SiCl_2^+ spectra, is reduced by two-thirds and that of polychlorides, appearing in the SiCl_4^+ spectrum, is enhanced around 580 K. These results indicate that the IR irradiation induces a

remarkable change of the surface component. The desorption of SiCl_4^+ is observed far less than that of SiCl_2 molecules, which is ascribed to worse detection sensitivity of QMS for heavier molecules like SiCl_4 . The actual amount of desorbed SiCl_4 molecules is therefore larger than that in Fig.1. Reduction in the desorption of SiCl_2 molecules means that considerable number of polychloride radicals have disappeared under the IR irradiation, because the each peak height of A, B and C is dominated by the amount of such adatoms. The enhancement of the desorption of SiCl_4^+ is not caused by the desorption from isolated SiCl_4 molecules on the surface. Because the desorption energy of SiCl_4 molecule was estimated to be 0.024 eV [15], so the isolated SiCl_4 molecules should be desorbed at lower temperature than 580 K. The desorption of SiCl_4^+ is therefore explained by silicon polychloride clusters formed from the polychloride radicals which should be different from those produced by thermal treatment. This cluster is therefore different from that appearing the thermal treatment at 600 K, which is more stable and desorbed around 900 K. The composition of the former cluster may be close to $\text{Si} : \text{Cl} = 1 : 4$, and that of the latter cluster may be close to $\text{Si} : \text{Cl} = 1 : 2$. The unit cell of $\text{Si}(111)\text{-}7\times 7$ DAS structure has 12 adatoms, and about 66 Cl atoms are adsorbed at the saturated coverage. If an adatom are removed and form a part of silicon polychloride cluster as SiCl_4 molecule by the IR irradiation, the 12 adatoms take 48 Cl atoms into the clusters and 18 Cl atoms are left in the unit cell. Then, about one-third of the rest atom layer is covered by Cl atoms. The one-third nearly corresponds to the peak heights of SiCl^+ and SiCl_2^+ spectra after the IR irradiation.

Fig.2 compares TPD spectra after the IR pulsed laser irradiation for 1 s, 10 s and 500 s. For all species, three TPD spectra have a same shape, indicating that the change of surface component induced by the IR irradiation does not depend on the duration of irradiation in the time scale of second. The change therefore occurs very fast, within 1 s, which suggests that the change proceeds via an electronic excitation process, not a thermal process. Possible process is as follows. Electrons excited in the bulk due to photon-absorption will be scattered at the surface inelastically, when the polychloride radicals may be removed from rest atoms and diffuse. The excitation to the anti-bonding states of the surface species might weaken the back bond of the adatom, resulting in the removal of the polychloride radicals. The IR irradiation for 1 s does not cause the desorption of chlorides, as is apparent in Fig.3 which is described later.

These results imply that, under the IR pulsed laser irradiation, the polychloride radicals are removed from the rest atom and diffuse on the surface without desorption, and may form the instable silicon polychloride clusters whose composition may be close to $\text{Si} : \text{Cl} = 1 : 4$.

Fig.3 shows the time courses of desorption yield under the IR irradiation at constant temperatures. When the surface was at room temperature (solid lines), the desorption of chlorides developed in the first 60 s of the IR irradiation. This is very slow reaction compared with the duration of the laser pulse. Chlorides were not desorbed at all at 150 K (dashed lines). The surface temperature gradually rises under the IR irradiation. The desorption of chlorides at room temperature is therefore ascribed to the temperature rise exceeding a desorption threshold. At 150 K, chlorides are not desorbed probably because the temperature rise is below the threshold.

The above results suggest the following processes underlying the change of surface component induced by the IR pulsed laser irradiation. Excited electrons generated from photo-absorption in the bulk propagate to the surface and activate the surface species, which proceeds very fast. At the same time, the energy of the excited electron is transformed into that of a lattice vibration, which yields the slow thermal effect.

4. CONCLUSIONS

We have observed the change of surface component of the Cl-saturated $\text{Si}(111)\text{-}7\times 7$ induced by the IR pulsed laser irradiation. Highly sensitive measurement of desorption species was attained by introduction of a pulse counting system, which helps us to obtain the information about the surface component in detail. When the surface is irradiated by the IR pulsed laser which excites electronic states in the bulk, two processes proceed on the surface. One is relevant to an electronic excitation and the other to a thermal effect. The following is concluded from the TPD spectral features and the short response time of the photo-stimulated change. In the electronic excitation process, the polychloride radicals are removed from the rest atom, diffuse and form silicon polychloride clusters on the surface. In the thermal process, a temperature rise of the surface causes the desorption of chlorides.

It is an interesting progress to have identified that silicon atoms move on the surface by an

electronic excitation in the bulk without a thermal effect. The present results will provide a deeper understanding of the photo-stimulated etching of a semiconductor surface.

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Figures and figure captions

Fig. 1. TPD spectra of Cl-saturated Si(111). Solid and dashed lines show the spectra for the surface as-exposed with Cl and the surface after the IR pulsed laser irradiation for 500 s, respectively.

Fig. 2. TPD spectra of Cl-saturated Si(111)- 7×7 surface after the IR pulsed laser irradiation for 1 s (thick lines), 10 s (thin lines) and 500 s (dotted lines). Four figures correspond to the spectra for SiCl^+ , SiCl_2^+ , SiCl_3^+ and SiCl_4^+ .

Fig. 3. Time courses of desorption yield under the IR pulsed laser irradiation at room temperature (solid lines) and 150K (dashed lines).