

Title	Modulation of Si-H vibrational mode as a function of the hydrogen coverage on a H-Si(111)1×1 surface
Author(s)	Miyauchi, Yoshihiro; Thi Thu Hien, Khat; Mizutani, Goro
Citation	Proceedings of SPIE, 8883: 88831D
Issue Date	2013
Type	Journal Article
Text version	publisher
URL	http://hdl.handle.net/10119/11439
Rights	Yoshihiro Miyauchi, Khat Thi Thu Hien and Goro Mizutani, " Modulation of Si-H vibrational mode as a function of the hydrogen coverage on a H-Si(111)1×1 surface ", Proc. SPIE 8883, ICPS 2013: International Conference on Photonics Solutions, 88831D (June 7, 2013); doi:10.1117/12.2021685. Copyright 2013 Society of Photo-Optical Instrumentation Engineers. One print or electronic copy may be made for personal use only. Systematic reproduction and distribution, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper are prohibited.
Description	

Modulation of Si-H vibrational mode as a function of the hydrogen coverage on a H-Si(111)1×1 surface

Yoshihiro Miyauchi^{*a}, Khuat Thi Thu Hien^b and Goro Mizutani^b

^a Department of Applied physics, National Defense Academy of Japan, Hashirimizu 1-10-20 Yokosuka, Kanagawa, 239-8686, Japan; ^b School of Materials Science, Japan Advanced Institute of Science and Technology, Asahidai, Nomi, Ishikawa 923-1292, JAPAN

ABSTRACT

In this study, we have observed a SFG microscopic image of the H-Si(111)1×1 surface after pump IR light irradiation. As the results, resonant SFG signals attributed to Si-H stretching vibration disappeared at the irradiated areas, and non-resonant signals were generated at these areas. We also found that there were boundary areas between laser irradiated and non-irradiated areas. Both SFG signals were weak at the boundary areas. As the reason of these modulations of SFG signals, we assumed that the temperature did not sufficiently increase for hydrogen desorption at the boundary areas, since the areas were located at edges of spatial distribution of the pump laser intensity. In order to verify the assumption, we heated the Si surface at 711K, slightly above threshold temperature for activation of hydrogen desorption, and then observe SFG spectra of the Si surface as a function of hydrogen coverage at room temperature. As the results, the intensity of the peak at 2083.7cm⁻¹ attributed to Si-H stretching vibration reduced as a function of hydrogen deficiency. Also, the peak position shifted toward red side. We simulated dipole-dipole interaction by using coherent potential approximation (CPA) method, and the simulated peak shift was qualitatively consistent with the experimental one. Thus, the peak shift corresponded to dipole-dipole interaction. On the other hand, the experimental peak width also broadened with the coverage reduction. However, the broadening was far wider than that of theoretical width. We suggest that the broadening was attributed to local structure defects and/or influence of neighbor dangling bonds.

*miyauchi@nda.ac.jp; phone +81-468-41-3810; fax +81-468-44-5912

Keywords: Hydrogen, Si surface, laser CVD, SFG spectroscopy, SFG microscopy, dipole-dipole interaction

1. INTRODUCTION

Laser chemical vapor deposition (CVD) is a well-established method for depositing high quality amorphous Si film on a Si surface at low temperature [1]. One of the crucial processes in the CVD method is hydrogen desorption. The hydrogen desorption promoted by the rapid temperature rise on a Si surface after light pulse irradiation is known as laser-induced thermal desorption (LITD). In the laser CVD growth of a uniform film, spatial uniformity of coverage and the orientation of H-Si bonds are important. However, because LITD is an indirect process, the spatial distribution changes dramatically as a function of the power density, wavelength, and duration of the incident light pulse [2,3]. Thus, the spatial distribution of the hydrogen atoms with the scale of pulse spot size is especially crucial for quality of the deposited film.

In order to observe a spatial distribution of hydrogen species on a Si surface, surface-sensitive microscopy is necessary. However, few of the conventional methods are effective. A scanning tunneling microscope (STM) can show the spatial distribution of hydrogen atoms, but it is difficult to distinguish between the bonding states with the substrate. A scanning type microscope using electron stimulated desorption (ESD) can also show the spatial distribution of hydrogen atoms [4]. With this method, hydrogen atoms on a Si surface are desorbed by ESD; they can then be detected by a time of flight technique. Using this method, a clear lithographed pattern of hydrogen on a Si surface was observed.

However, it is not only a destructive method but it also is difficult to analyze the species. Conventional vibrational microscopy such as IR and Raman also lack surface sensitivity. Thus, a new method for observing the spatial distribution of hydrogen molecules on a Si surface has to be established.

In this study, by using the sum frequency generation (SFG) microscopy as a new surface sensitive vibrational microscopy [5-9], we have observed a hydrogen terminated Si(111)1×1 surface after pump IR light irradiation. As the result, we found that there were boundary areas, where the SFG signals were modified. In order to analyze the boundary area, we heated the Si surface at 711K, and then observed SFG spectra at room temperature. We also analyzed the modulation of SFG spectra by calculating dipole-dipole interaction by using coherent potential approximation (CPA) method.

2. EXPERIMENTAL AND CALCULATION

The H-Si(111) 1×1 surface was prepared by a well-known wet chemical etching procedure [10]. Pieces of n-type Si(111) wafers with resistivity $\rho \sim 5 \Omega\text{cm}$ were etched by a few cycles of dipping in a hot solution of concentrated 97% H_2SO_4 : 30% $\text{H}_2\text{O}_2 = 4:1$ for 5 min, then in 50% hydrofluoric acid for 3 min, and finally dipping in 40% ammonium fluoride solution for 3 min.

The optical system for taking SFG spectra and intensity images under UHV conditions is already reported elsewhere [6-9]. In the system, we used doubled frequency output from a mode-locked Nd^{3+} :YAG laser as the visible light at wavelength 532 nm, and output ($\sim 4.8 \mu\text{m}$) from an optical parametric generator and amplifier system (OPG/OPA) as the wavelength-tunable infrared light (IR probe light). The spectral bandwidth of the IR probe light was $\sim 3 \text{ cm}^{-1}$. The pulse energies of the IR probe and visible light beams were $\sim 100 \mu\text{J/pulse}$ and $\sim 25 \mu\text{J/pulse}$, respectively.

The incident visible light was passed through a $\lambda/2$ plate, a Glan polarizer, a bandpass filter with a center wavelength of 532 nm, a lens with focal length $f=300 \text{ mm}$, and the CaF_2 window of the UHV chamber. The IR probe light was focused by a CaF_2 lens with a focal length of 300 mm. The angles of the incident visible and IR probe light beams were $\sim 45^\circ$ and $\sim 60^\circ$, respectively.

The SFG light from the sample in the reflective direction was first passed through the glass window of the chamber and dichroic filters to block the incident visible light, and then introduced into a long-distance Cassegrain-type microscope (Quester QM-1). The microscope was equipped with a time-gated image-intensified charge-coupled device (CCD) camera (Hamamatsu PMA-100-H) for accumulating the SFG signals. With this long-distance microscope, the image of an object 0.5 m away can be focused on the detector plane with a resolution of $\sim 3 \mu\text{m}$. The microscope was also equipped with band-pass filters with center wavelengths of 490 nm for SFG microscopy. The polarizations of the SFG, visible, and IR light were all, p, and p, respectively. The integration time for taking SFG intensity images was 500 seconds. It was confirmed that luminescence signals were very weak under these measurement conditions.

In order to promote hydrogen desorption, the Si surface was irradiated with IR light pulses (wavelength: 1064 nm, pulse duration: $\sim 6 \mu\text{s}$, repetition rate: 10 Hz, pulse energy: 6~12 mJ/pulse, focus size: $\sim 0.1 \text{ mm}$) from a Nd^{3+} : YAG laser.

For SFG spectroscopy, the SFG light was passed through a double monochromator, and detected by a photomultiplier and a gated integrator [8]. The polarizations of the SFG, visible, and IR light were s, s, and p, respectively. The peaks attributed to the Si-H stretching vibration in the SFG spectra were fitted using the equation

$$\chi^{SFG} = \chi^{NR} e^{i\phi} + \frac{\chi_v}{\omega - \omega_v + i\gamma}. \quad (1)$$

Here χ^{NR} , χ_v , ϕ , ω_v , and γ are nonlinear susceptibility, total hyperpolarizability of the Si-H molecules, phase difference between the resonant and non-resonant terms, the resonant frequency, and the damping constant of the resonant mode, respectively [11]. In order to reduce hydrogen coverage, the sample was directly heated by a DC current in it. After heated in several seconds, the sample was cooled down to RT and SFG spectrum was taken. The heating temperatures were calibrated from I-V curve measured in this Si(111) sample [12].

A simulation of the dipole-dipole interaction using the coherent potential approximation (CPA) method was developed by Persson and Ryberg [13]. The calculation of nonlinear susceptibility based on the CPA method has been reported by Backus and Bonn[14], and Cho, Hess, and Bonn[15]. The calculated susceptibility well described an experimental SFG spectrum. We calculated the nonlinear susceptibility using their method [16].

3. RESULTS AND DISCUSSION

Figure 1(a) depicts a schematic diagram of a H-Si(111)1×1 surface after pump IR light irradiation. Pump IR light irradiated the surface with circular arch pattern as shown in Fig. 1(a). The non-irradiated areas on the surface were terminated by hydrogen. On the other hands, at the areas irradiated by the pump light, the light beam gave rise to temperature increase, and then hydrogen desorbed [6,9]. Thus, the dangling bonds were generated at the irradiated areas.

Figure 1 (b) shows a SFG image of the Si surface after pump IR light irradiation with probe IR light of $\sim 2019\text{ cm}^{-1}$. The image represents non-resonant vibrational image, since the resonant frequency of Si-H stretching vibration is 2083.7 cm^{-1} [10]. In the image, strong non-resonant SFG signals were emitted from pump IR light irradiated areas. We suggest that the signals may have been enhanced by an electronic transition related to surface electronic levels of the dangling bonds [6,9].

Figure 1(c) represents that SFG images of the same surface with the IR probe light of $\sim 2084\text{ cm}^{-1}$. Resonant SFG signals with the Si-H stretching vibration appeared at non-irradiated areas in the image, while non-resonant signals also appeared at the irradiated areas. Moreover, boundary areas observed between irradiated and non-irradiated areas. Both signals were weak at the boundary areas. This represents that at the boundary areas, hydrogen atoms were still adsorbed but the signals resonance with Si-H vibration were also weak.

Pump IR light irradiation gave rise to temperature increase, and then hydrogen desorbed. However, the boundary areas were at edges of the spatial distribution of IR light intensity, so that the temperature dose not sufficiently increase for activation of hydrogen desorption on the surface. We assumed that the low temperature was crucial of the modulation of SFG signals at the boundary areas. Thus, in order to verify the assumption, we investigated how SFG signal modified with the coverage reduction by heating with low temperature at 711K, slightly above activation temperature of hydrogen desorption [8].

As the first step, we simulated dipole-dipole interaction of Si-H oscillators by using the CPA method, and the peak modification as a function of coverage. Figure 2(a) shows the calculated SFG spectra at each coverage [16]. With the reduction from 1 to 0.45ML, the peak intensity reduced, and the peak position also shifted to red side. The peak width was not increased dramatically. Figure 2(b) shows the experimental SFG spectra with coverage reduction during the heating of the sample at 711 K. From 1 to 0.48 ML, peak position was red sifted, and the shift was qualitatively consistent with the theoretical peak shift in Fig. 2(a). Thus, the peak shift was modified by dipole-dipole interaction. However, the peak width broadened far wider than the theoretical one. We suggest that the broadening was due to local structural defects and/or influence of neighbor dangling bonds [16]. We also suggest that not only the peak intensity reduction as a function of hydrogen deficiency but also the broadening and peak shift were origins of the weak resonant SFG signals at the boundary areas in Fig. 1(a).

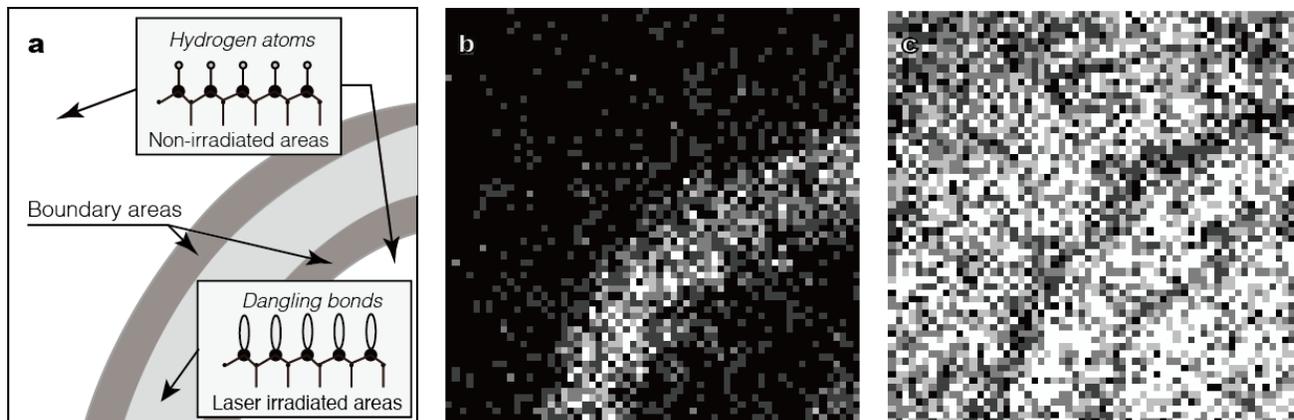


Figure 1. SFG microscopic images of a H-Si(111)1×1 surface after pump IR light irradiation. (a) a schematic diagram of the surface irradiated with circular arch by pump IR light. There were boundary areas at the edges of irradiated areas. (b) SFG images of the irradiated surface with probe light of $\sim 2019\text{ cm}^{-1}$. (c) SFG images of the same surface with probe light of 2084 cm^{-1} . Image scale is $200 \times 200\ \mu\text{m}^2$.

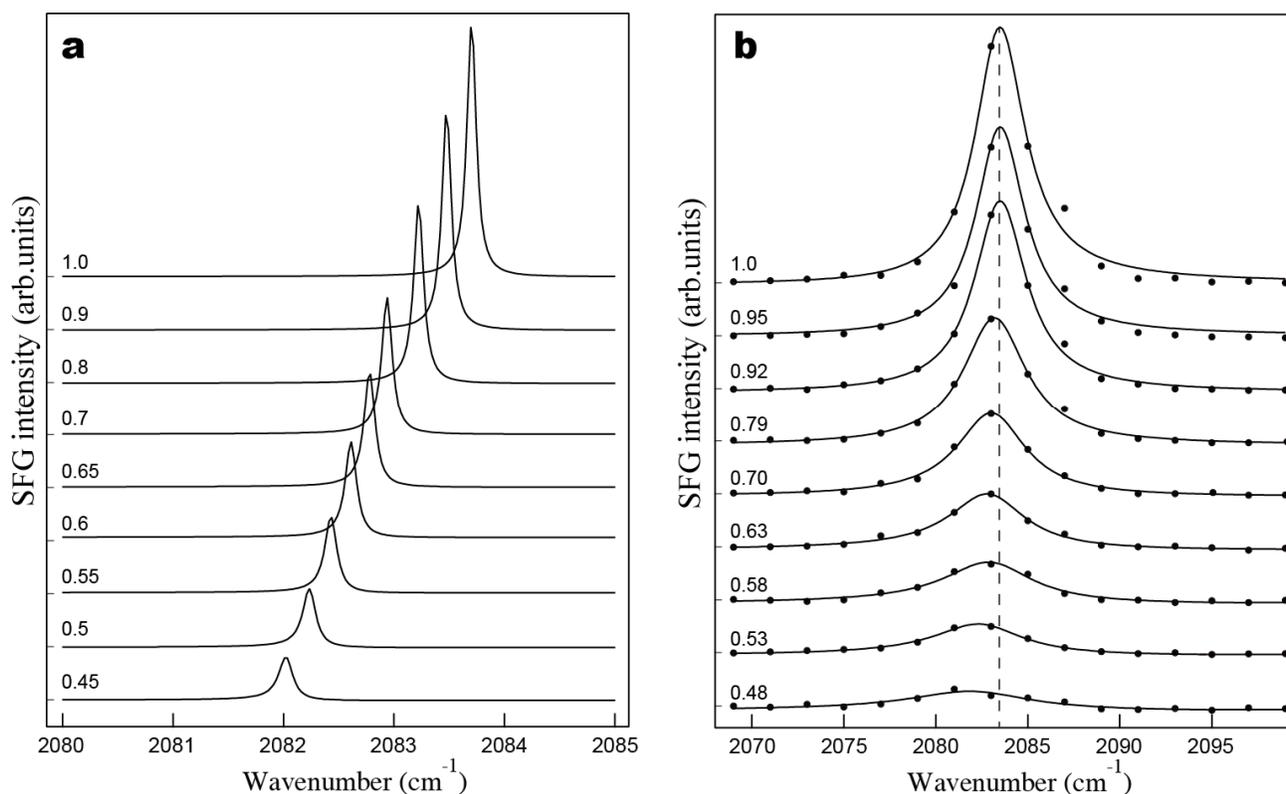


Figure 2. (a) Theoretical and (b) experimental SFG spectra as a function of the coverage. The horizontal axis represents the wavenumber of the IR probe light and the vertical axis shows the SFG intensity. Hydrogen coverage is denoted on the left side of each SFG spectrum. The solid curves shown in (a) represent the SFG intensity calculated by the CPA method. The solid dots in (b) represent the observed SFG intensity and the curve represents the fitting by eq. (1). The SFG spectra were observed at room temperature after heating the sample to 722K. The polarizations of SFG, visible, and IR light were s, s, and p, respectively. The wavelength of the visible light was 532.1nm. The dashed line represents guide to eyes.

4. CONCLUSIONS

In order to investigate the fundamental processes of laser CVD, especially hydrogen desorption process from a Si surface, we observed a SFG microscopic image of the H-Si(111)1×1 surface after pump IR light irradiation. As the results, non-resonant SFG signals appeared at the irradiated area, while resonant SFG signals attributed to Si-H stretching vibration disappeared at the irradiated area. We also found that there were boundary areas that both SFG signals were weak. For understanding the modification of the SFG signals at the boundary areas, we heated the Si surface at 711K, and then observed SFG spectra as a function of hydrogen coverage. As the results, the peak position shifted toward red side. The shift was well consistent with that calculated by the CPA method, and thus it corresponded to dipole-dipole interaction. On the other hand, the peak width was also broadened with the coverage reduction, but the widths at low coverages were far broader than the theoretical ones.

REFERENCES

- [1] M. Tsuji, M. Sakmoto, H. Obase, Y. Nishimura, "Direct Oxidation of Silicon Substrates Using ArF Excimer Laser Photolysis of N₂O at Low Temperatures," *Chem. Lett* **19**(6), 863-866 (1990).
- [2] Y. Miyauchi, H. Sano, and G. Mizutani, "Optical second harmonic intensity images of hydrogen deficiency on H-Si(111) surfaces," *e-J. Surf. Sci. Nanotech.* **4**, 105-109 (2006).
- [3] Y. Miyauchi, H. Sano, and G. Mizutani, "Numerical analysis of second harmonic intensity images of a H-Si(111) surface after UV light pulse irradiation," *Appl. Surf. Sci.* **255**, 3442 (2008).
- [4] K. Ishikawa, K. Ueda, M. Yoshimura, "New development of scanning-type microscope for two-dimensional hydrogen distribution using electron-stimulated desorption method," *Surf. Sci.* **433** 244-248 (1999).
- [5] M. Flörsheimer, C. Brillert, H. Fuchs, *Mater. Sci. Eng. C* **335**, 8-9 (1999). "Chemical imaging of interfaces by sum-frequency generation,"
- [6] Y. Miyauchi, H. Sano, J. Okada, H. Yamashita, and G. Mizutani, "Simultaneous optical second harmonic and sum frequency intensity image observation of hydrogen deficiency on a H-Si(1 1 1) 1 × 1 surface after IR light pulse irradiation," *Surf. Sci.* **603**, 2972-2977 (2009).
- [7] K. T. T. Hien, Y. Miyauchi, G. Mizutani, "Construction of a pump-probe system for observing time-resolved sum frequency images," *Surf. Int. Anal.* **42** (10-11), 1671-1674.
- [8] K. T. T. Hien, Y. Miyauchi, M. Kikuchi, G. Mizutani, "Hydrogen desorption from a Si(111)1×1 surface studied by sum frequency generation spectroscopy and microscopy," *Surf. Int. Anal.* **44** (6), 662-665 (2012).
- [9] Y. Miyauchi, "Second-Order Nonlinear Optical Microscopy of a H-Si(111)1 x 1 Surface in Ultra-High Vacuum Conditions," *PHys. Res. Int.* **2012**, 576547-1-14 (2012).
- [10] G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Raghavachari, *Appl. Phys. Lett.* "Ideal hydrogen termination of the Si (111) surface," *Appl. Phys. Lett.* **56**, 656-659 (1990).
- [11] S. Ye, T. Saito, S. Nihonyanagi, K. Uosaki, P. B. Miranda, D. Kim, Y. R. Shen, "Stability of the Si-H bond on the hydrogen-terminated Si(1 1 1) surface studied by sum frequency generation," *Surf. Sci.* **476**, 121-128 (2001).
- [12] A. Ichimiya, and S. Mizuno, "RHEED and AES Study of Si(111) $\sqrt{3}\times\sqrt{3}$ -R30° Structure Induced by Adsorption of Impurity Gases," *ISIJ international* **29** (7), 576. (1989).
- [13] B. N. J. Persson and R. Ryberg, "Vibrational interaction between molecules adsorbed on a metal surface: The dipole-dipole interaction," *Phys. Rev. B* **24**, 6954-6970 (1981).
- [14] E. H. G. Backus, M. Bonn, "A quantitative comparison between reflection absorption infrared and sum-frequency generation spectroscopy," *Chem. Phys. Lett.* **412** (1-3), 152-157 (2005).
- [15] M. Cho, C. Hess, and M. Bonn, "Lateral interactions between adsorbed molecules: Investigations of CO on Ru(001) using nonlinear surface vibrational spectroscopies," *Phys. Rev. B.* **65**, 205423-205433 (2002).
- [16] Y. Miyauchi, K. T. T. Hien, and G. Mizutani, "Si-H vibrational mode on a H-Si(111)1×1 surface with hydrogen deficiency," *Surf. Sci.* (on Publish).

ACKNOWLEDGEMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research (C) (#23540363) and Grant-in-Aid for Young Scientists (B) (#23740238) of Japan Society for the Promotion of Science.