Surface Raman scattering study on the hydrogenated semiconductor surfaces: vibrational dephasing dynamics

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Abstract

Surface Raman scattering has been systematically performed on Ge(100)-2 × 1:H and Ge(111)-1 × 1:H. The temperature-dependent spectral profiles of GeH stretches from 150 to 450 K were analyzed with the Persson–Ryberg dephasing model. The extracted exchange mode for the Ge(100) surface matches the GeH bending mode. However, the corresponding mode for the Ge(111) surface is within the phonon branch. The surface-specific vibrational dephasing behavior can be attributed to the difference in vibrational coupling between the adsorbates and the substrate. This behavior and the similar behavior found for the hydrogenated diamond and silicon surfaces can be explained by a multi-mode dephasing model. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

A study of dephasing of adsorbate vibrational motion is helpful in examining the inhomogeneous contribution and in separating the energy relaxation from the dephasing in the spectral analysis. An analysis of the vibrational spectral profiles can reveal this dynamical information [1]. On the surfaces of semiconductors or insulators, only the coupling to other surface vibrations causes the dephasing. Persson and Ryberg proposed a vibration-phonon stochastic coupling model to explain the temperature-dependent spectral variation: line center shifting and line width broadening [2]. In this simple model, a single exchange mode chosen from the low-frequency surface vibrations is responsible for elastically perturbing the high-frequency adsorbate vibration, leading to vibrational dephasing. With the coupling strength and the friction of this exchange mode, the line center shifting and the line width broadening of the high frequency adsorbate vibration can be characterized. Based on the generalized master equation approach, Liu et al. also derived a consistent model in describing the effects of dephasing on the line center and the line width [3]. Although there have been many experimental and theoretical studies, a complete understanding of the vibrational dephasing for different surface structures still remains elusive. In our recent work, we proposed a multi-mode dephasing model to explain...
the discrepancy between the frequency- and time-domain measurements in Si(100)-2 \times 1:H [4]. The temperature-dependent line center shifting and the line width broadening in the multi-mode dephasing model were generalized as

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

(1)

and

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

(2)

where

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

(3)

\( \delta \omega_i \) is the coupling parameter between the adsorbate vibration, \( \Omega_i \), and the exchange mode, \( \epsilon_i, \eta_i \) is the friction parameter of this exchange mode. In comparison with the study on Si(111)-1 \times 1:H, this multi-model dephasing model also provided a possible explanation for the vibrational dephasing mechanism at different surface configurations.

In principle, all the surface vibrational modes are able to couple with the stretching mode to cause the dephasing. An interesting question can then be raised: why do all the existing frequency-domain studies point to the single-mode dephasing model? In our previous study on Si(100)-2 \times 1:H, we proposed that at least two exchange modes exist simultaneously: the SiH bending mode (650 cm\(^{-1}\)) and the other a low-frequency surface phonon mode (~200 cm\(^{-1}\)). According to the temperature dependence in the dephasing model [Eqs. (1)–(3)], the high-frequency exchange mode is responsible for the dephasing at high temperatures, whereas the low-frequency mode would dominate at low temperatures. Limited by the inhomogeneous line width, the frequency-domain measurements can only reveal the line width broadening at high temperatures. In contrast, the time-domain spectroscopy (surface photon echo) can measure the pure dephasing time without any obstruction from the inhomogeneous contribution [5]. It is the discrepancy between the frequency-domain result at high temperatures and the time-domain result at 100 K that provides a direct proof for the existence of two exchange modes for Si(100)-2 \times 1:H. In this study, we employed surface Raman spectroscopy to examine the temperature-dependent spectral profiles of the GeH stretches on the hydrogenated Ge(100)-2 \times 1 and Ge(111)-1 \times 1 surfaces. Based on the proposed multi-mode dephasing model, we investigated the difference in the dephasing mechanism between the (100) and (111) semiconductor surfaces.

2. Experimental

Surface Raman spectra were measured with an experimental set-up similar to our previous studies on Si(100)-2 \times 1:H [4]. Briefly, the 514.5-nm line of an Ar-ion laser was used to perform the experiments. A cylindrical lens focused the laser beam to a n-type Ge(100) or Ge(111) sample in a UHV chamber (< 5 \times 10\(^{-10}\) Torr). The incident angle of this laser beam was 60°, and the scattered radiation was collected at 60° from the surface normal to maximize the total effective field intensity at surface as well as the Raman collection efficiency [1,10]. The scattered radiation was dispersed by a 640-mm monochromator with a spectral resolution of 5.2 cm\(^{-1}\) and was detected by a LN\(_2\) cooled CCD camera. As-received Ge samples were cleaned by As\(^+\) sputtering (5 kV, 10 \mu A) at 600 K for 1 h, followed by annealing at 1120 K for 10 min. This procedure was repeated more than six times. Inherent carbon on the Ge surfaces could be removed by this sputtering-annealing procedure, as evidenced by Auger electron spectroscopy measurements. After this sputtering-annealing procedure, the Ge surface was then exposed at 500 K to atomic hydrogen (3000 L). This treatment would result in well-ordered hydrogen-terminated Ge(100)-2 \times 1 and Ge(111)-1 \times 1 surfaces, also evidenced by LEED measurements. A series of Raman scattering measurements were performed for the temperatures ranging from 150 to 450 K. The temperature measurement accuracy was determined to be within 20 K. Each Raman spectrum was obtained by summing four 5-min integrated spectra. 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.
3. Results and discussion

The surface Raman spectra of Ge(100)-2 × 1:H and Ge(111)-1 × 1:H are shown in Figs. 1 and 2, respectively. A prominent feature at 1993 cm⁻¹ with a smaller feature at 1982 cm⁻¹ can be identified for Ge(100)-2 × 1:H at 160 K and are assigned to the symmetrical and the anti-symmetrical stretches, respectively. In comparison, the single spectral peak at around 1973 cm⁻¹ for Ge(111)-1 × 1:H is assigned to the GeH stretching mode. The results agree with the results obtained by direct IR absorption [6,7]. Because of the “image” effect on the reflective Ge surface [1], the observed Raman signal for the anti-symmetric mode is much smaller than that for the symmetric mode. For this reason, the temperature dependence on Ge(100)-2 × 1:H is investigated only for the symmetric stretching mode. These Raman spectral features show two characteristic temperature dependences: line center shifting and line width broadening.

The temperature dependences of the line center and the homogeneous line width for Ge(100)-2 × 1:H and Ge(111)-1 × 1:H were obtained after de-convolution of the instrument spectral resolution and the subtraction of the inhomogeneous contribution. Since the GeH bending modes resonate at ~530 cm⁻¹ (Table 1), it emits at least four bulk phonons to relax one vibrational energy of the GeH stretch, resulting in inefficient vibrational energy relaxation. Similar to the cases of Si(100)-2 × 1:H and Si(111)-1 × 1:H, the energy relaxation contribution can thus be negligible in the line width analysis [4,8]. Based on the single-mode dephasing model, the fit of the
Table 1

<table>
<thead>
<tr>
<th>Surface</th>
<th>( \tilde{\nu}_S ) (cm(^{-1}))</th>
<th>( \tilde{\nu}_B ) (cm(^{-1}))</th>
<th>( \tilde{\nu}_0 ) (cm(^{-1}))</th>
<th>( \Delta \tilde{\nu} ) (cm(^{-1}))</th>
<th>( \eta_0 ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge(111)-1×1:H</td>
<td>1973(^a)</td>
<td>...</td>
<td>128±2(^b)</td>
<td>−3.3±2(^b)</td>
<td>144±11(^a)</td>
</tr>
<tr>
<td>Ge(100)-2×1:H</td>
<td>(a) 1993(^a)</td>
<td>...</td>
<td>505±140(^b)</td>
<td>−20±11(^b)</td>
<td>59±3(^b)</td>
</tr>
<tr>
<td>Si(111)-1×1:H</td>
<td>2083(^c)</td>
<td>52(^e)</td>
<td>210±25(^f)</td>
<td>−5.0±0.05(^f)</td>
<td>52±2(^e)</td>
</tr>
<tr>
<td>Si(100)-2×1:H</td>
<td>(a) 2107(^c)</td>
<td>(a) 2099(^e)</td>
<td>647±79(^f)</td>
<td>−30±8(^f)</td>
<td>59±3(^b)</td>
</tr>
<tr>
<td>C(111)-1×1:H</td>
<td>2835(^g)</td>
<td>1332(^f)</td>
<td>1200±100(^g)</td>
<td>−23±7(^g)</td>
<td>120±30(^g)</td>
</tr>
<tr>
<td>C(100)-2×1:H</td>
<td>(a) 2922(^d)</td>
<td>1270(^h)</td>
<td>1300±200(^d)</td>
<td>−35±7(^d)</td>
<td>550±150(^e)</td>
</tr>
</tbody>
</table>

(1), symmetrical mode; (a), anti-symmetrical mode.

\( ^a \) This work.
\( ^b \) Ref. [17].
\( ^c \) Ref. [8].
\( ^d \) Ref. [9].
\( ^e \) Ref. [18].
\( ^f \) Ref. [4].
\( ^g \) Ref. [19].
\( ^h \) Ref. [15].

The line center shifting for Ge(100)-2×1:H, as shown in Fig. 3, yields \( \tilde{\nu}_0 = 505 \text{ cm}^{-1} \) and \( \Delta \tilde{\nu} = -20 \text{ cm}^{-1} \). The extracted \( \tilde{\nu}_0 \) is comparable to that obtained in a previous IR study [9]. Furthermore, the fit of the line width broadening yields \( \tilde{\nu}_0 = 144 \text{ cm}^{-1} \), based on the fitted results on \( \tilde{\nu}_0 \) and \( \Delta \tilde{\nu} \). The inhomogeneous broadening is 1.5 cm\(^{-1}\). In comparison, the line shape analysis for the symmetric stretching mode on Ge(111)-1×1:H leads to \( \tilde{\nu}_0 = 128 \text{ cm}^{-1} \) and \( \Delta \tilde{\nu} = -3.3 \text{ cm}^{-1} \) (Fig. 4). The inhomogeneous broadening is 7.5 cm\(^{-1}\), which is much broader than that of Ge(100)-2×1:H, indicating that an appreciable amount of non-uniform GeH exists on the hydrogenated Ge(111) surface. For comparison,

Fig. 3. Temperature dependence of the line center (solid circles) of the GeH stretch on Ge(100)-2×1:H. The solid curve was obtained from fits of the data to the Persson–Rydberg dephasing model.

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\(^2\) Because the line center for Ge(111)-1×1:H decreases almost linearly with the temperature (Fig. 4), we then fit the line center with the approximated formula \( \Delta \tilde{\nu} = \Delta \tilde{\nu}_0 + \left( \frac{kT}{\tilde{\nu}_0} + 1 \right) \) first to obtain the relation between \( \Delta \tilde{\nu} \) and \( \tilde{\nu}_0 \). The inhomogeneous broadening is 7.5 cm\(^{-1}\), which is much broader than that of Ge(100)-2×1:H, indicating that an appreciable amount of non-uniform GeH exists on the hydrogenated Ge(111) surface. For comparison, no appreciable variation in the total line width was observed over the whole temperature range, not allowing for extracting the friction parameter due to the large inhomogeneous line width.
The exchange mode at C(100)-2×1:H was determined to be \( \sim 1300 \text{ cm}^{-1} \), which is very close to the bending frequency obtained by theoretical calculations [13]. In summary, the exchange mode for the X–H stretch (X = Ge, Si, and C) on the hydrogenated (111) surface is found to be within its bulk phonon branch. However, the exchange mode for the X–H stretch on the hydrogenated (100) surface closely matches its bending frequency.

For C(111)-1×1:H and Si(111)-1×1:H, existing theoretical studies show no relaxation in the surface structure [14,15]. Although no theoretical study is available on Ge(111)-1×1:H, it is conceivable that a similar configuration can be expected.

Comparatively, retaining the tetrahedral bonding configuration of the surface C or Si dimer atoms results in comparable relaxation of the subsurface layers on C(111)-1×1:H or Si(111)-2×1:H [13,16]. A similar surface relaxation on Ge(100)-2×1:H can be expected as well. Because of this structural relaxation, the stretching motion of X–H is strongly coupled with the bending motion. The bending mode is thus the most likely candidate for the exchange mode. In contrast, the ideal tetrahedral configuration for the surface atoms of Ge(111)-1×1:H, the extracted exchange mode at 128 cm\(^{-1}\) is well below the maximum of the Ge bulk phonon [11]. In our previous work, the exchange mode at the high-temperature regime for the SiH stretch on the hydrogenated Si(100)-2×1 surface was attributed to the bending motion of SiH [4]. However, the extracted exchange mode on Si(111)-1×1:H at \( \sim 210 \text{ cm}^{-1} \) was assigned to a low-frequency surface phonon mode [9]. In another previous study [12], 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\(^{-1}\). The corresponding mode at Ge(100)-2×1:H can be identified as the isolated \( S_8 \) surface phonon mode [8,13]. For C(111)-1×1:H, the corresponding \( S_8 \) mode is, however, congested with other phonons [44], possibly yielding a large friction parameter, \( \gamma_0 \), thus preventing the \( S_8 \) mode from becoming the exchange mode and resulting in an exchange mode at a higher frequency (\( \sim 1200 \text{ cm}^{-1} \)), which corresponds to the \( R_1 \) surface phonon mode.

Fig. 4. Temperature dependence of the line center (solid circles) of the GeH stretch on Ge(111)-1×1. The solid curve was obtained from fits of the data to the Persson–Rydberg dephasing model.

Comparing the extracted dephasing parameters as well as the stretching and bending frequencies for the hydrogenated germanium, silicon and diamond surfaces are listed in Table 1.

According to the present Raman measurements, the exchange mode for Ge(100)-2×1:H resonates at 505 cm\(^{-1}\), which closely matches the GeH bending frequency measured by HREELS [10]. For Ge(111)-1×1:H, the extracted exchange mode at 128 cm\(^{-1}\) is well below the maximum of the Ge bulk phonon [11]. In our previous work, the exchange mode at the high-temperature regime for the SiH stretch on the hydrogenated Si(100)-2×1 surface was attributed to the bending motion of SiH [4]. However, the extracted exchange mode on Si(111)-1×1:H at \( \sim 210 \text{ cm}^{-1} \) was assigned to a low-frequency surface phonon mode [9]. In another previous study [12], 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\(^{-1}\). The corresponding

4. Conclusion

In this study, we carried out surface Raman measurements on Ge(111)-1×1:H and Ge(100)-2×1:H at various temperatures. The dephasing parameters for the GeH symmetric stretch were extracted. Comparing the dephasing behaviors on the various semiconductor surfaces, we apply the multi-mode dephasing model to explain the difference in the dephasing mechanism between the (111) and (100) surfaces. Detailed comparative theoretical investigations on the anharmonic couplings between various surface vibrational modes will be pursued in the future to examine the origin of the exchange modes.
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