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Description	

Pump-Probe Time-Resolved Sum Frequency Spectroscopy of the H-Si(111)1×1 surface

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We have performed time-resolved sum frequency (SF) spectroscopy of a H-Si(111)1×1 surface excited by pump visible pulses with the pulse width of ~ 30 ps in ultra-high vacuum. Broad non-resonant SF signals as a function of the infrared wavenumber increased soon after the pump light irradiation, and decreased in ~ 1 ns. A remarkable change in the intensity and the shape of the peak at 2085 cm^{-1} attributed to the Si-H stretching vibration is observed as a function of the delay time. After the pump light irradiation, the symmetric peak in the SF spectra disappeared at ~ 60 ps and recovered gradually with an asymmetric shape. [DOI: 10.1380/ejssnt.2010.89]

Keywords: Sum frequency generation; Pump-probe technique; Hydrogen; Silicon; Vibration

I. INTRODUCTION

Hydrogen desorption from a hydrogenated Si surface promoted by visible or UV light pulses is expected to be utilized in the optical CVD growth technique. It occurs because the excited electron-hole (e-h) pairs and temperature increase due to the pump light pulses irradiation modify the electronic and bonding states of hydrogen atoms on the surface. For instance, Timoshenko and his co-workers studied the photo-thermal desorption of hydrogen from a H-Si(100) surface induced by XeCl laser irradiation at the photon energy of 4.0 eV. They proposed that the local electronic excitation induces the annihilation of Si dangling bonds and assists the desorption of a neighboring H atom [1]. Ye and his co-workers found that the number of monohydrides on a H-Si(111) surface decreases under the irradiation by 2.33 eV light due to a photo-electrochemical reaction in the atmospheric condition [2].

Guyot-Sionnest studied a modification of the Si-H stretching vibration due to visible light irradiation by measuring time resolved sum frequency spectra [3]. This work is important because the modification of the surface vibration induced by light pulses is the central issue of the photo-thermal desorption. As the pump light, he used visible light with photon energy 2.33 eV, pulse width 20 ps, and fluence 0-50 mJ/cm². In the result, he observed a slight reduction of the lifetime of the Si-H stretching mode for the carrier densities above $0.9 \times 10^{20}\text{ cm}^{-3}$. He also found that weak anharmonic coupling with thermally excited surface optical phonon modulates the SF intensity resonant to the Si-H stretching vibration.

We are interested in the modulation of the Si-H stretching vibration by pump light irradiation with the fluence larger than $\sim 100\text{ mJ/cm}^2$, while Guyot-Sionnest used the

power of $\sim 50\text{ mJ/cm}^2$. The modulation due to such a strong power is expected to be different from that excited by the weaker power light irradiation, since laser fluence higher than $\sim 100\text{ mJ/cm}^2$ may cause not only Auger recombination but also plasmon-phonon-assisted recombination (PPAR) of the excited carriers [4].

In this study, we used a pump-probe technique and measured time resolved sum frequency (SF) spectra of the H-Si(111)1×1 surface in ultra high vacuum (UHV) as a function of the probe delay time. We used pump visible light with the photon energy 2.33 eV and the fluence of 120 mJ/cm^2 . Sum frequency generation (SFG) is one of the lowest-order nonlinear optical processes. SFG occurs in media without inversion symmetry and have a high sensitivity to the surface vibration [5]. SFG is a useful tool for studying the Si-H bonds [2, 6] and identifying hydride species [7] on a Si surface.

In the result of this study, non-resonant SF signal increased soon after the pump light irradiation, and then decreased in ~ 1 ns. The non-resonant signal is suggested to be due to the electric field generated by the excited electron-hole pairs. We also found that the shape of the Si-H stretching vibrational peak at 2085 cm^{-1} became asymmetric at the probe delay time larger than 100 ps. The obtained results and the related information are planned to be utilized in interpreting the images of the H-Si(111) surface by our pump-probe sum frequency microscopy in our future work.

II. EXPERIMENT

In our pump-probe SF spectroscopic system, we used a doubled frequency output with photon energy 2.33 eV of a mode-locked Nd³⁺: YAG laser operating at the repetition rate of 10 Hz and pulse width ~ 30 ps as the visible light, and an output with photon energy 0.26 eV from an optical parametric generator and amplifier system (OPG/OPA) driven by the same YAG laser as the wavelength-tunable

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infrared light. The time resolution of our experiment is thus ~ 30 ps. The visible light beam was divided into two beams and they were used as pump and probe beams. The probe visible light was passed through a $\lambda/2$ plate, a Glan polarizer, a bandpass filter with the center photon energy 2.33 eV, a lens with focal length $f = 250$ mm, and the CaF_2 window of an UHV chamber. The IR probe light was focused by a CaF_2 lens with focal length of 300 mm. The pulse energies of the probe visible and IR light were 20 and 120 $\mu\text{J}/\text{pulse}$, respectively. Incident angles of the probe visible and IR light were 38° and 52° , respectively. The SF light from the sample generated in the reflective direction was passed through the glass window of the chamber and dichroic filters to block the incident visible light. It was then introduced into a monochromator and was finally detected by a photo-multiplier. The SF, visible and IR light were all p -polarized. We measured the SF intensity spectrum of the reference GaAs and the H-Si(111) surface alternately, and normalized the latter by the former. In the result of this paper, we use the wavenumber unit (cm^{-1}) in designating the infrared light because this unit is more popular in vibrational spectroscopies than the photon energy (eV).

The power of the pump visible light was 120 $\mu\text{J}/\text{pulse}$ and the fluence on the sample surface was 120 $\text{mJ}/\text{cm}^2\text{-pulse}$. The pump light was nearly p -polarized and had the incident angle of 68.5° . The optical delay of the probe visible and infrared pulses was controlled by an automatic linear stage with the positioning accuracy of $\sim 5\mu\text{m}$. The timing of the pump and probe light was adjusted by observing the SFG of the pump visible and probe IR light from the sample with its surface tilted differently from the final SFG measurement. In the final SFG measurement this SF light did not hit the detector because it traveled off the optical path by the angle of $\sim 30^\circ$. No damage was observed in the linear microphotograph of the sample surface after the pump light irradiation. The invariance of the Si-H vibrational peak in the SF spectra before and after the pump-probe measurement indicated the absence of the change of hydrogen coverage and disorder of the Si-H bonds during the strong pump light irradiation. The power of the probe visible light was ~ 50 times smaller than the power of the pump light. The power of the probe IR light was smaller than that of the pump light. The photon energy of the probe IR light ~ 0.26 eV was far smaller than the band gap of Si ~ 1.1 eV, and thus the IR light could not excite e-h carriers. Hence, the effect of the probe beams on the Si surface could be disregarded in this measurement.

The H-Si(111) 1×1 surface was prepared by a wet chemical etching procedure. N -type Si(111) wafers with resistivity $\rho = 200\text{-}240 \Omega\text{cm}$ 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 dipped in 40% ammonium fluoride solution for 3 min. This chemical treatment is known to produce a well defined monohydride terminated Si(111) 1×1 surface [8]. After this treatment, the sample was immediately introduced into UHV with the pressure $\sim 10^{-8}$ Pa at room temperature. A 1×1 structure of the H-Si(111) surface thus prepared was confirmed through a low energy electron diffraction (LEED) measurement.

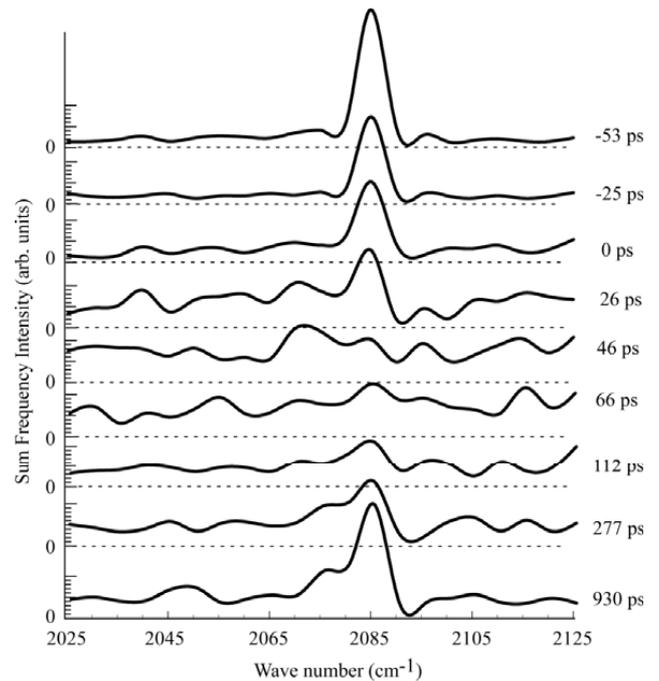


FIG. 1: SF intensity spectra of a H-Si(111) surface at several probe delay times with respect to the pump visible pulses of photon energy 2.33 eV. The delay times are indicated on the right hand side of each SF intensity spectrum.

III. RESULTS AND DISCUSSION

Before the pump light irradiation, we confirmed that there was a sharp peak at 2085 cm^{-1} attributed to the stretching vibration of the monohydride species in the SF spectrum of the sample (not shown). Then we studied the change of non-resonant and resonant SF signals as a function of the probe delay time. The monitoring of the non-resonant SF component is as important as the resonant one for an accurate analysis, since the SF intensity I_{SFG} is proportional to the square of the absolute value of the nonlinear susceptibility $|\chi^{(2)}|^2$ as

$$I_{\text{SFG}} \sim |\chi^{(2)}|^2 = |\chi_{\text{NR}}^{(2)} + \frac{A_0}{\omega - \omega_0 + i\Gamma_0}|^2. \quad (1)$$

Here, χ_{NR} is the non-resonant nonlinear susceptibility, and A_0 , ω_0 and Γ_0 are the strength, resonant frequency and damping constant of the resonant mode, respectively [2].

Figure 1 shows the SF spectra at several delay times. The delay time is indicated on the right hand side of each SF spectrum. Before the pump light irradiation (-53 ps), a symmetric peak is seen at 2085 cm^{-1} attributed to the Si-H stretching vibration. After the pump light irradiation, three significant modifications are observed in the SF spectra. First, the non-resonant signals jump up at ~ 0 ps, and then decreases gradually with the life time of ~ 1 ns. Second, from 0 ps to 66 ps, the peak rapidly decreases along with the increase of the non-resonant SF signal background. From 66 ps to 930 ps, the peak recovers gradually. Third, at 930 ps, the peak has a remarkably asymmetric lineshape. All these features except the rapid decrease of the resonant peak from 0 to 66 ps were not

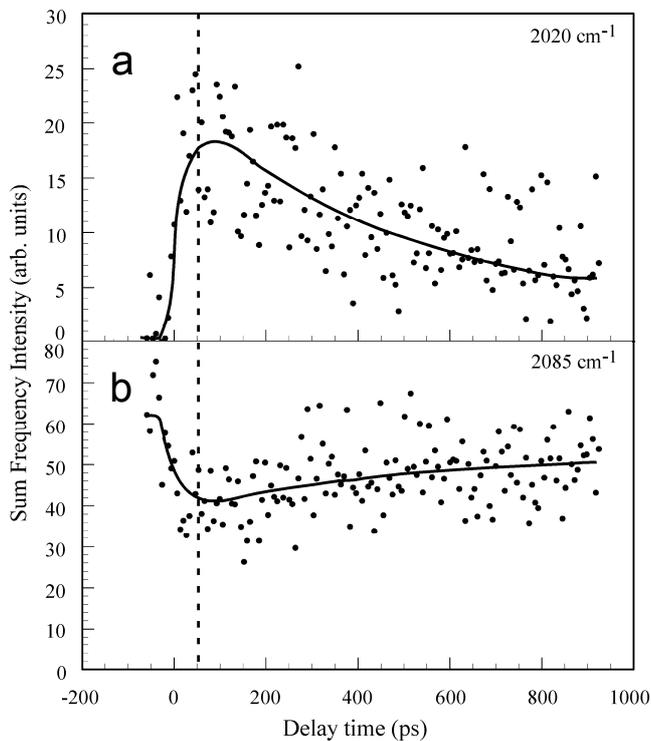


FIG. 2: SF intensity as a function of the delay time of the probe visible and IR pulses with respect to the pump visible pulses. The IR light wavenumbers are (a) 2020 cm^{-1} and (b) 2085 cm^{-1} . Solid curves represent a guide to the eye.

observed by Guyot-Sionnest [3]. We discuss the origins of these three modifications below.

In order to analyze the change of the non-resonant SF signal, we measured the SF intensity as a function of the probe delay time with the IR wavenumber of 2020 cm^{-1} as shown in Fig. 2(a). The solid curve represents a guide to the eye. This IR probe wavenumber is in off-resonance of the surface Si-H vibrational frequency. In Fig. 2(a) the signal jumps up at ~ 0 ps and then decreases gradually with the life time of ~ 1 ns.

The density of the excited e-h pairs by the pump pulses is estimated as $\sim 3 \times 10^{21}\text{ cm}^{-3} \cdot (\text{pulse})^{-1}$, and it is high enough to make a plasma state. Thus, as one candidate origin of the enhancement of the non-resonant SF signal at ~ 0 ps, the e-h plasma may modify the dielectric constant of the Si substrate at the probe IR light frequency [3]. It has been reported that the modulation of the dielectric constant for IR light enhances the SF signal [3]. However, the life time of the plasma should be smaller than ~ 100 ps due to the Auger recombination or faster processes like PPAR. This life time is not compatible with the observed life time of the signal. On the other hand, the modulation of the dielectric constant for visible and SF light by the plasma is negligible [3, 9].

As another candidate, the nonlinear susceptibility $\chi_{\text{NR}}^{(2)}$ in Eq. (1) may have been enhanced by the electric field accompanying the e-h pairs excited at ~ 0 ps, due to the electric field induced sum frequency generation [10]. After that the susceptibility $\chi_{\text{NR}}^{(2)}$ may have decreased due to the relaxation of the e-h pairs. As we mentioned above, the

number of the excited carriers reduces via Auger recombination or PPAR process in ~ 100 ps, but a small amount of carriers should remain after the recombination. The remaining carriers diffuse slowly with the life time of ~ 1 ns according to our calculation. The life time is consistent with the observed life time of the signal in Figs. 2(a). We also note that no background SF signal was observed for the *ssp* polarization (*s*-polarized SFG, *s*-polarized visible, and *p*-polarized IR) combination in a separate experiment (not shown). This result suggests that the non-resonant background signal observed for the *ppp* polarization combination in Fig. 2(a) does not originate from any trivial optical process such as scattering due to surface damages.

As the third candidate origin, we do not deny the effect of the temperature rise on the Si surface. Guyot-Sionnest pointed out that the surface temperature rises immediately after the visible excitation and is kept constant within the timescale of 500 ps. The high density phonons excited in the quasi-thermal equilibrium may induce some broad second-order nonlinearity. However, the non-resonant signal was not reported with the laser power used by Guyoto-Sionest [3]. Thus the non-resonant signal observed in this work may be a high fluence effect by the visible excitation light.

Figure 2(b) shows the SF signal as a function of the delay time with the IR wavenumber of 2085 cm^{-1} . The SF signal contains both the resonant and non-resonant contribution. Contrary to the change of the non-resonant SF signal, the signal drops down to a half of its initial value at ~ 0 ps and slowly recovers with the life time of ~ 1 ns. This result indicates that the Si-H stretching vibration is modulated strongly after the pump light irradiation.

In our separate calculation, the surface temperature reaches ~ 500 K at 20 ps after the pump light irradiation. With the temperature increase, the damping constant Γ of the resonant term in Eq. (1) may increase due to the weak anharmonic coupling between the Si-H vibration and the optical phonon of $\sim 200\text{ cm}^{-1}$ [3]. Thus, the peak of the Si-H stretching vibration is considered to drop due to the broadening. In addition, since the surface temperature is over 300 K, the strong anharmonic coupling with the bending mode may also modify the Si-H stretching vibration [11]. The peak of the Si-H vibration disappears at 46 ps in Fig. 1, while in the work of Guyoto-Sionest [3] the signal was more than a half of the initial intensity at every delay time after the light pulse irradiation. Indeed the stronger excitation gives rise to more severe modification of the Si-H vibration. Unfortunately, however, we cannot estimate the change of the damping constant Γ and the peak shift after the pump light irradiation due to the insufficient signal to noise ratio in our results.

The asymmetric lineshape at 930 ps in Fig. 1 could originate from a non-uniform temperature drop on the surface. However, as pointed out by Guyot-Sionnest [3] and in our previous theoretical work [12], the temperature drop should be very slow after the temperature jump to 500 K at 20 ps. For instance, the temperature is calculated to be still at 483 K at 500 ps. The Si surface is rather in quasi-thermal equilibrium up to 1 ns, and the peak recovery and the change of the lineshape due to the temperature change is not expected. In order to understand the recovery of the peak and the origin of the asymmetric lineshape, further theoretical study is necessary.

IV. CONCLUSION

In this study, we have performed time resolved sum frequency spectroscopy of a H-Si(111)1×1 surface in UHV conditions excited by visible pump pulses with the fluence of 120 mJ/cm². Non-resonant SF signal increased step-wise after the pump light irradiation, and then decreased on a time scale of ∼1 ns, partly due to the excitation and relaxation of the electron-hole pairs. We also found that the symmetric SF peak of the monohydride Si-H stretch-

ing disappeared at 60 ps and then recovered slowly with an asymmetric lineshape.

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