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Numerical analysis of Second harmonic intensity images of H-Si(111) surface after UV light pulse irradiation

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Abstract

By using laser induced thermal desorption (LITD) model, we have calculated spatial distributions of hydrogen deficiency and melting on a H-Si(111) surface after UV light pulse irradiation. We compared the calculated results with the observed second harmonic response from the Si surface after the UV light pulse irradiation with pulse duration of 30ps and wavelength of 355nm. The calculated profiles of hydrogen deficiency reproduced the spatial profiles of the observed SH light intensity from the Si surface very well. The calculated profiles of surface

melting were interpreted to be consistent with the spatial profiles of the observed SH light intensity from the bulk Si. Furthermore, the simulation clarified that the hydrogen desorption and the surface melting occur nearly simultaneously. The result also indicated that the surface melting did not give rise to the reduction of pre-exponential factor or activation energy of hydrogen desorption from the H-Si(111) surface. These results were consistent with the study of the spatially integrated H desorption yield from H-Si(111) by Koehler and George (Surf. Sci. **248** 158 (1991)).

PACS codes

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Keywords

optical second harmonic generation, laser induced thermal desorption, hydrogen , Silicon, surface melting

Introduction

Hydrogen terminated Si surface is a model system of chemical adsorption on a surface of semiconductor and the related bonding states [1]. The chemical reaction [2] on it has been studied well. Especially, the process of hydrogen desorption from a Si surface irradiated by light pulses is one of the most important topics of study concerning optical CVD growth and laser ablation.

Several different mechanisms of desorption processes of hydrogen from H terminated Si surface have been identified. One of them is photo-stimulated desorption [3]. In this process, incident photons of photon energy over 7eV directly break the Si-H bonds by electronic excitation. On the other hand, if the photon energy is below 7eV, laser induced thermal desorption (LITD) is the most dominant process [4, 5]. Recently, a new desorption process has been found on a Si(111) surface irradiated by IR light pulses with the energy of 0.26eV from a free electron laser (FEL), and the process could not be explained either by the PSD or LITD process [6]. Despite these vigorous studies, the detailed mechanisms of H desorption from a H-Si(111) surface are still not systematically understood.

Koehler and George investigated the influence of the surface melting on the hydrogen desorption on a Si(111) surface irradiated by visible light pulses [4]. Although the surface melting was expected to influence the process of hydrogen desorption, they did not find significant

correlation. We feel that this surprising result is worth checking by using more sophisticated experimental techniques. In this paper we pay attention to the point that they only detected desorbed H_2 molecules and could not check the spatial distribution of hydrogen deficiency and surface melting directly.

The efficiency of hydrogen desorption and surface melting on the Si surface should depend on the distribution of the light pulse intensity. In the lowest order approximation, these two phenomena should occur independently of each other, and their spatial distributions should not be correlated. However, if some interaction exists between the hydrogen desorption and the surface melting, such as a change of the activation energy of desorption, the desorption distribution should be influenced by the surface melting. In order to study this correlation, the analysis of the spatial distributions of the two phenomena is required.

In our previous work, we observed second harmonic intensity images of H-Si(111) surface irradiated by UV light pulses [7]. SH microscopy is a useful technique for observing the spatial distribution of hydrogen deficiency on the Si (111) surface quantitatively in an ultra high vacuum condition. The advantage of this SHM measurement is that we can observe the distributions of SH intensity from Si surface and bulk Si separately. The distributions of SH intensity from surface and bulk Si were interpreted to be those of hydrogen deficiency and surface melting, respectively. Hence we can judge whether there was any interaction between the hydrogen desorption and the

melting in the two-dimensional space, by analyzing this experimental result numerically.

In this study, the observed spatial profiles of the SH intensity of the surface and bulk Si(111) were compared with the calculated profiles of the hydrogen deficiency and surface melting by using LITD model. The spatially observed profiles of the SH light intensity from the bulk Si was consistent with the calculated profiles of the surface melting. This result indicates that LITD model is feasible for our system. The profiles of the SH light intensity from the surface was consistent with the calculated profiles of the hydrogen deficiency. The result again showed that the surface melting had no detectable influence on the process of hydrogen desorption from the Si surface with nearly 1ML coverage.

Calculation

In order to discuss the parameters for calculation, let us first review our previous experiment. A H-Si(111)1×1 surface was prepared by chemical treatment using NH_4F solution, and was immediately introduced into an UHV chamber. In order to induce desorption of the hydrogen atoms, the H-Si(111) surface was irradiated with the third harmonic frequency output from a mode-locked Nd^{3+}: YAG laser with a wavelength of 355nm, pulse duration of 30 ps, repetition rate of 10 Hz, pulse energy of 26~103μJ/pulse, spot size of ~1.9mm, p-polarization and the number of irradiating pulse of ~50. Enhanced SH light was observed at the area irradiated with the UV light pulses on the H-Si(111) surface [7].

Next we exposed the sample to ~70L of hydrogen, and observed SH intensity images of the Si surface again. The SH signals became weak but some SH signals remained. This remaining SH signal is interpreted to originate from the bulk Si near the interface between the amorphous Si layer formed by surface melting and the Si crystalline layer [8]. On the other hand, the decrease of the SH signals by hydrogen exposure attributed to the surface is a function of the number of dangling bonds on the surface. Hereafter we call these two types of SH signals as bulk SH (BSH) and surface SH (SSH) signals. The SSH intensity images were obtained numerically by subtracting the SH intensity images of the exposed Si substrate from those of the non-exposed Si surface.

The calculation by using the laser induced thermal desorption (LITD) model was based on the paper by Koehler and George [4] and an original source code was programmed. In order to estimate the temperature of the Si surface, three dimensional thermal diffusion was simulated by the finite difference method (called "explicit method"). The equation of thermal diffusion is:

$$\frac{\partial T}{\partial t} = D\nabla^2 T + Q \tag{1}$$

where T is the temperature [K], t is the time [s], D is the thermal diffusivity [cm^2/s], and Q is the source term[K/s]. The source term is defined as:

$$Q_{i,j,k}^{n} = \frac{E_{i,j,k}^{n}}{\rho C_P} \tag{2}$$

where E is the laser power absorbed per unit volume of Si [GW/cm^2], ρ is the density of the material [g/cm^3], and C_p is the heat capacity [J/gK]. The subscripts i, j, and k are the step number in z, x, and y directions, respectively, and n is the number of steps. The z direction is defined to be perpendicular to the surface and z is defined to increase in the direction from the surface into the bulk. The spatial distribution of the UV pulse energy is defined as in the Gaussian distribution:

$$E_{i,j,k}^{n} = \alpha(1-R)I_{0t}\exp(-\alpha\Delta z i)\exp(-(\frac{\Delta x^2}{2P_w^2}\cdot(j-j_c)^2 + \frac{\Delta y^2}{2P_w^2}\cdot(k-k_c)^2)) \tag{3}$$

where α is the absorption coefficient [cm^{-1}], and R is the optical reflectivity. The P_w^2 is the dispersion of the Gaussian distribution. The parameters j_c and k_c are the step numbers corresponding to the center position of the pulse spot in the x-y plane and Δx, Δy, and Δz are the step sizes in the directions of x, y and z, respectively. I_{ot} is the pulse intensity and is defined as:

$$I_{0t} = I_o \exp(-\frac{\Delta t^2}{2P_t^2} \cdot (n - n_c)^2) \tag{4}$$

where P_t^2 is the dispersion in the Gaussian distribution on the time axis. The parameter n_c is the step number at the peak time of the pulse.

The number of the spatial steps was 100 and the number of the time steps was 30000, and the solution was confirmed to converge. The initial surface temperature was assumed as 300K. The melting of Si bulk occurs at ~1684K [4, 9]. Thus, in the simulation, the upper limit of the temperature was 1684K, and the absorption coefficient, the reflectivity, the heat capacity, the thermal conductivity and the density changes occur at this temperature. The absorption coefficients of the material in the solid and liquid phases were set as 1.1×10^6[cm^{-1}] and 1×10^6[cm^{-1}] [10], respectively. The optical reflectivity of the material in the solid and liquid phases were $3.11\times10^{-1}+5.0\times10^{-5}\times(T-300)$ [11] and 0.73 [10], respectively. The other parameters were taken from the paper by Koehler and George [4].

The coverage change on the Si surface in the second order desorption kinetics is given by:

$$\frac{d\theta}{dt} = -\theta^2 \nu_d \exp(-E_d / RT_{surf}) \tag{5}$$

where θ is the coverage, E_d is the activation energy, R is the gas constant (8.31 J/molK), and T_{surf} is the temperature of the surface. Substituting the surface temperature as a function of time obtained by eq. (1) for T_{surf} in eq. (5), we obtained the time dependence of the coverage θ. The maximum surface density of the hydrogen atoms on Si(111) corresponding to ~1ML was assumed as 8×10^{14}

cm^{-2}. The activation energy E_d and the pre-exponential factor ν_d were set as 2.65eV and 12 cm^2/s, respectively. The wavenumber, the power, the spot size (FWHM), the pulse duration (FWHM) and the power of the UV light pulse were assumed to be 355 nm, 25~100 μJ/pulse, 294 μm, and 35.3 ps, respectively. The full width at half maximum (FWHM) of a Gaussian distribution is defined from the dispersion P^2 as:

$$FWHM = 2 \times P \times \sqrt{2\ln(2)} \quad (6).$$

The estimation of the focused spot size of the 355nm beam on the sample in the experiment was difficult, since the spot shape and size changed with each pulse irradiation. Thus, in the calculation, the spot size was adjusted so that the pulses of 25μJ/pulse caused the threshold surface melting.

There are several values of the activation energy, such as 2.40eV±0.1eV estimated by Reider et al. [12], 2.54eV estimated by Schulze et al. [13], and 2.65±0.17eV estimated by Koehler et al. [4, 14]. These activation energies were consistent with each other within the error ranges. Thus, we calculated the hydrogen deficiency for several activation energies in this error range.

Results and Discussion

The dotted curve in Fig. 1 shows the surface temperature at the center of the irradiating pulse spot as a function of time after UV light irradiation calculated by using LITD model. The power of UV light pulse was 50μJ/pulse and the pulse irradiates the sample at t=100ps. The dashed curve represents the power of the UV light. In Fig. 1, the surface temperature rises on and after t=100ps, reaches the melting point of bulk Si (1684K), and then drops down. It reaches the room temperature at t~700ps. From this curve, the heating and cooling rates are estimated to be $\sim 10^{13}$ and $\sim 10^{12}$[K/s], respectively.

The solid curve in Fig. 1 shows the hydrogen coverage as a function of time for E_d=2.65eV. In LITD process, the apparent threshold temperature of hydrogen desorption should be far higher than the β_1 peak (~800K) obtained in TPD [15]. In Fig 1, the threshold temperature of hydrogen desorption is the melting temperature of the Si bulk at 1684K and it is above the temperature of the surface melting at 1414K [16]. The two processes start almost simultaneously at t ~95ps in Fig. 1. Most of the hydrogen atoms cannot desorb before the surface melting occurs because the temperature rises too fast, even though the hydrogen atoms can desorb from the Si surface at ~800K in a more static condition. We note here that the absolute desorption rate depends sensitively on the activation energy, but the shapes of the time variation curves of the desorption were quite similar

between different activation energies (not shown).

Our calculation also showed that the threshold power of the UV light for hydrogen desorption is nearly equal to the threshold power for the surface melting. This indicates that the hydrogen desorption is accompanied by the surface melting on the Si surface after the UV light irradiation. Thus, the UV light pulse irradiation is suitable for investigating the correlation between the surface melting and the hydrogen desorption. In addition, since the absorption length of UV light in Si is shorter than those of IR and visible light, the desorption can be studied experimentally by using much smaller power of the incident light and hence with much smaller damage on the Si substrate.

Figure 2(a) shows the observed spatial profiles of the *bulk* SH (BSH) intensity after UV light irradiation with the power of 26, 46, 75 and 103μJ/pulse [7]. The horizontal axis represents the position on the Si substrate, and 0 μm corresponds to the center of the irradiating UV light spot. The vertical axis shows the BSH intensity. The vertical dashed guide lines at the positions of ±200μm are drawn in order to highlight the change of the area emitting the BSH signals.

At the power of 26μJ/pulse the BSH light emerges at the center, as it is seen in the top panel in Fig. 2(a). As the power of the UV light increases from the top to the bottom panels, the BSH signals increase and the areas emitting the BSH signals become wider. In the profiles of the BSH intensity for the UV power of 103μJ/pulse, the signals are seen with the width of ~420μm. Since

the BSH signals may be assigned to the interface between the amorphous and crystalline silicon, these profiles of the BSH signals may represent the profiles of the surface melting.

In order to analyze the BSH intensity distribution, the spatial profiles of the maximum surface temperature on the Si surface was calculated using LITD model for the UV light irradiation with the power of 25, 50, 75 and 100μJ/pulse as they are shown in Fig. 2(b). The horizontal and the vertical axes represent the position on the Si surface and the surface temperature, respectively. The horizontal dashed lines in Fig. 2(b) represent the surface melting temperature at 1414K. The surface melts when the temperature is above this line [16].

For the power of 25μJ/pulse as shown in the top panel of Fig. 2(b), the width of the area in the liquid state is ~150μm. In Fig. 2(b) the area in the liquid state becomes wider with the increase of the power of UV light. For the power of 100μJ/pulse, surface melting occurs in the width of ~420μm. We see that the profiles of the BSH signals in Fig 2(a) and the surface melting in (b) match each other for each power of the irradiating UV light. Consequently, the parameters assumed in solving eq. (1)~(4) have turned out to be appropriate.

Figure 3(a) shows the observed spatial profiles of *surface* SH (SSH) intensity generated from the H-Si(111) surfaces irradiated with UV light pulses of the power of 26, 46, 75 and 103μJ/pulse [7]. In Fig. 3(a), the SSH light is observable above the power of 26μJ/pulse. As the power increases, the area emitting SSH signals becomes wider and the SH intensity becomes stronger.

Figure 3(b) shows the calculated profiles of the hydrogen deficiency on the H-Si(111) surface after 50 pulses of UV light irradiation with the power of 25, 50, 75 and 100μJ/pulse. The solid, dashed and dotted curves show the calculated hydrogen deficiency for activation energies of E_d=2.65, 2.55 and 2.47eV, respectively. In the case of UV light irradiation with the power of 25μJ/pulse (the top panel in Fig. 3(b)), the profile of hydrogen deficiency is observed in an area of the width of ~100μm around the center of the UV light spot. As the power increased, the area of hydrogen deficiency becomes wider and the peak hydrogen deficiency becomes higher, in accordance with Fig. 3(a). The width of the hydrogen deficiency becomes ~400μm for the UV light irradiation with the power of 100μJ/pulse.

According to the paper by Bratu et al [17], the SSH light is not generated at a Si(111) surface below the hydrogen deficiency of 40%. For the activation energy of 2.47eV, the hydrogen deficiencies are above 40% at every power of the incident light in 25~100μJ/pulse. For this activation energy, the profiles of the observed SSH intensity in Fig. 3(a) and the calculated hydrogen deficiency on the Si surface in (b) are seen to match with each other. E_d=2.47eV is within the error range 2.65±0.17eV proposed by Koehler and George for hydrogen desorption from solid Si(111) surface [14]. Considering that the silicon surface is in a liquid state when the desorption occurs in the condition of Fig. 1, the activation energy E_d=2.47eV obtained in this study is that from the liquid Si surface. This indicates that the surface melting did not have a remarkable influence on the

process of hydrogen desorption from a Si(111) surface with coverage at ~1ML, and it is consistent with the result by Koehler and George.

The important contribution of this study is that the analysis by Koehler and George [4] has been applied to analyze numerically the observed spatial distribution of hydrogen deficiency by using SH microscopy. Our results using the UV light irradiation were consistent with those using visible light irradiation by Koehler and George in that the surface melting does not affect the activation energy of the hydrogen desorption. We suggest that the analysis of the deficiency distribution may determine the activation energy E_d more sensitively than the study of the spatially integrated yield. In addition, the present analysis is able to show the explicit spatial distributions of coverage θ and surface temperature T_{surf}. The obtained distributions of these parameters are expected to be utilized to analyze the optical CVD growth on the Si surface.

Conclusion

We have analyzed the profiles of the SH intensity from the surface and bulk of H-Si(111) after UV light pulse irradiation, by comparing them with the profiles of hydrogen deficiency and surface melting calculated by LITD model. Numerically, the spatially resolved desorption rate was found to be sensitive to the activation energy. However, the reduction of the activation energy due to the surface melting was not detected. The results obtained by Koehler and George [4] by analyzing the spatially integrated desorption were confirmed to be correct by our spatially resolved analysis of the hydrogen deficiency.

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Figures

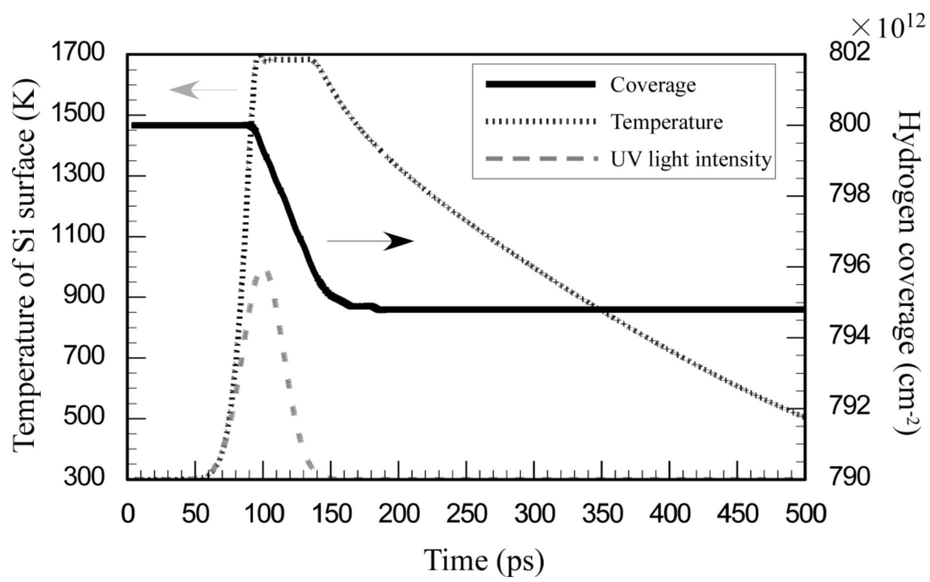

Fig.1 Change of the temperature (dotted curve) and the coverage of hydrogen (solid curve) on the Si surface after UV light irradiation (dashed curve) as a function of time calculated by LITD model. The wavelength of UV light pulse is 355nm, the power is 50 μJ/pulse, the spot size (FWHM) is 294μm, and the pulse duration (FWHM) is 35.3ps. The melting temperature of bulk Si is 1684K.

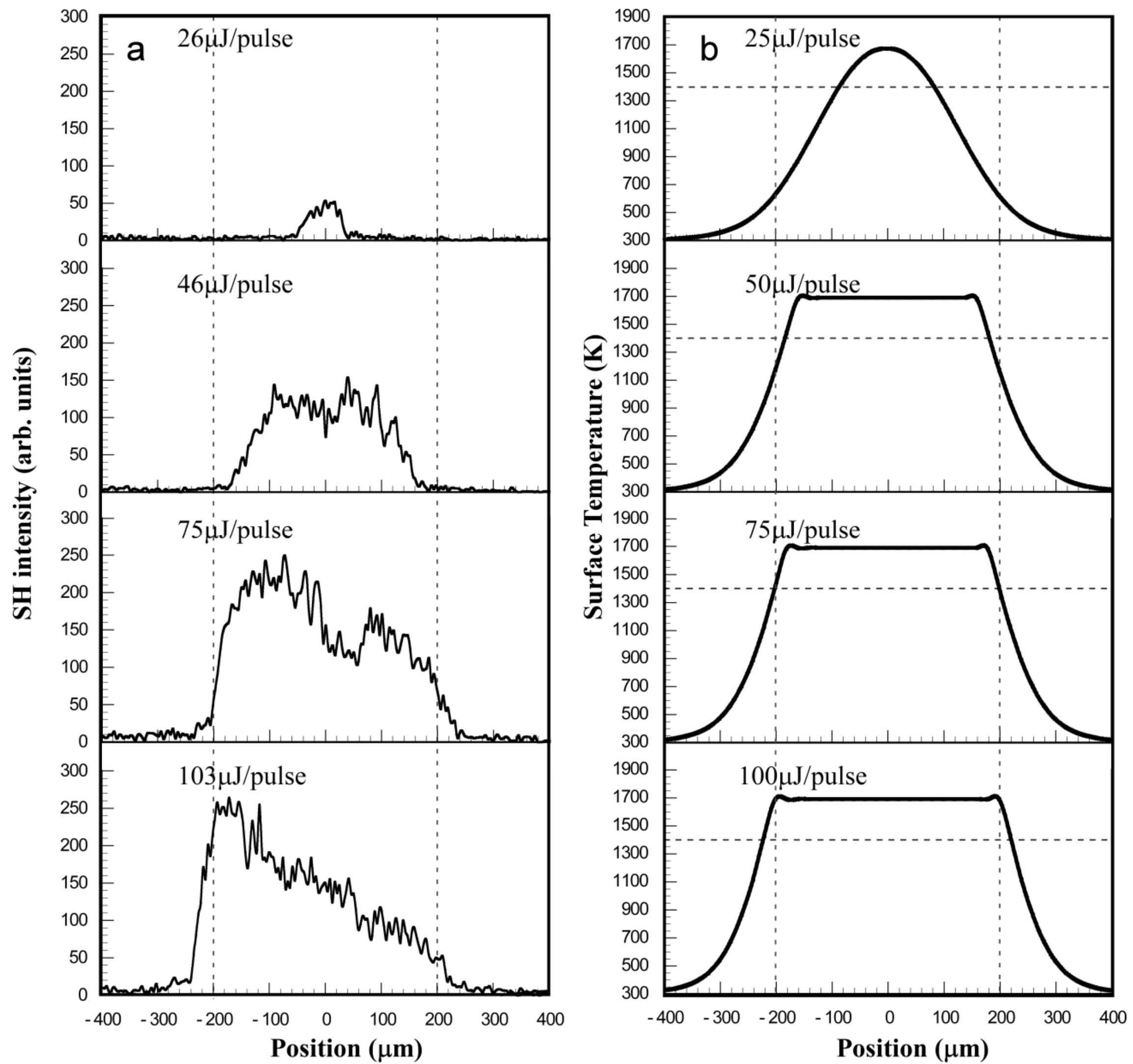

Fig. 2(a) Observed spatial profiles of the SH intensity of the bulk Si after UV light irradiation. (b). The profiles of the maximum surface temperature calculated by the LITD model. The horizontal dashed lines show the temperature of surface melting at 1414K.

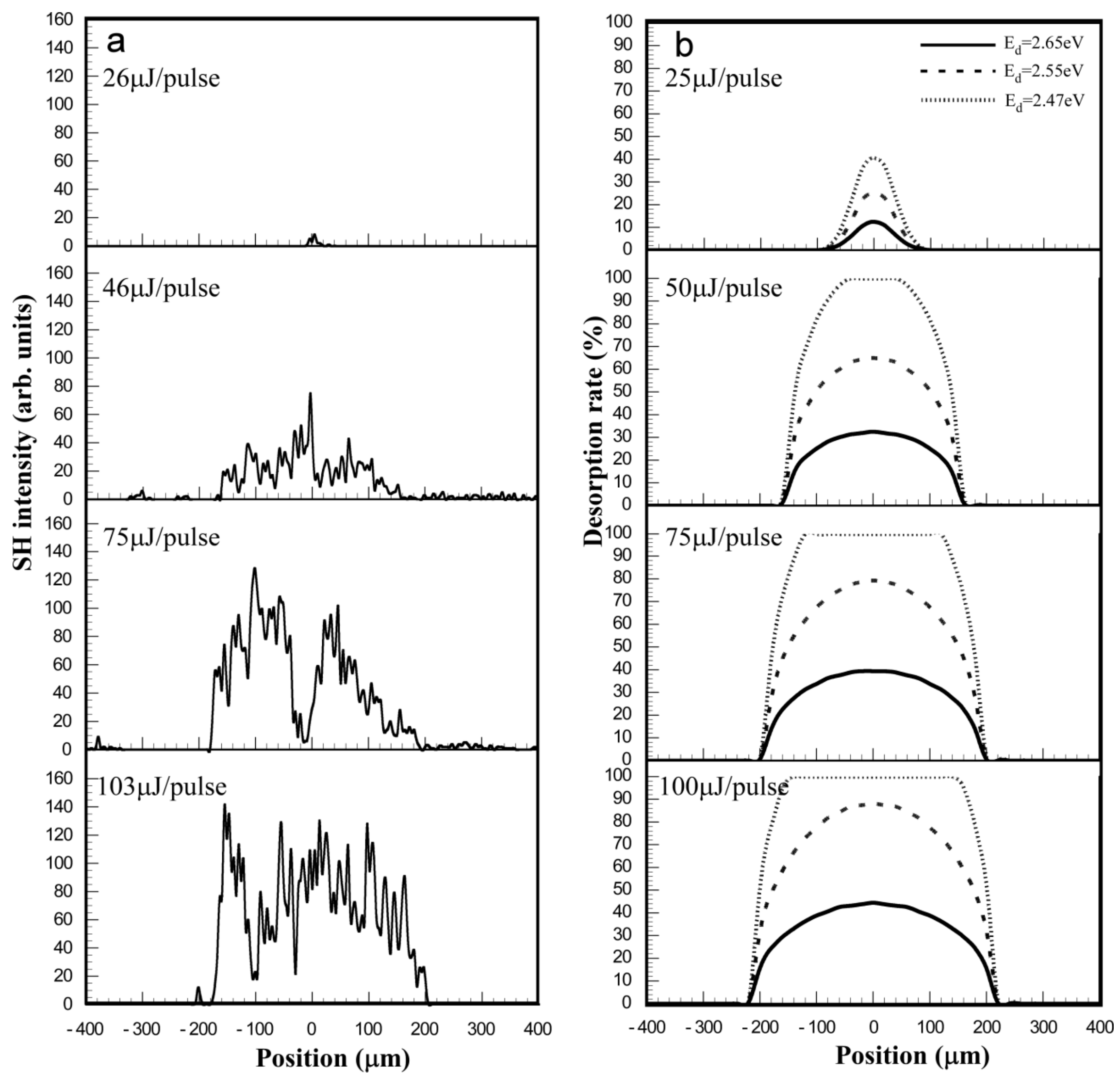

Fig. 3(a). Observed spatial profiles of the surface SH (SSH) intensity of H-Si(111) after UV light irradiation. (b). The calculated profiles of the hydrogen deficiency (%) by LITD model.