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Description	

Desorption activation energy of hydrogen from the Si (111)1x1: H surface studied by optical sum frequency generation and second harmonic generation

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Abstract:

The desorption kinetics of hydrogen from the H-Si (111)1x1 surface prepared by molecular hydrogen exposure has been studied by combining optical sum frequency generation (SFG) for higher coverage and second harmonic generation (SHG) for lower coverage at several sample temperatures from 711 K to 770 K. The hydrogen desorption activation energy was found as $E_d = 60.1 \pm 8.8$ kcal/mol (2.60 ± 0.38 eV) for the second order desorption for the coverage above 0.44 ML. For the first order desorption at the coverage below 0.18 ML the desorption activation energy was found as $E_d= 32.6 \pm 8.1$ kcal/mol (1.41 ± 0.35 eV).

Keywords: Sum frequency generation (SFG); Second harmonic generation (SHG); Si (111)1x1; desorption order; activation energy; hydrogen.

Introduction

Hydrogen terminated silicon surfaces are oxide free for up to several hours in air and are used as a substrate for deposition of organic monolayers. The desorption of hydrogen from the Si surface is one of the essential phenomenon in the hydrosilylation reaction for forming an organic monolayer in a biological sensor [1]. In this context the desorption mechanisms of hydrogen from H-Si (100)3x1, H-Si (100)2x1 and H-Si (111)7x7 surfaces have been studied, and desorption activation energy was obtained using various methods including laser induced thermal desorption (LITD) [2][3], second harmonic generation (SHG) [4], surface infrared (IR) spectroscopy [5], scanning tunneling microscopy (STM) [6], and temperature–programmed desorption (TPD) [7]. For example, Koehler *et.al.* [2] obtained a desorption activation energy of $E_d = 61$ kcal/mol (2.6 eV) for the second order desorption kinetics above 0.2 ML coverage of hydrogen, using laser-induced thermal desorption (LITD) process on the H-Si (111) 7x7 surfaces. Gupta *et.al* [8] found a desorption activation energy of $E_d = 65$ kcal/mol (2.82 eV) for silicon monohydride species as a second order kinetics by using temperature programmed desorption (TPD) for a porous silicon sample using FTIR spectroscopy. They also obtained an activation energy $E_d = 43$ kcal/mol (1.86 eV) for silicon dihydride species.

However, at lower coverages the results are not so unanimous. Schulze *et.al* [9] gave a hydrogen desorption activation energy of $E_d = 48.5$ kcal/mol (2.1 eV) for dihydride species in the first order kinetics. They studied the desorption of hydrogen by using temperature programmed desorption (TPD) from H-Si (111) 7x7 surfaces at lower coverages. Gupta et al. [8] objected to Schulze et al. and judged that silicon dihydride species should show second order kinetics and reported a measured activation energy of $E_d = 43$ kcal/mol (1.86 eV). Reiders *et. al.* [4] obtained a desorption activation energy of $E_d = 2.40 \pm 0.1$ eV from H-Si (111) 7x7 surfaces at hydrogen coverage below 0.2 ML in the temperature range of 680 K<T<800 K by using second harmonic generation (SHG). They reported that the desorption followed an intermediate reaction of order 1.5 ± 0.2. Thus, the study of the desorption kinetics of hydrogen from the Si (111) surface does not seem to have converged and until now there is still a debate on the values of the desorption activation energy of the first order desorption, especially at lower hydrogen coverage.

In our previous trial in addressing this problem [10], we studied hydrogen desorption from flat H-Si (111)1x1 at 711K by monitoring SFG and SHG. By combining SFG and SHG spectroscopies, we have

obtained the orders of hydrogen desorption over the hydrogen coverage range from 1 ML to 0 ML for a single Si(111) sample. The hydrogen was confirmed to desorb with second order kinetics for higher coverages of 1 ML-0.18 ML by SFG and with first order kinetics for the lower coverage of 0.18 ML-0.0 ML by SHG. In order to make this result contribute to the development in solving the problem mentioned in the previous paragraph, we need to obtain the activation energies of the two desorption processes.

In this paper, we will evaluate the activation energies of these second and first order hydrogen desorptions experimentally by studying the desorption curves at several different surface temperatures. We experimentally studied the hydrogen desorption kinetics from a flat H-Si (111)1x1 surface at 711 K, 730 K, 750 K and 770 K by using both SFG and SHG spectroscopies. The SFG spectroscopy was used to monitor the H-Si vibration at 711 K to 770 K at the coverages from 1 ML to below 0.44 ML. The SFG signal diminished and became close to the background as the coverage approached ~0.44 ML. The end coverage obtained by this SFG measurement was used as the starting coverage in the subsequent SHG measurement. The SHG spectroscopy was used to monitor the number of dangling bonds at the coverages below ~0.4 ML. Reider et al.'s experiment [4] used TPD data to get the initial coverage of the SHG measurements. In their case there must be two separate desorption experiments for one sample, namely one for getting a whole TPD spectrum and another for TPD and SHG combination. In our method we can get SFG and SHG data in one desorption experiment for one sample. Thus, if the desorption depends sensitively on the adsorption condition, our method has advantage.

Experimental setup

The methods of sample preparation and hydrogen dosing used in this study were already explained in our previous paper. [11]. Here we briefly describe important points of the sample preparation and measurements. In order to hydrogenate Si surfaces, pure molecular hydrogen was introduced into an ultra-high vacuum chamber holding cleaned Si(111) substrates at 873K [12][13][14][15]. The SFG intensity spectra were measured [10] from wavenumbers 2060 cm^{-1} to 2110 cm^{-1} with a scanning step of 1 cm^{-1}. The polarization combination was *ppp* with each "*p*" indicating the polarization of SFG, visible and IR light. After the sample was heated for 10 s repeatedly, it was cooled down to room temperature (RT) every time and the SFG spectrum was taken. This procedure was repeated until the SFG signal was close to the background at lower coverage of hydrogen. Then we switched to SHG measurement. The sample was heated for 50 seconds repeatedly, cooled down to RT every time, and

the SHG intensity was measured. The length of the heating time was increased as the hydrogen coverage decreased and we measured SHG intensity until the SHG intensity signal increased and saturated. The substrate temperature was 711 K, 730 K, 750 K, or 770 K. A typical net measurement time for one combination of SFG and SHG spectroscopies in a full H_2 desorption from one sample was more than 30 hours at the sample temperature of 711K.

Theoretical treatment of the desorption curves

Miyauchi *et. al.* obtained a relation between θ and $\overleftrightarrow{\chi}^{(2)}$ assuming coherent potential approximation taking dipole coupling among Si-H oscillators on Si (111) 1x1 into account [16]. The present paper follows his method to analyze the SFG and SHG signal intensity.

The hydrogen coverage follows the Polanyi-Wigner desorption rate equation [2][17],

$$-\frac{d\theta}{dt} = \vartheta_d\, \theta^n e^{-E_d/RT_{surf}} \tag{2}$$

Here θ is the surface hydrogen coverage, ϑ_d the pre-exponential factor, E_d the activation energy for desorption, R the gas constant (8.31 J/mol K), and T_{surf} the surface temperature. For $n = 1$, the solution of the desorption rate equation (2) gives:

$$\text{first order desorption:} \quad \theta_t = \theta_0\, e^{-k_1 t} \tag{3}$$

The solution of the equation (2) when n is not 1 is:

$$\theta_t = \theta_0\{1 + (n-1)\theta_0^{(n-1)}\, k_n t\}^{\frac{1}{1-n}} \tag{2'}$$

Thus for $n = 2$ the equation (2') becomes:

$$\text{second order desorption:} \quad \theta_t = \theta_0(1 + \theta_0 k_2 t)^{-1} \tag{4}$$

The desorption rate constant k can be defined considering Eq. (2) as

$$k = \vartheta_d\, e^{-E_d/RT_{surf}} \tag{5}$$

Taking logarithm of both sides of eq. (5) we get:

$$\ln(k) = \ln(\vartheta_d) + \frac{-E_d}{R}\frac{1}{T_{surf}} \quad\quad\quad (6)$$

The plot of *ln (k)* versus (1/T_{surf}) should give a straight line according to Eq. (6). Its slope and y-intercept can be used to evaluate the activation energy (E_d) and pre-exponential factor ϑ_d.

Results

(1)Activation energy of the second order hydrogen desorption

In order to evaluate the hydrogen desorption activation energy of H-Si (111)1x1 at coverages above 0.2ML, we observed isothermal desorption of hydrogen as a function of time by monitoring the SFG peak of Si-H (monohydride) vibration at 2083.7 cm^{-1} [11][12]. The sample temperatures were 711 K, 730 K, 750 K and 770 K.

Figure 1 shows hydrogen coverage on the H-Si(111)1x1 surface estimated from the SFG signal as a function of time when the sample was heated at 711K. The coverage decreases gradually over time and is fitted by theoretical curves of first (solid line) and second (dashed line) order kinetics. We also fitted the data with general coverage equation (2′) with an adjustable parameter n. The best fit value of n is 2.056 and it is very close to 2. Thus one can see that the desorption follows second order kinetics in the coverage range of 1.0 ML to 0.18 ML.
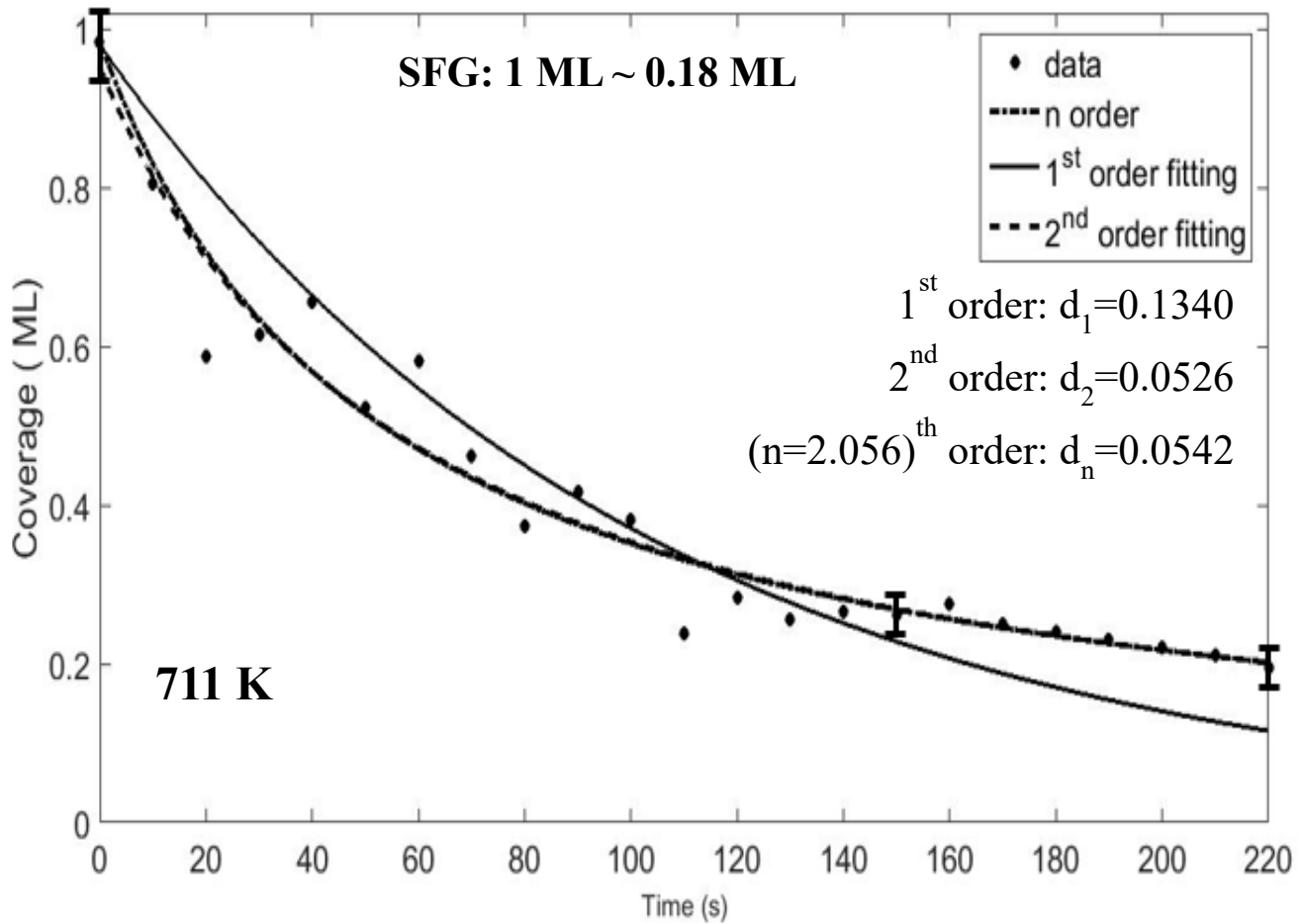
Fig. 1. SFG intensity of H-Si (111) 1x1 surface measured after every 10 seconds of heating at 711K. Dots are experimental results and error bars represent their standard deviation. The solid line, the broken line, and the dash-dotted line are simulation curves of the first, 2nd, and n^{th} order desorptions, respectively. d_n (n = 1, 2, 2.056) is the calculated standard deviation of the experimental data points in ML from the fitting curves assuming n^{th} order desorption. n=2.056 is the optimum desorption order obtained by the fitting, but the corresponding d_n is a little larger than that for n=2 due to a noise.

Figure 2 shows the time dependency of reciprocal coverages of hydrogen on the H-Si (111)1x1 surface at temperatures of (a) 711 K, (b) 730 K, (c) 750 K and (d) 770 K.   At all these four temperatures, the desorption order is judged to be 2, since ($1/\theta$) plotted versus heating time gives straight lines in all the

panels and it is consistent with the second order kinetics. The second order desorption was confirmed in the ranges above 0.18 ML for 711K, above 0.43 ML for 730K, above 0.44 ML for 750K and above 0.29 ML for 770K. The constant k values are obtained from the slopes of the lines in Fig. 2 and are used to make Fig. 3.
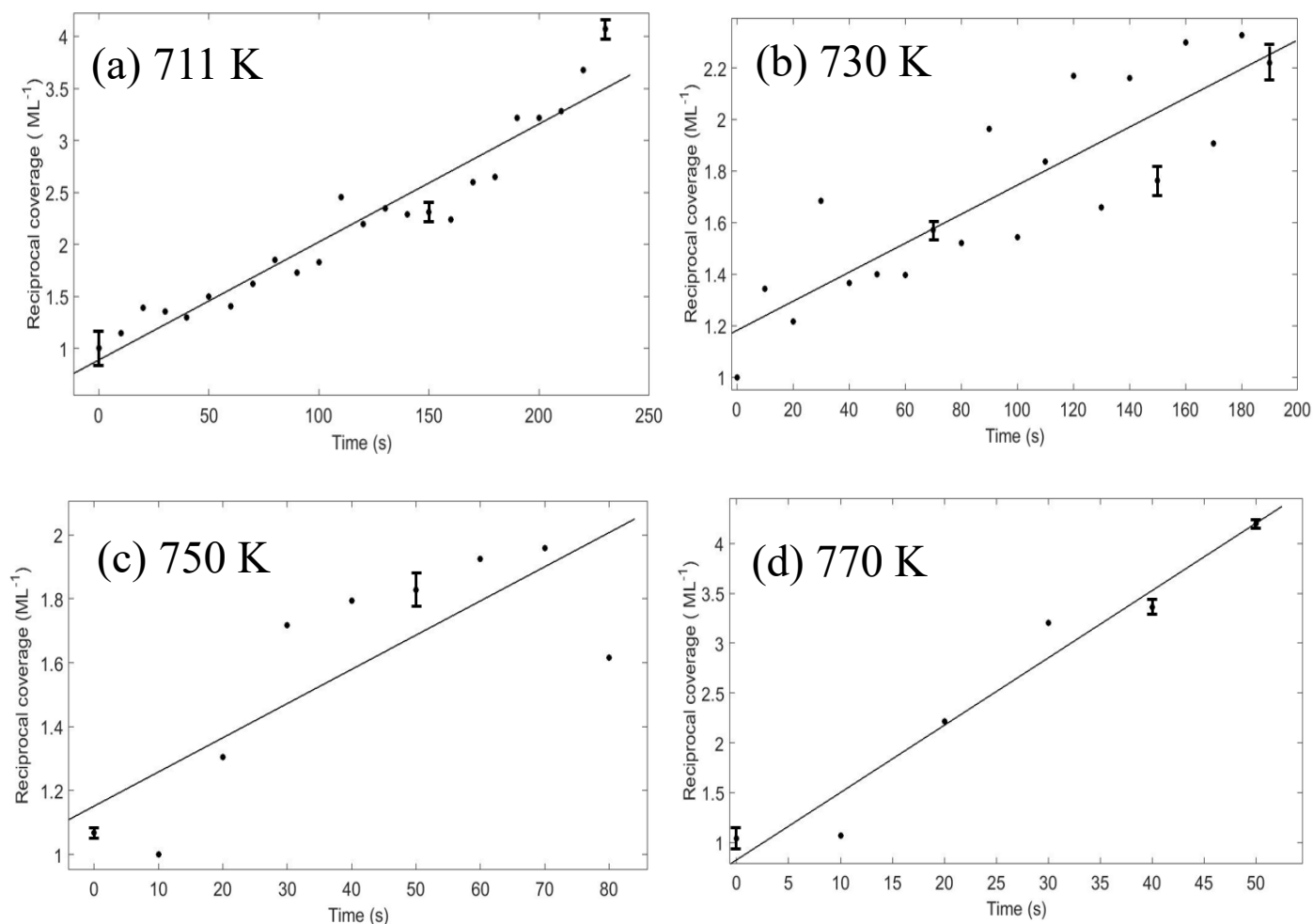

Fig.2. Time dependence of the reciprocal of the hydrogen coverage $(1 / \theta)$ estimated from the SFG intensity of H-Si (111) measured during H_2 desorption at surface temperatures of (a) 711 K, (b) 730 K, (c) 750 K and (d) 770 K.

The second order kinetics shown in Figs.1 and 2 is consistent with the result by Koehler *et.al* [2]. Namely, by using laser-induced thermal desorption (LITD), Koehler et al. assigned the hydrogen

desorption from Si (111) 7x7 surface with hydrogen coverage above 0.2 ML as second order at 710, 720, 730 and 750 K. Our results are also consistent with those by Wish *et al.* [18] by LITD at surface temperatures of 690, 705 and 725 K.

Figure 3 shows ln (k_2) versus inverse temperatures (1/T), or an Arrhenius plot at hydrogen desorption temperatures of 711, 730, 750 and 770 K. The values ln (k_2) as a function of inverse heating temperature (1/T) are roughly on a straight line. From the slope of the fitted line we get the desorption activation energy (E_d) for the second order desorption as $E_d = 60.1 \pm 8.8$ kcal/mol (2.60 ± 0.38 eV) in the coverage above 0.44 ML.
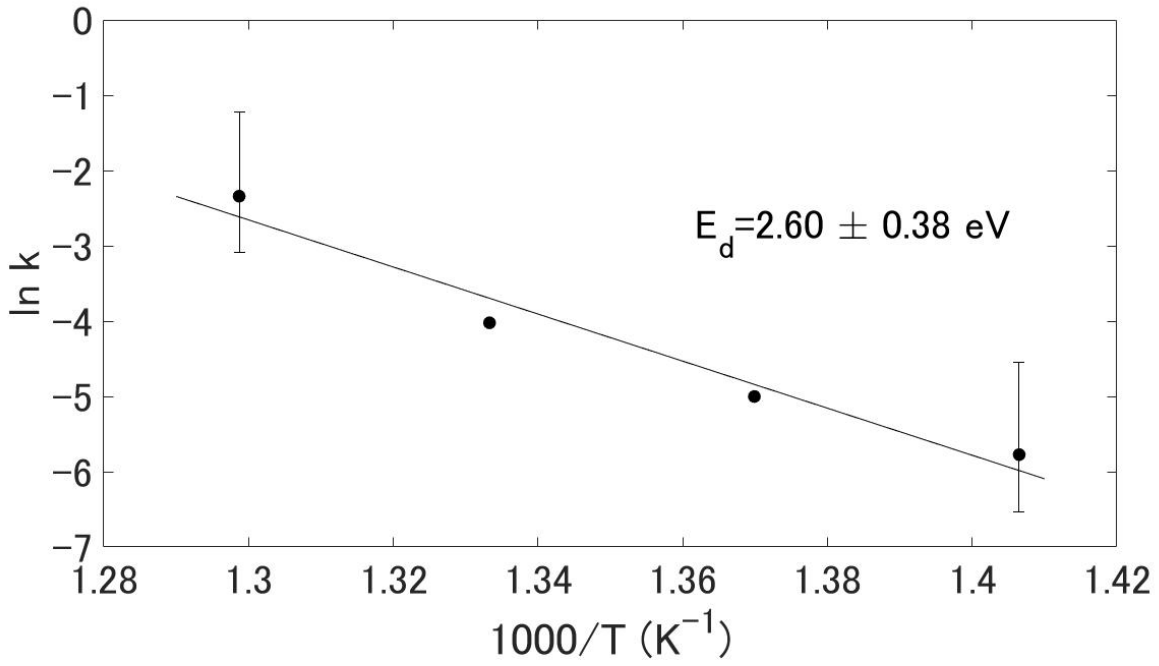

Fig. 3 Arrhenius plot of secondary hydrogen desorption rate from the H-Si (111) 1x1 surface at sample temperatures 711, 730, 750 and 770K.

So far as we know, there has been one report by Morita et al. on the activation energy of Si (111)1x1 surface [6]. The activation energy by Morita et al. is 2.89 eV and it is consistent with the value 2.60 ± 0.38 eV obtained in our study. We note here that the second order assignment and its consistent activation energy in our work guarantee the reliability of our experimental system and samples. As a reference the activation energies of the second order desorption of the Si(111) 7x7 surfaces can be also found in Table I [2][18]. Among them Koehler *et.al* [2] studied the hydrogen desorption from H-Si (111) 7x7 by using laser-induced thermal desorption (LITD) with activation energy $E_d = 61$ kcal/mol (2.6 eV), and it is very similar to the one obtained in this study for H-Si(111)1x1, or 60.1 ± 8.8 kcal/mol (2.60 ± 0.38 eV). For further reference Table I shows second order desorption activation energies from 2.16 eV to 2.89 eV including types of Si surfaces other than (111) 1x1 or 7x7. For example, Schulze *et.al* [9] studied the desorption activation energy of the H-Si (111) 2x1 surface using temperature-programmed desorption (TPD) measurements. They report that the monohydride species follows second order kinetics with an activation energy $E_d = 59$ kcal/mol (2.54 eV).

(2) Activation energy of the first order hydrogen desorption

After we finished taking SFG spectra at each sample temperature, we switched to SHG system to monitor the hydrogen coverage of the same sample at lower coverages. This continuous switch from SFG to SHG at a certain coverage of hydrogen in one desorption experiment is the biggest feature of the method in this work. The insets in Fig. 4(a) and (b) show the SHG intensity of the H-Si (111)1x1 surface as a function of time after the sample was heated repeatedly for 50 seconds at 711 and 730 K, respectively. The pulse energy of the fundamental light at the photon energy of 1.17eV was 380 μJ/pulse. In this experiment we used the polarization configuration $P_{in} P_{out}$. Since the SHG originates from the dangling bonds of the Si surface created after hydrogen desorption, SHG intensity curves rose initially as a function of heating time and then gradually saturated.

We now evaluate the hydrogen coverage from the observed SHG signal intensity, using the equation (7) below [19], just as we did it in our previous work [10].

$$\overleftrightarrow{\chi}_s^{(2)}(\theta) \simeq \overleftrightarrow{\chi}_{s,0}^{(2)} (1 - \beta\theta), \text{ for } \theta \ll 1 \qquad (7)$$
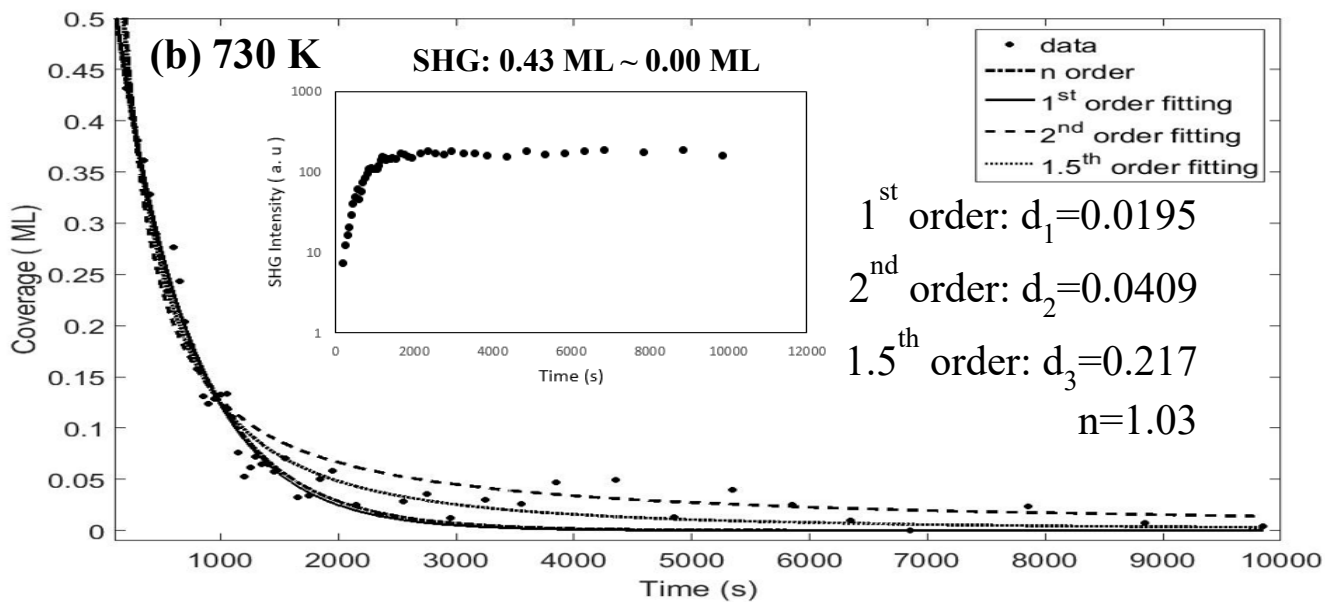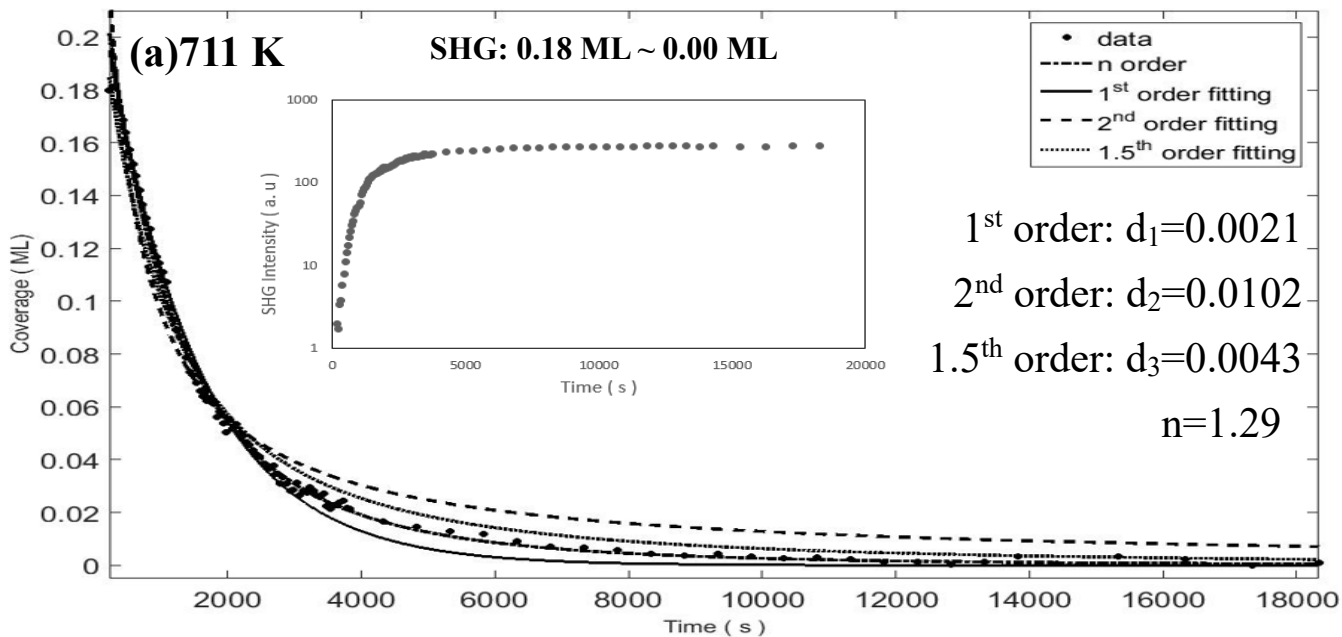
Fig. 4 Isothermal hydrogen desorption from H-Si (111) 1x1 surface at (a) 711 K and (b) 730 K obtained by SHG spectroscopy. The dots are hydrogen coverage obtained from the SHG intensity. The solid line, the broken line, the dotted line, and the dash-dotted line are simulation curves corresponding to the desorption rates of the 1st, 2nd, 1.5^{th}, and nth orders, respectively.

Here θ is the coverage of the Si(111) surface by hydrogen, $\overleftrightarrow{\chi}_s^{(2)}(\theta)$ is the second-order nonlinear susceptibility at coverage θ, $\overleftrightarrow{\chi}_{s,0}^{(2)}$ is the one at zero coverage, and β is a constant of proportionality, that is, the ratio between the susceptibility and the coverage. In the case of H-Si (111)7x7, it has been found that the slope is $\beta \simeq 1.3$ [19]. For hydrogen on the H-Si (100)2x1 surface the proportionality constant is $\beta \simeq 3.1$ [20]. In our case of H-Si (111)1x1 surfaces, the proportionality constant of $\beta \simeq 5.08$ was obtained by using the equation (7) and the inset in Fig. 4(a). The hydrogen coverage was then calculated from the observed SHG intensity data following the process described in our previous paper [10].

Figure 4(a) and (b) shows typical hydrogen coverage data on the Si(111) surfaces as a function of the heating time at temperatures 711 and 730K, respectively. The initial coverage of hydrogen in Fig. 4 was (a) 0.18 ML and (b) 0.43 ML. The data in Fig. 4(a) and (b) were fitted with calculated curves in equations (3), (2') and (4) according to the first (solid line), intermediate (dotted line) and second (dash line) order kinetics, respectively. For both cases in Fig. 4(a) and (b) the first order desorption shows the best fit among first, 1.5 th, and second order kinetics.
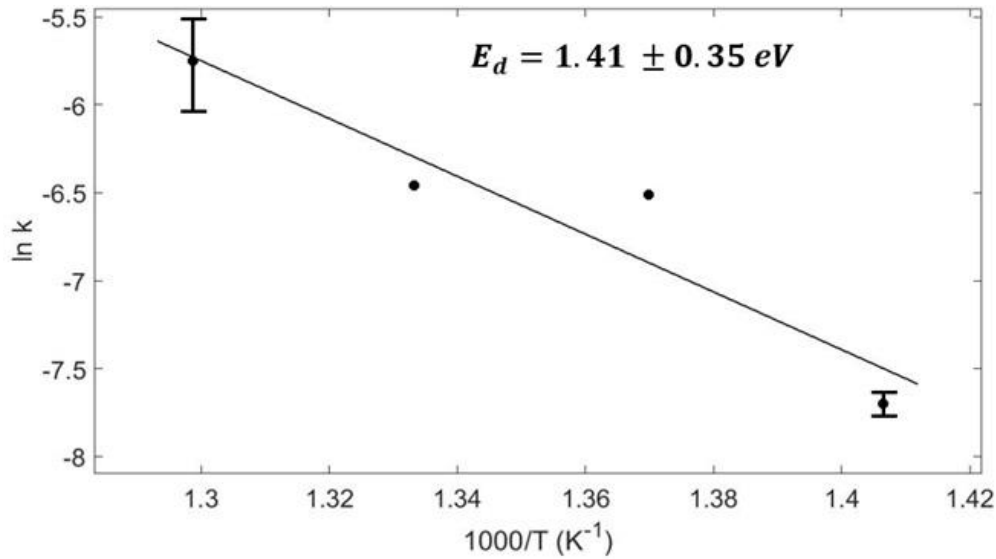

Fig. 5 Arrhenius plot of the first order hydrogen desorption rate from the H-Si (111) 1x1 surface at 711, 730, 750 and 770K obtained by SHG spectroscopy.

Next, we calculate the desorption activation energy of this first order desorption observed at the lower coverage. We first evaluated the hydrogen desorption rate constants (k) from the slopes of $ln(\theta)$ as a function of heating time at different temperatures of 711, 730, 750 and 770 K. Using the obtained k values we made an Arrhenius plot in Fig. 5. In Fig. 5 the data are roughly on a straight line. From the slope of the line and Eq. (6), we obtained the desorption activation energy (E_d) for the first order desorption as $E_d = 32.6 \pm 8.1$ kcal/mol (1.41 ± 0.35 eV). Hence the hydrogen desorption was assigned as the first order below 0.18 ML with an activation energy of $E_d = 32.6 \pm 8.1$ kcal/mol (1.41 ± 0.35 eV). This activation energy is not too different from $E_d = 1.7$ eV obtained by a TPD measurement with ethene or methanol on Si films by Klient *et. al* [17]. Schulze *et.al* also obtained an activation energy of the first order kinetics on the H-Si (111) 7x7 surface by TPD as $E_d = 48.5$ kcal/mol (2.1 eV) [9].

Here we explain why the number of data points is as little as four in the Fig. 5, although bigger number of measurement temperatures is more desirable to get a reliable activation energy. In order to get Figs. 1 and 3, many SFG and SHG spectra were taken during the hydrogen desorption for one sample. The quality of the Si wafer degraded after each set of measurements. After SFG and SHG measurements at one desorption temperature, the Si wafer was cleaned again by heating at 600 °C for 6 hours and flashed at 1100 °C for H_2 adsorption. The wafer became molten at the electrical contact points after the repetition of this process for many times. In addition, the SFG measurement took almost three working days. After the hydrogen coverage became low, we used another full day for getting SHG spectra. It is rather difficult to keep the stability of the light source for a longer time than this. So we could not just simply increase the number of the measurement temperatures. The number of the observation temperatures, i. e. four, is the best compromise in this trade-off situation.

Discussion on the hydrogen desorption kinetics and activation energy

In this and previous studies, we found that the desorption of hydrogen from the H-Si(111) 1x1 surface is in second order for the coverage larger than 0.44 ML and is in first order for the coverage smaller than 0.18ML. In the second order kinetics one hydrogen atom is expected to leave a surface Si atom, diffuses to another Si-H site, then the two hydrogen atoms meet and form a dihydride (Si-H_2), and a molecular hydrogen desorbs. From the results of this study, the activation energy of the second order desorption

was found to be 2.60 ± 0.38 eV, and the activation energy of the first order desorption was 1.41 ± 0.35 eV. We would like to get an image of this first order desorption, comparing the desorption order obtained from our experiments with those in the literature. So far there are several models for the first order kinetics as listed in Table 1 but a final image does not seem to be reached.

Many references in Table 1 claim second order desorption for the hydrogenated silicon surfaces, but some papers report on first order desorption at lower coverage and others propose 1.5^{th} order. The studies proposing the second order desorption are performed with TPD or LITD, and they can have lower sensitivity at lower coverages and might have failed to detect the first order contribution. Since STM or SHG have good sensitivity at lower coverages and that may be why the first or 1.5^{th} order desorption have been detected. Reider et al. and this work employed both molecular hydrogen adsorption and SHG method for detection. The observed desorption time was up to 5000 s for Reider et al and 18000 s for this study. Thus we may be able to say that our study is more accurate in the assessment of the long tail-part of the curves in Fig. 4. This benefit is remarkably visible for the lower temperature desorption curve in Fig. 4(a). In Fig. 4(b) it is the data points for time before 2000 s that are more favorable to the first order desorption. This point was already argued in our previous paper.

Table 1 Hydrogen desorption studies of the H-Si(111) and the obtained desorption energies and models

reference	Surface	adsorption	method	desorption odrder and energy	
G. Schulze et al (1983)[9]	Si(111) 2x1	atomic H	TPD	2nd (2.5eV)	surface is rough
B. G. Koeler et al (1988)[2]	Si(111) 7x7	atomic H	LITD	2nd (2.68eV)	
J. L. Wise et al (1991)[18]	Si(111) 7x7	atomic H	LITD	2nd (E=2.73eV)	
G. A. Reider et al (1991)[4]	Si(111) 7x7	atomic H	SHG	m=1.5 (E=2.4eV)	
A. Morita et al (1995)[6]	Si(111) 1x1	atomic H	STM	2nd(E=2.89eV) to 1st	critical coverage=0.8α (α=adatom saturation coverage)
A. Vittadini et al (1997)[21]	Si(111) 7x7		DFT calc.	2nd (E=2.4eV)	transition state at adatom site
H. Kim et al (2001)[22]	Si(113)	atomic D	TPD	1st(β1,E=2.58eV), 2nd(β2,E=2.16eV)	1st order = from tetramer units
M. Y. Mao et al (2001)[12]	Si(111)	H2 molecule	SFG, SHG	m=1.5 (E=2.38eV)	
L. Tsetseris et al (2006)[23]	Si(111) 1x1 with excess H		DFT calc.	E=1.68eV	3H complex
This work	Si(111) 1x1	H2 molecule	SFG, SHG	1st (E=1.41$\pm$0.35 eV), 2nd (E=2.60$\pm$0.38 eV)	

Next, we compare the second-order desorption activation energy obtained in this study with those listed in Table 1. There have been two ways to adsorb hydrogen in the studies listed in Table 1. One is the adsorption of atomic hydrogen and the other is the adsorption of molecular hydrogen. Molecular hydrogen adsorption is done by Reider et al. and Mao et al., and is claimed to cause less surface roughening than atomic hydrogen adsorption. However, so far as the desorption activation energy is

concerned, the two methods do not seem to have fatal difference. Some of the activation energies of the second order desorption [22] is smaller than that obtained in this study and others have similar values to this study within the statistical errors. This variation of the values may be due to the differences in the surface quality or experimental systems.

Morita et al. reported first order desorption at lower coverages [6]. They studied Si(111)-H surfaces prepared in UHV with an atomic hydrogen source by scanning tunneling microscopy. They pointed out that the Si-H species are rather mobile and give second order desorption of H_2 at higher coverage. At lower coverage the surface shows $\sqrt{3} \times \sqrt{3} R \, 30°$ domains and these domains do not allow Si-H species to enter. Then the desorption kinetics of second order does not work and it is rather first order as it is explained by a further phenomenological analysis. Unfortunately they did not report on the activation energy of the first order desorption and we cannot compare our work with theirs from a point of view of the desorption activation energy.

Kim et al reported on first and second order desorption from a deuterium adsorbed Si(113) surface, but we do not compare their resulting first order desorption activation energy of 2.58eV with that of our study because the difference between hydrogen and deuterium is not systematically known. Here we note only that Kim et al say that the origin of the first order desorption is deuterium adsorbed on tetramer units within the atomic step regions.

We note that our group recently reported a tentative value of dihydride desorption energy as ~1.6eV by analyzing an isothermal desorption of Si-H_2 vibration by SFG from Si steps on a *miscut* Si(111) surface [24]. In this paper the desorption order of the hydrogen from the steps could not be determined, but the desorption activation energy was roughly estimated to be 1.6 eV. The proximity of this 1.6 eV and the activation energy 1.41 eV obtained for the first order desorption in the current work may mean that the latter originates from some defects on the Si(111) surface.

There can be another model of the first order kinetics as we have already suggested in our previous paper. Namely, at very low coverage Si-H_2 or Si-H_3 groups exist on the surface and they can decompose and emit H_2 in the first order kinetics. This picture is consistent with another report by Kawasuso *et. al.* [25]. They studied hydrogen terminated Si(111) surface prepared by NH_4F solution by reflection high energy positron diffraction (RHEPD). They found that the rocking curves cannot be explained unless

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they assume the coexistence of Si-H$_3$ groups on the surface. Actually, in ref. [24] as mentioned in the previous paragraph, we could not detect dihydride or trihydride peaks in the SFG spectrum of H-Si(111) prepared in the same way as in this paper [11]. However, the dihydride below 0.2 ML may rather not be visible by SFG because the SFG from Si-H vibration at the coverage of 0.2 ML is close to the background. On the other hand, SHG has a sensitivity to detect the disappearance of dihydride or trihydride below 0.2 ML by getting a signal from the dangling bonds created by the desorption from the dihydride or trihydride.

No other experimental results of Si(111) surfaces are left to be compared with the activation energy of our first order desorption. There is a first principle calculation result by Tsetseris et al. Tsetseris et al assumed excess hydrogen adsorbed on the Si (111) 1x1 surface, and found that "3H complex" state is stable in the adsorbed layer. They claimed that its desorption activation energy is 1.68 eV. This value agrees well with our 1.41 eV within the statistical error range, and is considered to be informative. However, according to Tstseris et al., this 3H complex state shifts to monohydride state at the early stage of desorption and does not contribute to desorption until the coverage of hydrogen becomes low enough. So we cannot say that our experiment is explained by the theory by Tsetseris et al.

Conclusions

In this study combined SFG and SHG measurements in one hydrogen desorption from 1 ML to 0 ML on a flat H-Si (111)1x1 surface has been done at different surface temperatures of 711, 730, 750 and 770 K. The hydrogen desorption was confirmed to follow the second order kinetics for the coverage from 1 ML to 0.44 ML and the heating temperatures at 711, 730, 750, and 770 K. The corresponding activation energy was estimated to be $E_d = 60.1 \pm 8.8$ kcal/mol (2.60 ± 0.38 eV). At low coverages below 0.18 ML hydrogen desorption was assigned as the first order for the heating temperatures at 711, 730, 750 and 770 K. The corresponding activation energy was estimated to be $E_d = 32.63 \pm 8.1$ kcal/mol (1.41 ± 0.35 eV).

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