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Description	

Optical second harmonic intensity images of hydrogen deficiency on H-Si(111) surfaces*

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In order to obtain the spatial distribution of hydrogen desorption by ultraviolet (UV) laser pulses from a hydrogen terminated Si (H-Si) surface, optical second harmonic (SH) intensity images of the surface have been observed in ultra high vacuum. The observed SH signal included both contributions of the hydrogen deficiency on the H-Si surface and the surface damage. The spatial distribution of the hydrogen deficiency has been obtained from the difference between the SH intensity images before and after the hydrogen re-termination. The hydrogen desorption occurred above the threshold fluence of ~ 40 mJ/cm², and the total amount of the hydrogen desorption increased monotonically as a function of the UV laser pulse energy. It is suggested that the observed hydrogen desorption may have resulted from the laser induced thermal desorption (LITD) mechanism. [DOI: 10.1380/ejsnt.2006.105]

Keywords: Second harmonic generation; Desorption induced by photon stimulation; Surface melting; Thermal desorption; Silicon; Hydrogen molecule; SHG microscope; H-Si(111)

I. INTRODUCTION

The hydrogen terminated silicon (H-Si) single crystal surface is an important model system of adsorbed semiconductor surfaces. Its bonding states [1, 2] and chemical reactions [3] have been studied very well. Especially, photo-thermal desorption of hydrogen from this surface is an important basic process in optical CVD and laser ablation, and have been studied extensively [4]. In addition to the hydrogen desorption, surface melting often occurs under strong light irradiation. This makes the mechanism of the hydrogen desorption by intense laser light pulses very complicated.

It has been reported that the rates of hydrogen desorption and surface melting depend in different ways on the beam pattern of the incident laser light [5]. Thus, in order to analyze the hydrogen desorption and surface melting under inhomogeneous UV irradiation, the information on the spatial distribution of hydrogen deficiency on a H-Si surface and of surface melting are important. Laser-induced thermal desorption (LITD) have been studied extensively [4], but few experimental study of the spatial distribution of hydrogen deficiency on a H-Si surface has been reported [5].

In the present study, we have observed spatial distribution of hydrogen deficiency on a H-Si surface irradiated with ultraviolet (UV) light beam by using optical second harmonic (SH) microscopy. Optical second harmonic generation (SHG) is one of the lowest-order nonlinear optical processes. Although it is forbidden in a medium with center of inversion such as a Si crystal, SH light can be generated at the surface lacking inversion symmetry. Because of its high surface sensitivity, SHG has been used as a useful tool to investigate the surface structures and surface electronic states of various materials [6]. Recently, this nonlinear optical phenomenon has been applied to mi-

croscopy [7–11]. By using the SH microscope, one can obtain spatial distribution images of surface electronic states or adsorbates [11]. In this study, we demonstrate that spatial distributions of hydrogen deficiency and surface melting on a H-Si(111) surface can be separately obtained from the observed SH intensity images.

II. EXPERIMENT

Details of our SH microscope system for observing the surfaces in ultra-high vacuum (UHV) has been reported in Ref. [11]. The excitation light for SHG was generated by a mode-locked Nd³⁺:YAG laser (EKSPLA PL2143B) with wavelength of 1064 nm, the pulse duration of 30 ps, and repetition rate of 10 Hz. The light pulses were passed through neutral density filters, Glan polarizers, a lens with focal length $f = 300$ mm, a colored glass filter to block the visible light, and a glass window of a UHV chamber. They were focused loosely onto the sample surface in the UHV chamber. The pulse energy of the excitation light beam at the sample was 0.5 ~ 2 mJ/pulse. The angle of light incidence onto the sample was 45°. The reflected light was first passed through a glass window of the chamber and through colored glass filters to block the fundamental light, and then introduced into a long-distance microscope of Cassegrain type (Quester QM-1). With this long-distance microscope, the image of an object 0.5 m away can be focused on a detector plane with a resolution of 3 μ m. The microscope is equipped with a time-gated image intensified charge coupled device (CCD) camera (Hamamatsu PMA-100-H) for accumulating SH signals. It is also equipped with a band-pass filter with the center wavelength of 532 nm.

To prepare the H-Si(111) surface, non-doped Si(111) wafers with resistivity $\rho = 200 \sim 240$ Ω cm were etched in a clean room by a few cycles of dipping in a hot solution of 97% H₂SO₄ : 30% H₂O₂ = 4:1, then in hydrofluoric acid [2], and finally in NH₄F solutions for producing a monohydride terminated Si(111) surface. After this preparation, the sample was immediately introduced into the UHV chamber with the base pressure of $\sim 1 \times 10^{-7}$ Pa. In order to induce desorption of the adsorbed hy-

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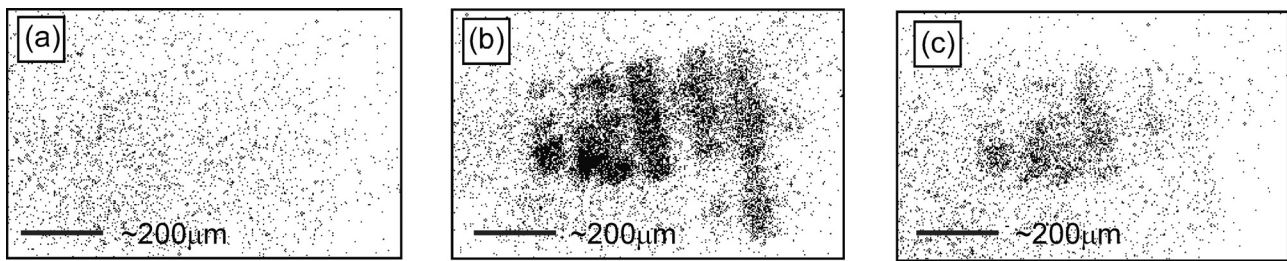


FIG. 1: SH intensity images of a H-Si(111) surface (a) before and (b) after UV light irradiation through a striped mask and (c) after air exposure. The dark dots represent the observed SH photons.

drogen atoms, the H-Si(111) surface was irradiated with focused UV light pulses with the wavelength of 355 nm from the YAG laser.

III. RESULTS AND DISCUSSION

Let us start with the demonstration that hydrogen deficiency on a H-Si(111) surface is detectable in the measured SH intensity images. Figure 1(a) is a SH intensity image of a H-Si(111) surface before UV light irradiation. The observed SH photons are represented by dark dots. No obvious structure is seen in Fig. 1(a), and the total SH intensity is very weak. In order to remove a part of the adsorbed hydrogen atoms, the H-Si(111) surface was irradiated with UV laser light pulses with wavelength of 355 nm masked by a striped pattern. The repetition of the laser light pulses was 10 Hz, the irradiation time was 5 min, and the fluence of UV light was 1.6 J/cm^2 . The result is shown in Fig. 1(b) and one can see an enhanced SH intensity image. The total SH intensity in Fig. 1(b) was five times as large as that in Fig. 1(a). This result is interpreted as follows. The UV light gave rise to hydrogen desorption from the H-Si(111) surface and produced a lot of dangling bonds. Since surface electronic levels due to the dangling bonds are formed around the Fermi level, resonant optical transition mediated by these surface electronic levels becomes allowed at the incident photon energy $\hbar\omega = 1.17 \text{ eV}$ so that SHG is enhanced [12, 13]. On the other hand, the H-terminated surface has no surface state in the energy band gap. Thus SHG enhancement due to the resonant optical transition of the surface states does not occur for the H-terminated surface at $\hbar\omega = 1.17 \text{ eV}$. It is noted that the incident photon energy $\hbar\omega = 1.17 \text{ eV}$ is suitable for the SHG experiment to detect hydrogen deficiency on Si(111) [14].

In order to confirm the validity of the above interpretation, the following experiment was performed. After observing the image of Fig. 1(b), air was introduced into the chamber to the atmospheric pressure and the sample was exposed to air for 5 min. Then, the chamber was evacuated again, and the SH image of the same surface area was observed. The result is shown in Fig. 1(c). The total SH intensity in Fig. 1(c) is one-third of that in Fig. 1(b). The decrease in the SH intensity is due to the disappearance of the dangling bonds by the adsorption of chemically active molecules such as oxygen in air. Thus most part of the SH intensity images in Fig. 1 is the spatial mapping of the surface electronic states reflecting the

distribution of dangling bonds created by the hydrogen deficiency.

In order to check the crystallinity of the Si(111) substrate after the UV light irradiation, it was examined by transmission electron microscopy (TEM) [15]. The surface layer with the thickness of a few ten nanometers was found to be amorphous and defects were seen in the deeper layer [15]. The surface melting must have occurred due to the irradiation of UV light pulses. The SH signal seen after disappearance of the dangling bonds in Fig. 1(c) is suggested to result from the surface melting due to the UV light irradiation, although its detailed mechanism of SHG enhancement is not clear at present.

Next, we demonstrate experimentally that spatial distribution of the hydrogen deficiency can be separated from that of the surface melting in the SH intensity images. First, a H-Si(111) surface in the UHV chamber was irradiated with UV laser light pulses for 5 sec and SH intensity image was observed immediately. This first image should contain the contribution of both the hydrogen deficiency and the surface melting. Secondly, hydrogen gas was introduced into the chamber with the exposure of $\sim 70\text{L}$ for hydrogen re-termination of the dangling bonds on the surface and SH intensity image was recorded. The contribution of the hydrogen deficiency should have disappeared in this second image. Thirdly, we subtracted the second SH intensity images from the first SH intensity images by using image processing technique, and obtained the differential images, i.e. the spatial distribution of the hydrogen deficiency.

The SH intensity images of the H-Si(111) surface irradiated with UV light pulses are shown in Figs. 2(a) to (g). The fluence of the UV light was varied from 41 to 164 mJ/cm^2 . White dots represent detected SH photons. The area emitting bright SH light became larger as the energy of UV light pulses was increased. Figures 2(a') to (g') are the SH intensity images of the same surface areas after hydrogen exposure. Figures 2(a'') to (g'') are the differential images obtained by subtracting Figs. 2(a') to (g') from Figs. 2(a) to (g), respectively. As shown in Figs. 2(a'') to (g''), clear spatial distribution of the hydrogen deficiency due to the UV light irradiation was obtained. Figure 2(a'') is very dark, but a few SH photons from the hydrogen deficiency were detected. One can clearly see that the area of hydrogen deficiency due to the UV light irradiation was expanded as the energy of UV light pulses increased.

In order to check the validity of the obtained SH images of hydrogen deficiency and also discuss the mechanism of

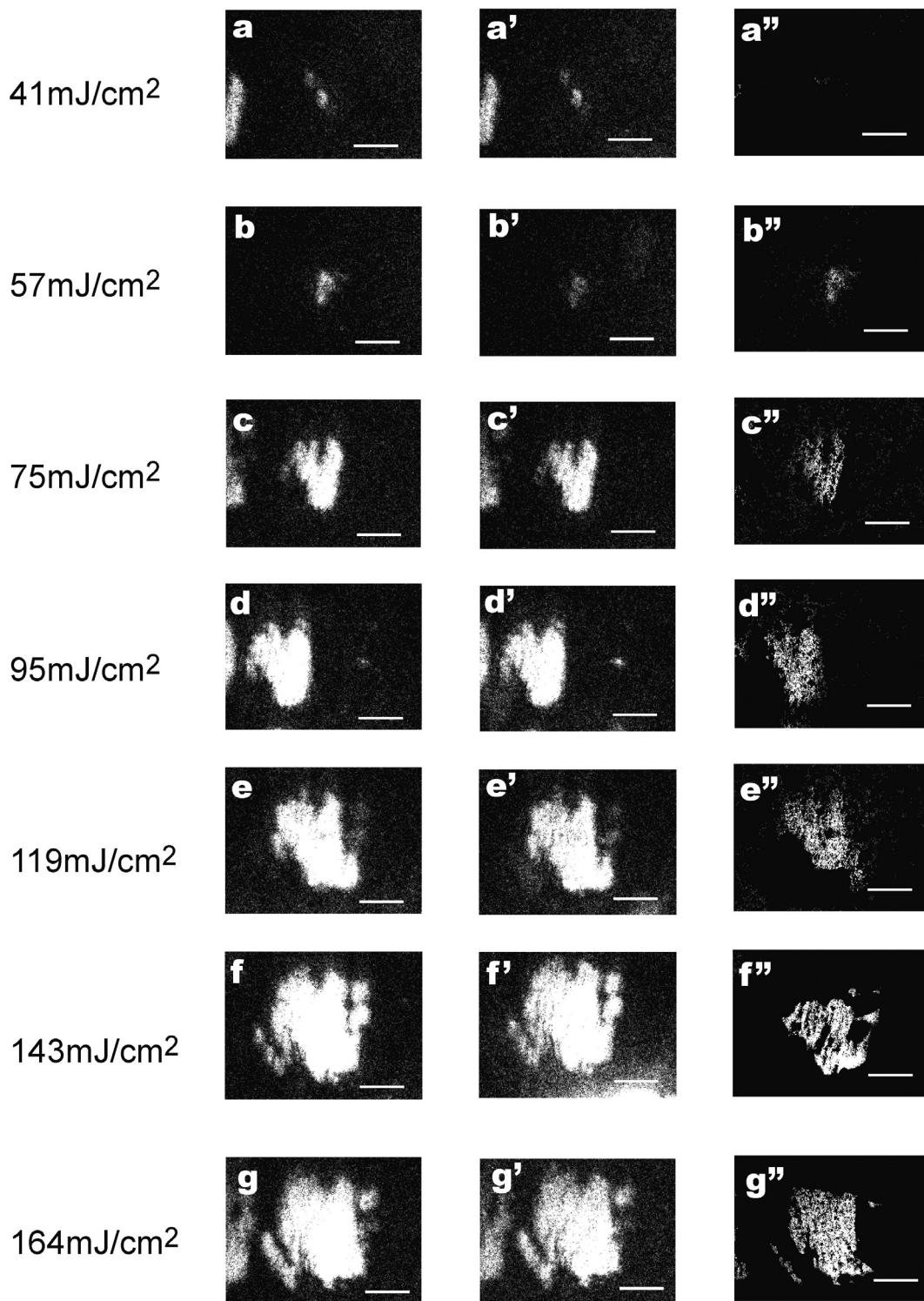


FIG. 2: SH intensity images of H-Si(111) surfaces after (a)-(g) UV light irradiation with various pulse energy and (a')-(g') after the subsequent exposure to hydrogen gas. Panels (a'')-(g'') are the differential SH intensity images obtained by subtracting the panels (a')-(g') from the panels (a)-(g), respectively. White dots represent the SH photons. All scale bars in the images are 200 μm .

the desorption in the present experiment, we have calculated the energy dependence of the amount of hydrogen deficiency from the SH intensity images. Figure 3 shows the total signal in the differential images of Figs. 2(a'') to (g'') as a function of the fluence of the UV light. Vertical axis in Fig. 3 represents the total amount of hydrogen des-

orption. The solid line was obtained by the least squares fitting. Fig. 3 indicates that hydrogen desorption occurs above the threshold fluence of $\sim 40 \text{ mJ/cm}^2$ and the total amount of hydrogen desorption increased monotonically as the fluence of UV laser light increased.

So far, two mechanisms, i.e. photo-stimulated desorp-

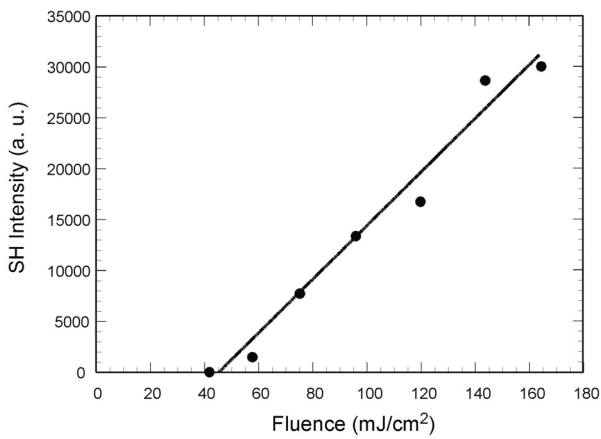


FIG. 3: SH signal due to the hydrogen deficiency as a function of the fluence of UV light. Solid squares are the experimental data obtained from Figs. 2(a'')-(g''). The solid line was obtained by the least squares fitting.

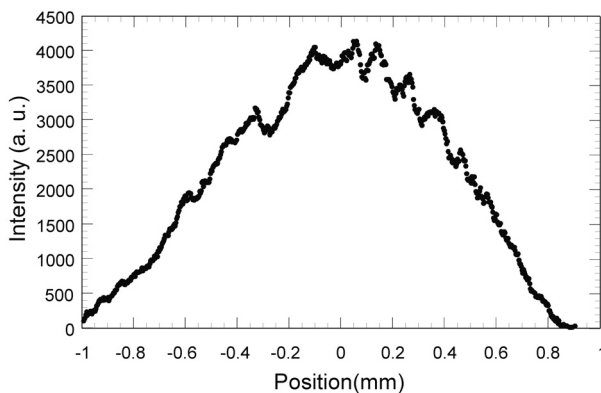


FIG. 4: The profile of UV light intensity with wavelength of 355 nm on a Si surface.

tion (PSD) and laser induced thermal desorption (LITD) were proposed as the origins of hydrogen desorption from a H-Si surface due to the light irradiation [16]. In the LITD mechanism, the hydrogen desorption is expected to have an energy threshold because the surface temperature should exceed a level sufficient for the hydrogen desorption [5]. On the other hand, PSD should show no energy threshold because in the PSD process a photon directly breaks the Si-H bond [16]. Since Fig. 3 shows the fluence threshold of ~ 40 mJ/cm², the hydrogen desorption observed in the present study probably results from the LITD mechanism.

Next, let us discuss the surface temperature under UV light pulse irradiation. We roughly estimated the temperature rise of a Si surface irradiated by one UV light pulse with the energy density of 0.82 mJ/pulse·cm² corresponding to the fluence of 41 mJ/cm². In the calculation, the photo-absorption coefficient and heat conductivity were

assumed to be constant, and heat diffusion was neglected for simplicity. Figure 4 is a spatial distribution of UV light intensity on a sample surface measured by a laser beam profiler. By using the profile of Fig. 4, the surface temperature rise in the center of the irradiated area was estimated to be ~ 1400 K. This roughly estimated surface temperature is close to the melting temperature of a Si surface layer (1414 K) [17]. Therefore, the experimental result in Fig. 2(a'') indicating the surface melting is reasonable. Ref. [5] also reports that the surface melting of Si can occur in typical experimental conditions used for LITD from silicon surfaces. Our results are consistent with this report in Ref. [5]. Although the estimated temperature of Si irradiated with the UV fluence of 41 mJ/cm² is much higher than the hydrogen desorption temperature of ~ 800 K (β_1) [18], only a small amount of hydrogen desorption were observed. Si surface was heated to the desorption temperature in such a short time (1.5 nsec in total) under our experimental condition that it was difficult to find out appropriate pulse energy of UV light causing enough amount of hydrogen desorption to be detected by SHG without the surface melting. For complete understanding of the experimental results, further experimental and theoretical studies are required.

IV. CONCLUSION

We have observed SH intensity images of a H-Si(111) surface irradiated with UV laser light pulses. In the surface area irradiated with UV laser pulses, SH intensity was enhanced. This SHG enhancement is due to the hydrogen deficiency on a H-Si surface and surface melting. Hydrogen re-termination reduced the SHG enhancement. By subtracting the SH intensity image after the hydrogen re-termination from that before the hydrogen re-termination, the spatial distribution of hydrogen deficiency on a H-Si(111) surface irradiated with the UV laser light pulses were obtained. Since the hydrogen desorption occurred with the fluence threshold of ~ 40 mJ/cm², the most likely origin of the hydrogen desorption in the present system is suggested to be the laser induced thermal desorption (LITD). In order to confirm the validity of this tentative explanation, it is necessary to fully analyze the measured spatial distributions of the hydrogen deficiency by performing model calculation of thermal diffusion in the surface layer. In the present study, we have demonstrated that SH microscopy is a powerful tool to investigate dynamics and chemical processes on a surface.

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