Vibrational dephasing dynamics of the hydrogenated Si(100)-2 × 1 surface revisited: multi-mode dephasing model

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Abstract

Surface Raman scattering was performed on Si(100)-2 × 1:H. The analysis of the temperature-dependent spectral profiles of the Si-H stretch with the Persson–Rydberg dephasing model has led to an exchange mode (ω0) at 647 ± 79 cm−1, a coupling parameter (δω) equal to −30 ± 8 cm−1, and a friction parameter (η0) equal to 59 ± 3 cm−1. The extrapolated pure dephasing time at 100 K, however, was found to be inconsistent with the direct time-resolved measurement [P. Guyot-Sionnest, P.H. Lin, E.M. Hiller, J. Chem. Phys. 102 (1995) 4269]. This controversy can be resolved by proposing another exchange mode at ~200 cm−1, coexisting with the one at ~650 cm−1. This multi-mode dephasing model generalizes the existing single-mode model. © 1998 Elsevier Science B.V. All rights reserved.

The vibrational spectroscopy at surfaces provides characteristic features in understanding both the structures and dynamics of surface adsorbates [1]. For the surface dynamics, the vibrational energy relaxation and dephasing of the adsorbate vibrational modes can be revealed by the temperature-dependent measurements on their spectral profiles [2,3]. On the surfaces of semiconductors or insulators, the coupling to other surface vibrational motions causes the vibrational energy relaxation and dephasing of the adsorbates. This is because in these systems no significant amount of free electrons exists to perturb the adsorbate vibrational modes. In most cases, the vibrational dephasing process is the dominant mechanism in determining the temperature-dependent spectral behaviors: line center shifting and line width broadening. Persson and Rydberg have proposed a vibration–phonon stochastic coupling model to explain this vibrational pure dephasing phenomenon [4]. Based on the generalized master equation approach, Liu et al. have also derived a consistent anharmonic coupling model in describing the effects of dephasing and energy relaxation on the line center and the line width [5]. Under quasi-mode approximation, they reached similar equations for pure dephasing. According to their derivation, the line center shift (∆Ω) and the line width (Γ) are given by

\[ ∆Ω = \delta \omega \cdot (n_0 + 1/2) \]  

and

\[ Γ = 2(\delta \omega)^2 n_0(n_0 + 1)/\eta_0, \]

where

\[ n_0 = 1/(e^{k_w/RT} - 1). \]
δω is the coupling parameter between an adsorbate vibration, $\Omega$, and an exchange mode, $\omega_{\text{ex}}$. $\eta_0$ is the friction parameter of the exchange mode. Their complete model further indicated the possibility of multiple exchange modes to elastically perturb the surface adsorbate vibrations, although previous experimental observations pointed to a single exchange mode [4,6–8].

Surface Raman spectroscopy has been developed as a unique surface analytical tool in the last decade, benefited by the advancement in charge-coupled device (CCD) technology [1,9]. It offers a number of advantages: high spectral resolution, high sensitivity, and background-free. In comparison, although infrared absorption spectroscopy offers similar resolution, its limited sensitivity feature often requires a complicated multi-pass geometry [10]. Using Raman spectroscopy to study the SiH stretches on the hydrogenated Si(111)-1×1 surfaces has been successfully demonstrated by Hines et al. [11]. It has been further utilized to study the H-terminated Si(100) surfaces produced by etching solutions [12]. In this study, we used surface Raman spectroscopy to examine the temperature-dependent spectral profile of the symmetric SiH stretch on the Si(100)-2×1 surface. We propose a multi-mode dephasing model to explain our experimental observations.

Surface Raman spectra were measured with an experimental setup similar to that employed by Hines et al. [11]. Briefly, the 514.5 nm line of an Ar ion laser at $\sim$350 mW was used to perform surface Raman experiments. A laser line filter blocked the residual plasma lines accompanying the laser beam. A cylindrical lens focused the laser beam to a p-doped Si(100) sample in a UHV chamber ($<5 \times 10^{-10}$ Torr). The incident angle of the laser beam was 60° and the scattered radiation was collected at 60° from the surface normal with an achromatic lens. This Raman geometry was selected to maximize the total effective field intensity at surface as well as the Raman collection efficiency [9,11]. In order to eliminate the Rayleigh scattering from the laser beam, a holographic super-notch filter was placed in front of the entrance slit of a 640 mm monochromator. The instrument spectral resolution was calibrated to be 5.2 cm$^{-1}$. In the end, a liquid-nitrogen cooled CCD camera detected the dispersed radiation. In preparing a clean Si(100) surface, a standard cleaning and flashing procedure was followed [7]. The hydrogenation was then performed at 600 K for 10 min with a dosing pressure of $5 \times 10^{-6}$ Torr. This treatment would result in a well-ordered hydrogen-terminated Si(100)-2×1 surface, also evidenced by independent LEED measurements in a separate UHV chamber. Through the combination of liquid-nitrogen cooling and resistive heating, a series of Raman scattering measurements were performed for the temperatures ranging from 100 to 500 K. Proper cares were taken to estimate the temperature difference caused by the incident laser power. The temperature measurement accuracy was determined to be within ±20 K. Each Raman spectrum was obtained by summing over 16 times of 5 min integrated spectra. In each 5 min spectrum, cosmic spikes were removed before averaging. All the Raman spectra were fitted by the Voigt profile. The line center and the de-convoluted line width were thus obtained for each sample temperature. The surface Raman spectra of Si(100)-2×1:H, as shown in Fig. 1, exhibit a prominent feature at $\sim$2100 cm$^{-1}$. The results are in good agreement with the frequencies recorded by direct IR absorption [13], high-resolution electron energy loss spectroscopy (HREELS) [14], and sum-frequency generation [7]. Because of the 'image' effects on the reflective surfaces [15], the Raman signal of the anti-symmetric stretching mode is much smaller than the symmetric one. The observed feature at 2100 cm$^{-1}$ was thus assigned to the SiH symmetric stretching mode. Furthermore, the Raman spectral feature shows two characteristic temperature dependencies: line center shifting and line width

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2 With 350 mW of laser power, the sample surface temperature, measured by a C-type thermocouple, was raised by $\sim$50 K throughout the whole temperature range. We also measured the anti-Stokes to Stokes intensity ratio of the Si bulk phonon Raman line to determine the actual sample temperature at the laser spot, resulting in a $\sim$20 K difference from the thermocouple readings. This represents the upper bound of our temperature measurement error.

3 The line profile obtained from one of the plasma lines in the Ar spectral calibration lamp was well fitted by a Gaussian function. Furthermore, the inhomogeneous contribution to the spectra is presumably a Gaussian as well. With the knowledge of this combined Gaussian width contributed by the instrument-limited resolution and the inhomogeneous broadening, the Lorentzian line width can be thus determined by the fitting of the Voigt profile on the SiH Raman spectra.
broadening, which have been observed by Tully et al. [16], as well and are similar to the cases of Si(111)-1×1:H [6] and C(111)-1×1:H [8]. Fig. 2 shows the temperature dependence of the line center and the Lorentzian line width, obtained after the deconvolution of the instrument spectral resolution and the inhomogeneous contribution 4. From 160 to 460 K, the line center is smoothly red shifted by 4.7 cm\(^{-1}\) and its Lorentzian width increases from 0.5 to 6.3 cm\(^{-1}\).

In a previous study, Guyot-Sionnest et al. obtained a vibrational energy relaxation time of >6 ns at 100 K for the symmetric SiH stretch on Si(100)-2×1:H, corresponding to a line width of <10\(^{-4}\) cm\(^{-1}\) [7]. Considering the four-phonon relaxation process of the SiH stretching mode [17], the energy relaxation contribution should be negligible in the total homogeneous line width over the whole temperature range (160–460 K). Thus, only the pure dephasing contribution was considered in analyzing our temperature-dependent spectral profiles. Based on the simple Persson–Rydberg model, the fit of the line center shift, as shown in Fig. 2, yields \(\omega_0 = 647 \pm 79\) cm\(^{-1}\) and \(\delta\omega = -30 \pm 8\) cm\(^{-1}\). The extracted \(\omega_0\) is comparable to the one (550 cm\(^{-1}\)) obtained in the previous IR study on Si(100)-2×1:H [16]. Furthermore, the fit of the line width broadening in temperature using Eq. (2) yields \(\eta_0 = 59 \pm 3\) cm\(^{-1}\), based on the fitted results on \(\omega_0\) and \(\delta\omega\) (Fig. 3). The resultant inhomogeneous broadening is 0.33 cm\(^{-1}\), which is well within our experimental error. The homogeneous line width at 300 K can thus be determined to be 1.53 cm\(^{-1}\), leading to a dephasing

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4 There are two side peaks in our Raman spectra (Fig. 1), which can be attributed to be from the defect sites. They most likely have the same dephasing mechanism as that for the main stretching vibration and therefore have the same temperature-dependent behaviors. The spectrum for each substrate temperature was hence fitted by three Voigt profiles with an identical Lorentzian width. Because the Gaussian portion that composes of the instrument spectral resolution and the inhomogeneous broadening is constant throughout different substrate temperatures, the Gaussian widths of these three Voigt profiles during the fitting process were maintained to be constant and larger than the instrument Gaussian width of 5.2 cm\(^{-1}\).

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**Fig. 2.** Temperature dependence of the line center (solid circles) of the SiH stretch on Si(100)-2×1. The solid curves were obtained from fits of the data to the Persson–Rydberg dephasing model.
fig. 3. Temperature dependence of the line width (open squares) of the SiH stretch on Si(100)-2 × 1. The solid curves were obtained from fits of the data to the Persson–Rydberg dephasing model.

Time ($T_2 = 1/\pi c \Gamma$) of 6.9 ps. This number is only slightly smaller than the corresponding one (12 ps) for Si(111)-1 × 1:H [6]. However, it is much smaller than the one (340 ps) for C(111)-1 × 1:H in our previous investigation on the hydrogenated diamond surfaces [8].

In analyzing the infrared line centers of the SiH stretches on the Si(100)-2 × 1 surface, Tully et al. assigned this extracted exchange mode to the bending motion of SiH [16]. By high-resolution electron energy loss spectroscopy (HREELS), Stucki et al. measured a SiH bending mode of 633 cm$^{-1}$ on the hydrogenated Si(100) surface [18]. Recently, Gräuschus et al. used a semi-empirical total energy approach to calculate the surface phonons of Si(100)-2 × 1:H. Four bending modes were found at around 615 cm$^{-1}$ [19]. According to these investigations, the SiH bending frequencies therefore agree with the exchange mode extracted in our Raman measurements. Guyot-Sionnest et al., on the other hand, used photon echo spectroscopy to directly measure the pure dephasing time to be 75 ps at 100 K [7]. They combined their data with the IR data by Tully et al. [16], and obtained an exchange mode at 200 cm$^{-1}$, which is very similar to the corresponding one for Si(111)-1 × 1:H [6]. However, based on our extracted dephasing parameters at high temperatures, the pure dephasing time of the SiH stretch on the hydrogenated Si(100) surface at 100 K is estimated to be longer than 3.7 ns, which is fifty times of the dephasing time (75 ps) measured by photon echo spectroscopy. To resolve this discrepancy, we tentatively propose that there exist at least two exchange modes responsible for the dephasing dynamics of the SiH stretch on Si(100)-2 × 1:H. The first one is the SiH bending motion at $\sim$ 650 cm$^{-1}$. According to the temperature-dependent behavior in the line center of the IR data by Tully et al. [16], and our Raman data, it would be of little doubt that it is this high-frequency exchange mode responsible for the vibrational dephasing at the high temperatures (200–500 K). Inferring from the time-resolved data of the vibrational dephasing time at 100 K [7], it is thus proposed that there should exist at least another surface mode at a lower frequency perturbing the SiH stretching motion. Fig. 4 shows the simulated curves for the vibrational dephasing of the SiH stretch on Si(100)-(2 × 1)-H caused by the two exchange modes. Because the similarities in the surface phonon dispersion [19,20], we thus assign the second exchange mode for the SiH stretch on H$_2$/Si(100) to be at $\sim$ 200 cm$^{-1}$. Furthermore, the dephasing parame-

Fig. 4. Simulated temperature dependencies of the homogeneous line width of the SiH stretch on Si(100)-2 × 1:H caused by single- and two-mode couplings, respectively. The experimental data from Tully et al. (open triangles), Guyot-Sionnest et al. (open square) and from our work (filled circles) are shown as well.
ters for the phonon coupling are: \( \delta \omega = -3.5 \text{ cm}^{-1} \) and \( \eta_0 = 52 \text{ cm}^{-1} \), which are close to the ones obtained for Si(111)-1 \times 1:H [6], since the pure dephasing time for the two cases are almost identical [7,21]. In addition to the present results, the experimental data from Tully et al. [16] and Guyot-Sionnest et al. [21] are also shown in Fig. 4 for comparison. For the substrate temperatures ranging from 230 to 400 K, the homogeneous line width obtained from our Raman spectra coincides with that from the IR absorption measurements. Due to the relatively small homogeneous broadening compared to the instrument resolution, the large error bars for the data below 250 K would prevent one from identifying the second exchange mode by the frequency-domain measurements. However, it seems that the time-resolved data point at 100 K follows more closely the simulation result based on the phonon coupling mode (Fig. 4). We can thus conclude that the major contribution in dephasing at high temperatures is due to the anharmonic elastic interaction between the bending mode and the stretching mode of SiH, although the dephasing caused by the low-frequency phonon mode still exists. At temperature as low as 100 K, on the other hand, the coupling by the low-frequency phonon mode dominates. The crossover temperature is \( \sim 230 \text{ K} \).

Accordingly, for the vibrational dephasing induced by many exchange modes, the total center shifting (\( \Delta \Omega_{\text{tot}} \)) and the total line width broadening (\( \Gamma_{\text{tot}} \)) are equal to the sum of the contribution from each exchange mode. The corresponding dephasing equations can thus be written as

\[
\Delta \Omega_{\text{tot}} = \sum \delta \omega_i \cdot (n_i + 1/2)
\]

and

\[
\Gamma_{\text{tot}} = \sum 2(\delta \omega_i)^2 n_i (n_i + 1)/\eta_i,
\]

where

\[
n_i = \left[ \exp(\hbar \omega_i/kT) - 1 \right]^{-1}.
\]

\( \delta \omega_i \) is the coupling parameter between the adsorbate vibration, \( \Omega_i \), and the exchange mode, \( \omega_i \). \( \eta_i \) is the friction parameter of this exchange mode. With this multi-mode dephasing model, it is conceivable that a single theoretical curve is expected to interpolate the high- and low-temperature data, as shown in Fig. 4.

According to the Persson–Rydberg model, there are two important parameters in determining the dominant exchange mode at a certain temperature range: \( \delta \omega \) (coupling parameter) and \( \eta_0 \) (friction parameter). Eq. (2) indicates that the smaller \( \eta_0 \) is, the larger the dephasing rate is. This suggests that the surface vibrational modes, which are isolated and do not couple strongly with other heat-bath modes, would be the dominant dephasing sources to the adsorbate vibrational mode. In this regard, since the bending mode of SiH is closest in frequency to its stretching mode, the coupling parameter between the two vibrational motions would be most likely to be the largest one. In addition, according to the theoretical calculations, the bending mode is isolated from the rest of the heat-bath modes on semiconductor or insulator surfaces [22]. Consequently, the most possible candidate for the exchange mode is the bending mode. Since this bending motion has the highest frequency next to the stretching motion, its dephasing process will be most important at high temperatures. At low temperatures, however, its dephasing contribution is much smaller, as shown in Fig. 4. Although other isolated surface vibrational modes (such as surface phonon modes) have a smaller coupling strength with the stretching mode, their dephasing contributions may be more significant than the one from the bending mode at low temperatures. This can be readily understood through the dependence of the Bose–Einstein distribution in Eq. (2).

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5 The frequency- and time-domain data were fitted with the dephasing equation for the multi-mode dephasing model (Eq. (5)), described in the text below. The friction parameter \( \eta_0 \) for the phonon coupling was assumed to be the same as the one for Si(111)-1 \times 1:H. For the bending coupling, \( \omega_0 \) and \( \delta \omega \) obtained with single bending mode was used in this two-mode line width fitting. \( \eta_0 \) for the bending coupling in this case was extracted to be \( \sim 91 \text{ cm}^{-1} \), which is larger than that from line width fitting with single bending mode. Since the experimental data at low temperatures are not enough for a good fitting, \( \delta \omega \) for the phonon coupling and \( \eta_0 \) for the bending coupling thus obtained is meant for a tentative purpose.

6 Because of the deviation at high temperatures for the IR data, it is conceivable that its fitting to the Persson–Rydberg model would not be satisfied.
This is most likely the cause for the above-mentioned discrepancy between the frequency- and time-domain data. Consequently, the proposed multi-mode dephasing model can therefore resolve this issue (see Table 1).

In comparison, the extracted exchange mode on Si(111)-1 × 1:H is at ~ 210 cm⁻¹ [6]. According to previous frequency- and time-domain studies [6,21], this exchange mode is valid for both the low- and high-temperature ranges (from 130 to 470 K) on this surface. The difference in the extracted exchange modes and the associated dephasing coupling mechanisms between Si(111)-1 × 1:H and Si(100)-2 × 1:H thus deserves a further investigation. For Si(100)-2 × 1:H, retaining the tetrahedral bonding configuration of the surface Si dimer atoms results in small relaxations of the subsurface layers [23]. For the Si(111)-1 × 1:H surface, on the other hand, the surface silicon atoms maintain a sp³ configuration. This difference in the local surface structure may lead to a much larger coupling parameter between the SiH stretching and bending modes in Si(100)-2 × 1:H than in Si(111)-1 × 1:H. For a smaller δω in the bending coupling found in Si(111)-1 × 1:H, the dominant dephasing source can thus come from other low-frequency-surface vibrational modes, such as the surface phonon at ~ 200 cm⁻¹. In our previous study [8], the exchange mode for the CH stretch at C(111)-1 × 1:H was determined to be 1200 cm⁻¹, appreciably lower than its bending mode at 1330 cm⁻¹ [24]. The corresponding one at C(100)-2 × 1:H was determined to be ~ 1300 cm⁻¹, which incidentally is very close to the bending frequency obtained by the theoretical calculation [25]. Accordingly, the extracted coupling parameter δω at C(100)-2 × 1:H is also larger than that at C(111)-1 × 1:H. This result agrees with the silicon case and assures the validity of our generalization in the dephasing model.

In this study, we carried out surface Raman measurements on Si(100)-2 × 1:H at various temperatures. The dephasing parameters of the SiH symmetric stretch were thus extracted. We generalized the Perssson–Rydberg model to a multi-mode dephasing model to explain both the frequency- and time-domain data, leading to a better understanding in the dephasing mechanisms for adsorbate systems. In order to further understand the dephasing process on surfaces, the measurements on hydrogenated Ge(111) and Ge(100) surfaces will be performed in the future. Due to the inhomogeneous contribution in the line width, the frequency-domain measurements are thus not feasible at low temperatures. Direct time-resolved measurements using ultrafast laser spectroscopy, therefore, will be carried out in the future to determine the pure dephasing time at all temperatures without the obstruction from the inhomogeneous line width, especially for the very low-temperature regime. Finally, detailed comparative theoretical investigations on the anharmonic couplings between various surface vibrational modes will be pursued in the future to examine the exchange modes at various temperature ranges.

Table 1

<table>
<thead>
<tr>
<th>Surface</th>
<th>( \Omega_\omega ) (cm⁻¹)</th>
<th>( \omega_0 ) (cm⁻¹)</th>
<th>( \delta \omega ) (cm⁻¹)</th>
<th>( \eta_0 ) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(111)-1 × 1:H</td>
<td>2083.7⁺</td>
<td>210 ± 25⁺</td>
<td>-5.03 ± 0.05⁺</td>
<td>52 ± 2⁺</td>
</tr>
<tr>
<td>Si(100)-2 × 1:H</td>
<td>2099⁹</td>
<td>550 ± 150ᵇ</td>
<td>-50 ± 8⁷</td>
<td>59 ± 3⁷ (~ 90)⁷</td>
</tr>
<tr>
<td></td>
<td>2107.6ᶜ</td>
<td>647 ± 79ᶜ</td>
<td>~ 200⁸</td>
<td>~ 35⁸</td>
</tr>
<tr>
<td>C(111)-1 × 1:H</td>
<td>2835.5ᵈ</td>
<td>1200 ± 100⁴ᵈ</td>
<td>-23 ± 3⁴ᵈ</td>
<td>120 ± 3⁴ᵈ</td>
</tr>
<tr>
<td>C(100)-2 × 1:H</td>
<td>2922ᵈ</td>
<td>1300 ± 200⁴ᵈ</td>
<td>-35 ± 9⁴ᵈ</td>
<td></td>
</tr>
</tbody>
</table>

Note that the dephasing parameters at high- and low-temperature ranges for Si(100)-2 × 1:H are listed. The parameters for the low-frequency exchange mode and the number in parentheses were obtained from Eq. (5), described in the text.

⁺Ref. [6]. ⁺Ref. [16]. ⁷This work. ⁸Ref. [8].
Acknowledgements

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