Vibrational dephasing dynamics at hydrogenated and deuterated semiconductor surfaces: Symmetry analysis

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Raman scattering has been performed on single crystal hydrogenated silicon and germanium surfaces to investigate the temperature dependence of their vibrational spectral profiles. Based on a single-mode dephasing model for pure vibrational dephasing, the frequency shift and line broadening were analyzed to extract the following dephasing parameters: exchange mode frequency, coupling strength, and friction parameter. The exchange modes for the XH stretches on hydrogenated X(100) surfaces (X=Ge, Si, and C) are found to match their respective bending frequencies. The corresponding ones for hydrogenated X(111) surfaces, on the other hand, are located within the bulk phonon. This surface dependence of the exchange mode in surface vibrational dephasing dynamics is correlated with the structural relaxation and its associated symmetry variation at surfaces. It is further confirmed by the experiments performed on deuterated semiconductor surfaces. A site-symmetry induced representation method is exploited to analyze the symmetry properties of the surface vibrations on these two surfaces. This group-theoretical analysis has revealed the selection rules of choosing the dominant exchange modes on hydrogenated semiconductor surfaces. We have identified the exchange modes in the surface phonon spectra of these surfaces according to their symmetry properties. © 2000 American Institute of Physics.

I. INTRODUCTION

When an atom or molecule is adsorbed on a surface, new vibrational normal modes are created. Surface vibrational spectroscopy provides information about the adsorbate–substrate bond from the frequency spectra of such modes. While surface nonuniformity causes the inhomogeneous broadening of these vibrational spectra, vibrational energy relaxation and dephasing contribute to the homogeneous linewidth. The vibrational energy relaxation rate governs surface phenomena such as sticking, desorption, and diffusion, which influence surface chemistry. Because vibrational dephasing usually dominates the homogeneous linewidth, the study of dephasing dynamics, on the other hand, helps in determining the inhomogeneous contribution to the line shape and in revealing surface uniformity.1 Furthermore, Persson et al. have recently shown that the vibrational energy relaxation rate of an ordered adlayer may be strongly affected by pure dephasing processes.2 The theoretical and experimental investigations of surface vibrational dephasing are therefore crucial in extracting dynamical information at surfaces.

Vibrational dephasing dynamics at surfaces in the past two decades has been largely carried out in the systems of molecules adsorbed on metallic surfaces (such as CO/metal and NO/metal). Temperature dependence of the vibrational spectra was measured. The experimental data were consistently interpreted based on a so-called "exchange-mode dephasing model," where the observed high-frequency vibrations of adsorbed molecules are coupled locally to thermally excited low-frequency surface vibrational modes.3 On the other hand, H/Si(100)4 and H/Si(111)5 were the only two dynamic studies at semiconductor surfaces: The dynamics of both vibrational dephasing and energy relaxation of the SiH stretch were further investigated with time-resolved spectroscopic techniques.6 The dynamics of vibrational dephasing were also studied based on the exchange-mode dephasing model. However, at that time, it still remained to be resolved whether one or many modes contribute to the pure dephasing in these two systems. Further, the principles in selecting the exchange mode had not been worked out.

There are two questions regarding the issue of selecting the exchange mode from among all the vibrational modes existing at surfaces. First, what is the difference in the exchange modes for the molecules adsorbed on surfaces of the same substrate material but with different structures? For example, the extracted exchange modes of Si(100)-2×1:H4 and Si(111)-1×1:H3 resonate at two different frequencies, while no explanation was given for this discrepancy. Second, in addition to the propensity rules from the exchange-mode dephasing model, what are the consistent selection rules for...
the exchange mode according to the symmetry properties of surface vibrations? The vibrational dephasing dynamics at metallic surfaces seemingly do not depend on the surface structures underneath. Can this behavior be predicted similarly in the cases of semiconductor surfaces, in which strong reconstruction is undergone?

To construct a consistent vibrational dephasing model for various chemisorbed semiconductor surfaces and to extend it to molecules adsorbed on metals, we performed a series of systematic surface Raman spectroscopic studies on hydrogenated and deuterated semiconductor surfaces (silicon and germanium). Together with the vibrational dephasing studies on hydrogenated diamond surfaces, sensible answers can then be provided for the above-posed questions. In this investigation, the reasons for choosing hydrogen as the adsorbed species to study are twofold. First, hydrogen is the simplest element such that no complication is expected in the sample preparation as well as in the structures and properties of hydrogen-terminated semiconductor surfaces. Hydrogenated semiconductor surfaces are therefore well studied both experimentally and theoretically. Using hydrogenated semiconductor surfaces as a model system, should pave the way for investigating the vibrational dynamics at surfaces adsorbed by other molecules. Second, the preparation of hydrogen-terminated semiconductor surfaces is an essential intermediate step in growing epitaxial semiconductor thin films with chemical vapor deposition. Studying the vibrational dynamics on these hydrogenated surfaces would help in revealing the kinetics of surface chemistry.

In Sec. II, the exchange-mode dephasing model is first described briefly. The symmetry analyses of hydrogenated semiconductor surfaces and their associated surface vibrations are presented. With these two theoretical investigations, we attain the consistent selection rules for the exchange modes for these surfaces. The experimental setup and procedures are given in Sec. III. Section IV presents the results of surface Raman measurements and the analysis based on the exchange-mode dephasing model. In Sec. V, we discuss and compare the extracted dephasing parameters of these hydrogenated and deuterated semiconductor surfaces. The selection rules are exploited to interpret the experimental results and the exchange modes are thus assigned. Finally, Sec. VI concludes this study.

II. THEORY

A. Vibrational dephasing of surface adsorbates

The vibrational line shape of a molecule on a flat surface is the result of several microscopic dynamical couplings. The coupling mechanisms include emission of electron–hole pairs, emission and absorption of phonon, dephasing by surface phonons or other vibrational modes, and dephasing by electron–hole pairs. On the surfaces of semiconductors or insulators the vibrational energy of the surface vibrational mode is usually much smaller than the energy band gap, the minimum energy required for electron–hole pair excitation of the substrate. The line shapes of these surface modes are therefore affected mainly by (1) dephasing via other surface vibrational motions and (2) emission and absorption of other surface phonons. For these two coupling-induced line-broadening mechanisms, the characteristic dephasing time \( T_2 \) obtained from spectral linewidth analysis is composed of two parts,

\[
\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{1}{2T_1},
\]

where \( T_2^* \) is the pure dephasing time and \( T_1 \) is the energy relaxation time. In this study, because the systems under study are diamond, silicon, and germanium, we will focus only on the vibrational dephasing and energy relaxation induced by vibron–phonon coupling.

In the exchange-mode dephasing model, the (thermally induced) temporary excitation of a low-frequency mode \( \omega_0 \) (exchange mode) modulates the resonant excitation of a high-frequency oscillator \( \Omega \) under consideration. This results in both a frequency shift and a broadening of the high-frequency vibration. This exchange-mode dephasing model was first derived by Anderson and Kubo to explain dynamical phenomena in nuclear spin relaxation. Later on, it was applied to the energy and phase relaxation of vibrational excitations of molecules in condensed phases. Persson, Hoffmann, and Ryberg extended this exchange-mode dephasing model to the analysis of the observed temperature-dependent frequency shift and line broadening of CO stretch on metals. Based on a generalized master equation approach, Liu et al. have derived a consistent anharmonic vibron–phonon coupling model in describing the effects of dephasing and energy relaxation on the vibrational line shape of adsorbed surfaces. Under quasimode approximation, they reached similar equations for pure dephasing. According to their derivation, the line center shift (\( \Delta \Omega \)) and the linewidth (\( \Gamma \)) are given by

\[
\Delta \Omega = \delta \omega \cdot (n_0 + 1/2)
\]

and

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

where

\[
n_0 = 1/(e^{h \omega_0/kT} - 1).
\]

\( \delta \omega \) is the coupling parameter between the high-frequency adsorbate vibration, \( \Omega \), and the exchange mode, \( \omega_0 \). \( \eta_0 \) is the friction parameter of the exchange mode. This model is also called the “single-mode dephasing model.” Their complete model further indicated the possibility of existing multiple exchange modes to elastically perturb the high-frequency adsorbate vibration, although previous experimental observations pointed to a single exchange mode.

In our recent work, we have proposed a “multimode dephasing model” to explain the discrepancy between the frequency- and time-domain measurement on Si(100)-2×1:H. The temperature-dependent line center shifting \( \Delta \Omega_{\text{tot}} \) and the linewidth broadening \( \Gamma_{\text{tot}} \) in the multimode dephasing model were generalized as

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

and

\[
\Gamma_{\text{tot}} = \sum_i \frac{1}{T_i} + \sum_{i,j \neq i} \frac{1}{2T_{ij}},
\]
\[
\Gamma_{\text{tot}} = \sum_{i} 2(\delta \omega_{i})^{2} n_{i}(n_{i}+1)/\eta_{i},
\]
where
\[
\delta \omega_{i} = 1/(e^{\hbar \omega_{i}/kT} - 1).
\]

\(\delta \omega_{i}\) is the coupling parameter between the adsorbate vibration and the exchange mode, \(\omega_{i}\), \(\eta_{i}\) is the friction parameter of this exchange mode. Depending on the temperature range, the experimental observation may result in single exchange mode because the thermal population of the exchange mode [Eq. (7)] is highly temperature sensitive.

In sum, the guidelines for selecting the exchange mode for a high-frequency adsorbate vibration can be described in the following. First, according to Eq. (3), the exchange mode should have a strong coupling strength (\(\delta \omega\)) with the adsorbate vibration. Second, according to the same equation, the exchange mode should have a small friction parameter (\(\eta\)). That is, the exchange mode should be fairly isolated from other low-frequency vibration modes. This is the so-called “motional narrowing” in the studies of nuclear spin relaxation. The second selection principle for the exchange mode in fact rules out the possibility of the projected bulk phonons contamination. The exchange mode should have a strong coupling strength (~\(\delta \omega\)) and the exchange mode should have a small friction parameter (~\(\eta\)).

In the present study, this approach is followed to analyze the symmetry properties of surface vibrations. In many problems of solid-state physics it is often necessary to determine the irreducible representations of the space group of a crystal contained in a tensor field representation, a reducible representation of the space group whose basis functions are components of a tensor defined on the atoms of the crystal. In lattice vibrational problems, for example, the basis functions of the tensor field representation are components of a three-component polar vector defined on each atom. The vibrational field representation \(D_{V}^{G_{0}}\) is the direct product of a vibrational representation \(D_{V}^{G_{0}}\) and a permutational representation \(D_{p}^{G_{0}}\), i.e., \(D_{V}^{G_{0}} = D_{V}^{G_{0}} \times D_{p}^{G_{0}}\). The vibrational representation \(D_{V}^{G_{0}}\) is the representation of the space group \(G_{0}\) with the wave vector \(\mathbf{k} = 0\) and in the general case is a sum of several irreducible representations of the space group \(G_{0}\), i.e., \(D_{V}^{G_{0}} = \sum_{i} D_{V}^{G_{0}}(\mathbf{q}_{i})\), where \(\mathbf{q}_{i}\) represent the Wyckoff positions occupied by crystal atoms and \(D_{V}^{G_{0}}(\mathbf{q}_{i})\) are the simple induced representations with respect to \(\mathbf{q}_{i}\). Accordingly, the vibrational field representation is a direct sum of the band representations, \(\langle \mathbf{q}_{j}, \beta_{j}^{(i)} \rangle\), induced by the site symmetry group \(G(\mathbf{q}_{j})\), i.e.,

\[
D_{V}^{G_{0}} = \sum_{i,j} \langle \mathbf{q}_{j}, \beta_{j}^{(i)} \rangle = \sum_{i,j} \left\langle \mathbf{q}_{j}, \sum_{i} \beta_{j}^{(i)} \right\rangle.
\]
are three Wyckoff positions:

\[ \begin{align*}
K & = (0,0,0) \\
M & = (1/2,1/2,0) \\
L & = (1/2,0,1/2)
\end{align*} \]

Hydrogenated semiconductor reconstruction-induced symmetry variation exists on the hydrogen atom. The direct projection of the Wyckoff positions is the first- and second-layer substrate atoms. The region encircled by the dashed line is the unit cell. \( a_1 \) and \( a_2 \) are the basis vectors of the unit cell.

2. Phonon symmetries of X(111)-1\times1:H and X(100)-2\times1:H

To model the vibrational structure of a crystalline surface, the surface is approximated by a slab of finite thickness (a diperiodic system)\(^{25}\) instead of atoms on a surface plane, because in general cases more than one layer of atoms are involved in the surface vibrations. A system with diperiodic symmetry has an infinite periodicity in only two dimensions but additionally allows symmetry elements that may affect the nonperiodic third dimension, e.g., a reflection plane in the two dimensions. There exist 80 diperiodic space groups (DG)\(^{25}\). The table of simple induced representations of DG can be deduced from the simple induced representations of the related 3D space group \( G_0 \) (Ref. 21) by striking out the simple induced representations of \( G_0 \) for the points \( \mathbf{q} \) which are not contained in the set of Wyckoff positions for the group DG and then, crossing out those \( \mathbf{k} \) vectors that do not lie in the 2D Brillouin zone of the group DG\(^{20}\).

The surface structures of the group IV semiconductors have many similarities. Although they all have a bulk diamond structure, their bare surfaces may exhibit different phases, because of the difference in bonding strength and distance. Through proper annealing and hydrogen adsorption processes, the hydrogenation of X(111) and X(100) surfaces can result in identical monohydride phases: X(111)-1\times1:H or X(100)-2\times1:H (X=Ge, Si, and C). The hydrogenated surface of X(111) has the unreconstructed (1\times1) structure with one normally oriented bond on each surface atom (see Fig. 1), and these bonds are capped by hydrogen atoms. X(111)-1\times1:H belongs to the diperiodic space group \( p3m1 \), corresponding to the 3D space group \( C_{3v}^{1} \). The 2D space group of each layer of atoms is the direct projection of the 3D space group on the (111) surface. That is, no reconstruction-induced symmetry variation exists on the hydrogenated semiconductor (111) surfaces. In this DG, there are three Wyckoff positions: (a) \((0,0,0)\), (b) \((1/3,2/3,z)\), and (c) \((2/3,1/3,z)\). Their site symmetry groups are all \( 3m \left( C_{3v}^{1} \right) \). The surface unit cell and the corresponding 2D Brillouin zone are shown in Fig. 1. The most interesting points in the Brillouin zone are \( \Gamma (k=0) \), \( M (k=b_1/3+b_2/3) \), and \( K (k=b_1/2) \), where \( b_1 \) and \( b_2 \) are the basis vectors in the reciprocal space. The induced representations induced by the site symmetry groups at these Wyckoff positions are shown in Table I.

In contrast, the X(100) monohydride phase has a dimer structure where the dangling bonds (one on each surface atom) are capped by hydrogen (see Fig. 2). X(100)-2\times1:H, therefore, belongs to the diperiodic space group \( p\overline{1}1m \) with a mirror symmetry operation \( \sigma_g \) corresponding to the 3D space group \( C_5 \). The surface unit cell and the corresponding 2D Brillouin zone are shown in Fig. 2. The direct projection of this 3D space group on the (100) surface is, on the other hand, the 2D space group \( p4mm \). That is, the surface reconstruction lowers the surface symmetry from \( p\overline{4}mm \) to \( p11m \). Notice that since Kovalov only gives the 3D induced representations with a mirror symmetry operation \( \sigma_g \), the induced representations have to be modified accordingly. In this DG, there are two Wyckoff positions: (a) \((a,0,0)\) and (b) \((a,1/2,0)\). Their site symmetry group is \( m \left( C_{1} \right) \). The most interesting points in the Brillouin zone are \( \Gamma (k=0) \), \( J (k=b_1/2) \), \( J' (k=b_2/2) \), and \( K (k=b_1/2+b_2/2) \), where \( b_1 \) and \( b_2 \) are the basis vectors in the corresponding reciprocal space. The representations induced by the site symmetry groups at these Wyckoff positions are shown in Table II.

Within the unit cell of X(111)-1\times1:H (Fig. 1), the H atom as well as the first-layer X atom (X\(_1\)) occupies the Wyckoff position (b). On the other hand, the second-layer X atom (X\(_2\)) occupies the Wyckoff position (a). Combined with the simple induced representation of \( p3m1 \) (Table I) and Eq. (8), the phonon symmetry of X(111)-1\times1:H is depicted in Table III. For the hydrogen atom, its vibrational field representation at the zone center (\( \Gamma \)) is then given by

### Table I. Simple induced representations of the \( p3m1 \) diperiodic space group

<table>
<thead>
<tr>
<th>( \tilde{q} )</th>
<th>( \beta )</th>
<th>( \Gamma )</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a ( a_1(z) )</td>
<td>( \Gamma_1 )</td>
<td>( M_1 )</td>
<td>( M_3 )</td>
<td>( M_2 )</td>
<td>( K_1 )</td>
<td></td>
</tr>
<tr>
<td>b ( a_2 )</td>
<td>( \Gamma_2 )</td>
<td>( M_1 )</td>
<td>( M_3 )</td>
<td>( M_2 )</td>
<td>( K_2 )</td>
<td></td>
</tr>
<tr>
<td>c ( e(x,y) )</td>
<td>( \Gamma_3 )</td>
<td>( M_2+M_3 )</td>
<td>( M_1+M_2 )</td>
<td>( M_1+M_3 )</td>
<td>( K_1+K_2 )</td>
<td></td>
</tr>
</tbody>
</table>

![FIG. 1. Top view of X(111)-1\times1:H surface (left-hand panel). The closed circles show the positions of the hydrogen ions and open circles represents X (C, Si, and Ge) ions. The right-hand panel is its related two-dimension Brillouin zone. \( X_1 \) and \( X_2 \) are the first- and second-layer substrate atoms. The region encircled by the dashed line is the unit cell. \( a_1 \) and \( a_2 \) are the basis vectors of the unit cell.](image1)

![FIG. 2. Top view of X(100)-2\times1:H surface structure (left-hand panel), with the two-dimension Brillouin zone (right-hand panel). Closed circles indicate H atoms, while open circles indicate X (C, Si, and Ge) ions. \( X_1 \), \( X_2 \), and \( X_3 \) are the first-, second-, and third-layer substrate atoms. The region encircled by the dashed line is the unit cell. \( a_1 \) and \( a_2 \) are the basis vectors of the unit cell.](image2)
their site symmetries are all \( Cs \) group. There are three Wyckoff positions corresponding to two sagittal vertical modes and one mixed \( M \) is given by

\[
G(X) = 2K_1 + K_2, \tag{10}
\]

(9) corresponding to one stretching mode \( (\Gamma_1) \) and two degenerate bending modes \( (\Gamma_3) \). The two degenerate bending modes are split at \( M \) and \( K \) points. For the \( X \) atom on the first layer \( (X_1) \), its vibrational field representation at \( K \) is given by

\[
K(X_1) = 2K_1 + K_2, \tag{10}
\]

(9) corresponding to two sagittal vertical modes and one mixed mode. The vibrational field representation of the \( X_1 \) atom at \( M \) is given by

\[
M(X_1) = M_1 + M_2 + M_3. \tag{11}
\]

It also corresponds to single sagittal vertical mode and two mixed modes.

Within the unit cell of \( X(100)\text{-}2\times1\text{-}H \) (Fig. 2), the two \( H \) atoms as well as the two first-layer \( X \) atoms \( (X_1) \) occupy the Wyckoff position \( b \). On the other hand, the second- and third-layer \( X \) atoms \( (X_2 \) and \( X_3 \) occupy the Wyckoff position \( a \). Combined with the simple induced representation of \( p\overline{1}lm \) (Table II) and Eq. (8), the phonon symmetry for the \( X(100)\text{-}2\times1\text{-}H \) surface is listed in Table IV. For the two hydrogen atoms, their vibrational field representations at the zone center \( (\Gamma) \) are then given by

\[
G(2H) = 4\Gamma_1 + 2\Gamma_2 = 2a'(x) + 2a'(z) + 2a''(y), \tag{12}
\]

(12) corresponding to one symmetric stretching \( [\Gamma_1(z)] \), one symmetric bending \( [\Gamma_1(x)] \), one antisymmetric stretch \( [\Gamma_1(x)] \), one antisymmetric bending \( [\Gamma_1(x)] \), one symmet-

\begin{table}[h]
\centering
\caption{Phonon symmetry of \( X(111)\text{-}1\times1\text{-}H \) with space group \( p\overline{3}m1 \). \( X_1 \) and \( X_2 \) represent the \( X \) atoms at the first and second layers, respectively. The related Wyckoff positions are given in the parentheses of the second column from the left. The positions of \( \Gamma, M, \) and \( K \) in the Brillouin zone are given in the first row from the top. The symmetries of the two Wyckoff positions and the three points in the Brillouin zone are also given.}
\begin{tabular}{|l|l|l|l|l|l|l|}
\hline
\( q \) & \( \beta \) & \( \Gamma \) & \( J \) & \( J' \) & \( K \) & \\
\hline
\( a \) & \( a'(x,z) \) & \( \Gamma_1 \) & \( J_1 \) & \( J'_1 \) & \( K_1 \) & \\
\hline
\( b \) & \( a''(y) \) & \( \Gamma_2 \) & \( J_2 \) & \( J'_2 \) & \( K_1 \) & \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Phonon symmetry of \( X(100)\text{-}2\times1\text{-}H \) with space group \( p\overline{1}lm \). \( X_1, X_2, \) and \( X_3 \) represent the \( X \) atoms at the first, second, and third layers, respectively. The related Wyckoff positions are shown in the parentheses of the second column from the left. The positions of \( \Gamma, J, J', \) and \( K \) in the Brillouin zone are shown in the first row from the top. The symmetries of the two Wyckoff positions and the four points in the Brillouin zone are also given.}
\begin{tabular}{|l|l|l|l|l|l|l|l|l|l|l|l|l|}
\hline
\( q \) & \( \beta \) & \( \Gamma \) & \( J \) & \( J' \) & \( K \) & \\
\hline
\( (0, 0) \) & \( (1/2, 0) \) & \( (0, 1/2) \) & \\
\hline
\( \alpha \) & \( a'(x,z) \) & \( \Gamma_1 \) & \( J_1 \) & \( J'_1 \) & \( K_1 \) & \\
\( \beta \) & \( a''(y) \) & \( \Gamma_2 \) & \( J_2 \) & \( J'_2 \) & \( K_1 \) & \\
\hline
\end{tabular}
\end{table}

\begin{table}[h]
\centering
\caption{Phonon symmetry of \( X(111)\text{-}1\times1\text{-}H \) with space group \( p\overline{3}m1 \). \( X_1 \) and \( X_2 \) represent the \( X \) atoms at the first and second layers, respectively. The related Wyckoff positions are given in the parentheses of the second column from the left. The positions of \( \Gamma, M, \) and \( K \) in the Brillouin zone are given in the first row from the top. The symmetries of the two Wyckoff positions and the three points in the Brillouin zone are also given.}
\begin{tabular}{|l|l|l|l|l|l|}
\hline
\( q \) & \( \beta \) & \( \Gamma \) & \( M \) & \( K \) & \\
\hline
\( (0, 0, z) \) & \( C_3 \) & \( a_1(z) \) & \( \Gamma_1 \) & \( M_1 \) & \( K_1 \) & \\
\hline
\( (1/3, 2/3, z) \) & \( C_3 \) & \( e(x,y) \) & \( \Gamma_3 \) & \( M_2 + M_3 \) & \( K_1 + K_2 \) & \\
\hline
\end{tabular}
\end{table}

Surface phonon spectra of several hydrogenated semiconductor surfaces have been calculated using the semi-empirical total-energy approach,\textsuperscript{26} density functional theory,\textsuperscript{27} and tight-binding model.\textsuperscript{28} The results by Pollmann and co-workers will be used in this investigation, because their semiempirical method gives the best match with the experimental data and their results cover most systems of interest. Relating to this study, they have calculated the surface phonon spectra of \( C(111)\text{-}1\times1\text{-}H \),\textsuperscript{29} \( C(100)\text{-}2\times1\text{-}H \),\textsuperscript{30} \( Si(111)\text{-}1\times1\text{-}H \),\textsuperscript{31} and \( Si(100)\text{-}2\times1\text{-}H \).\textsuperscript{32} The surface phonon spectra of \( Ge(111)\text{-}1\times1\text{-}H \) and \( Ge(100)\text{-}2\times1\text{-}H \) are still not available to our knowledge. For \( Si(111)\text{-}1\times1\text{-}H \),\textsuperscript{31} the stretching and bending modes are energetically decoupled from the substrate modes. According to the above-mentioned symmetry analysis, the stretching mode at the zone center has an irreducible representation \( \Gamma_1 \) related to the site symmetry \( a_1(z) \), while the bending mode has an irreducible representation \( \Gamma_1 \) related to the site symmetry \( e(x,y) \). Similarly, the stretching mode of \( C(111)\text{-}1\times1\text{-}H \) also corresponds to the irreducible representation \( \Gamma_1 \) . However, according to the calculation,\textsuperscript{29} its bending vibration is split into three modes \( (B_1, B_2, \) and \( B_3 \) ) because of the strong coupling with the bulk phonons. As pointed out by Sandfort, Mazur, and Pollmann,\textsuperscript{28} the H adlayer and the first two diamond layers strongly contribute to \( B_2 \) and \( B_3 \), which is also reflected by the strong dispersion in these bending modes. In addition to the Rayleigh wave and the Lucas mode, there exist several isolated surface phonons in the gaps of the projected bulk-phonon spectra (PBPS) of H:C(111)\textsuperscript{29} and H:Si(111).\textsuperscript{31} Their respective symmetry properties will be further discussed later to explain the anharmonic coupling behaviors in vibrational dynamics. For \( X(100)\text{-}2\times1\text{-}H \), the surface possesses a dimer structure with two tilted XH bonds in the unit cell. The stretching mode is split into symmetric and antisymmetric...
stretches modes ($S_x$ and $S_a$) with the irreducible representations $\Gamma_1(z)$ and $\Gamma_1(x)$, respectively. The SiH bending vibration of Si(100)-2×1:H is split into four modes: $B_1(\Gamma_1(z))$, $B_2(\Gamma_1(x))$, $B_{1g}(\Gamma_2(y))$, and $B_{2g}(\Gamma_2(y))$.\textsuperscript{32} Because of the strong coupling with the bulk phonons, the bending vibration of C(100)-2×1:H is, on the other hand, split into seven bending modes: $B_{1s}$, $B_{2s}$, $B_{a1}$, $B_{a2}$, $B$, $B_1$, and $B_2$.\textsuperscript{30} Similar to the case of C(111)-1×1:H, the carbon atoms have to be involved in the phonon symmetry analysis of the bending motion.

### III. EXPERIMENTAL SETUP AND PROCEDURES

The vibrational spectra of SiH/D and GeH/D stretches on Si and Ge surfaces were measured with surface Raman scattering. The experiments were carried out in two separate ultrahigh vacuum chambers. The detailed description of both chambers and the Raman setup have been described previously.\textsuperscript{14(c)} Briefly, the first chamber (base pressures <2 × 10^{-10} Torr) was equipped with a reverse view low-energy electron diffraction optics for surface structure determination and an Auger electron spectrometer (AES) for surface chemical characterization. The single-crystal sample was first degreased by ultrasonic cleaning in acetone and methanol solvents. The crystal was then mounted on a temperature-controlled sample holder. By the combination of resistive heating and liquid nitrogen, the sample temperature can be varied from above 1300 to 100 K. After inserted into the chamber, the sample was alternatively cleaned by Ar\textsuperscript{+}-ion sputtering at 600 K, followed by annealing at ~1300 K for Si surfaces and at ~1100 K for Ge surfaces. The sample was then essentially free of contamination within our AES detection limit. After the sample cleaning and annealing process, the hydrogen or deuterium gas was leaked to the chamber at 5×10^{-6} Torr at the threshold of the hydrogen/deuterium desorption temperature (600 K for Si and 500 K for Ge). Atomic hydrogen was then produced by the decomposition of molecular hydrogen (deuterium) on an 1800 K tungsten filament placed ~3 cm in front of the sample. For all the hydrogenated and deuterated semiconductor surfaces, the sample preparation procedures were determined after the confirmation of surface structures and cleanliness. The same procedures were then followed to prepare samples in the second chamber.

The optical setup is shown in Fig. 3. The Ar-ion laser beam at ~350 mW was incident to the sample through a viewport on the second chamber and the scattered radiation was collected through another viewport, 90° to the incident laser beam direction. We chose a Raman geometry such that the total effective field intensity at surface as well as the Raman collection efficiency can be maximized.\textsuperscript{15(c)33} A laser line filter blocked the residual plasma lines accompanied in the laser beam and a half-wave plate varied the laser polarization. The collected radiation was sent through a super-notch filter or a long-pass filter to a 640 mm monochromator. The dispersed spectra were detected and accumulated by a liquid-nitrogen cooled charge-coupled device (CCD) camera. To prevent huge spikes caused by a cosmic ray coinciding with the vibrational peaks, each accumulation of spectrum from the CCD was limited to 5 min. The reported spectra were represented an average of 4 to 16 times for 5-minute integrations, depending on the signal level. For each sample, the number of average times was fixed over the whole temperature range. To obtain the temperature dependence of the adsorbate vibrational spectra, a series of Raman scattering measurements were performed for the temperatures ranging from 150 to 500 K. In all of our studies on X(100)-2×1:H/D, the observed signal of the XH/D symmetric stretch is always much larger than that of the antisymmetric stretch. This is because the “image” effects on the reflective surfaces\textsuperscript{33} enhance the vertical transition dipole from the symmetric stretch and partially cancel the parallel transition dipole from the antisymmetric stretch. On the X(100) surfaces, we therefore focus only on the XH/D symmetric stretch.

The instrument spectral resolution for the slit width at 100 μm was calibrated to be 5.2 cm\textsuperscript{-1} by measuring the linewidth of the residual plasma lines. A combination of sharp plasma emission lines from Ar and Hg arc lamps was used to precisely calibrate the wavelength positions in the spectral region of interest. The resultant spectral error with this method was less than 0.1 cm\textsuperscript{-1}. Furthermore, the inhomogeneous contribution to the spectra is presumably Gaussian as well. With the knowledge of this combined Gaussian width caused by the instrument-limited resolution and the inhomogeneous broadening, the Lorentzian linewidth and the band center can thus be determined by fitting a Voigt profile to the Raman spectra. The detailed considerations in fitting the spectral profile have been described in Ref. 16.

### IV. RESULTS AND ANALYSIS

According to the infrared absorption study by Dumas et al.,\textsuperscript{34} the extracted exchange mode on Si(111)-1×1:H\textsuperscript{11} resonates at ~210 cm\textsuperscript{-1}, which is much smaller than the SiH bending frequency.\textsuperscript{34} Their result is consistent with the time-domain study by Guyot-Sionnest.\textsuperscript{35} The earlier study on Si(100)-2×1:H, on the other hand, yielded an exchange mode at ~550 cm\textsuperscript{-1}, which is close to the SiH bending mode.\textsuperscript{4} 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 further investigation. In our previous work,\textsuperscript{5} the exchange mode for...
the CH stretch on C(111)-1×1:H was determined to be \( \sim 1200 \text{ cm}^{-1} \), appreciably lower than its bending mode at 1330 cm\(^{-1}\). In contrast, the corresponding one for C(100)-2×1:H was determined to be \( \sim 1300 \text{ cm}^{-1} \), which incidentally is very close to the bending frequency obtained by theoretical calculation.\(^{29}\) The extracted coupling parameter \( \delta \omega \) for C(100)-2×1:H is also larger than that for C(111)-1×1:H. This result agrees with the silicon case, leading to the conclusion that the exchange modes for Si(100)-2×1:H and C(100)-2×1:H are their respective bending modes and those for Si(111)-1×1:H and C(111)-1×1:H are from lower-frequency vibrational modes that are located in their respective bulk phonon branches.

In the present study, after saturation exposure to atomic hydrogen at \( \sim 500 \text{ K} \), germanium surfaces exhibit monohydride phases. A series of temperature-dependence measurements on the Ge stretch have been carried out on Ge(100) and Ge(111) surfaces\(^{37}\) to extend the surface vibrational dynamics study. Similar to the case of Si(100)-2×1:H, the temperature dependence on Ge(100)-2×1:H was investigated only for the symmetric stretching mode. The temperature dependencies of the line center and the homogeneous linewidth for Ge(100)-2×1:H and Ge(111)-1×1:H were obtained after the deconvolution of the instrument spectral resolution and the subtraction of the inhomogeneous contribution. Similar to our previous study on Si(100)-2×1:H,\(^{16}\) the energy relaxation contribution is neglected in the linewidth analysis, because it involves at least four-phonon emission and is much slower than the dephasing process. For the GeH symmetric stretch on Ge(100)-2×1:H, the fit of the line center shifting yields \( \omega_0 = 505 \pm 145 \text{ cm}^{-1} \) and \( \delta \omega = -20 \pm 11 \text{ cm}^{-1} \). The extracted \( \omega_0 \) is comparable to the one obtained in the earlier IR study.\(^{4}\) Furthermore, the fit of the linewidth broadening yields \( \eta_0 = 144 \pm 11 \text{ cm}^{-1} \), based on the fitted results on \( \omega_0 \) and \( \delta \omega \). The inhomogeneous broadening is 1.5 cm\(^{-1}\). In comparison, the line shape analysis of the GeH stretching mode at Ge(111)-1×1:H results in \( \omega_0 = 128 \pm 93 \text{ cm}^{-1} \) and \( \delta \omega = -3.3 \pm 2.6 \text{ cm}^{-1} \). In this case, no appreciable variation in the total linewidth was observed over the whole temperature range, thus not allowing for extraction of the friction parameter due to a large inhomogeneous linewidth. The inhomogeneous broadening is 7.5 cm\(^{-1}\), which is much broader than that of Ge(100)-2×1:H, indicating that a large amount of nonuniform GeH adsorbates exist on the hydrogenated Ge(111) surface. With surface Raman scattering, a detailed investigation on the kinetics of the hydrogenation process on this surface has been performed.\(^{16}\)

The extracted dephasing parameters as well as the stretching and bending frequencies for the hydrogenated germanium, silicon, and diamond surfaces are summarized in Table V. According to these 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 high-resolution electron energy-loss spectroscopy.\(^{38}\) For Ge(111)-1×1:H, the extracted exchange mode at 128 cm\(^{-1}\) is well below the maximum of the Ge bulk phonon.\(^{39}\) In summary, the exchange mode for the X–H stretch (X=Ge, Si, and C) at the hydrogenated (111) surface is found to be within its bulk phonon branch. On the other hand, the exchange mode for the X–H stretch at the hydrogenated (100) surface closely matches its bending frequency.

In order to confirm the above-mentioned conclusions, we have further performed the temperature dependence measurements of the SiD and GeD stretches at Si(100), Ge(100), and Ge(111) surfaces, respectively. For Si(100) and Ge(100), the exchange modes come from their corresponding bending modes and, therefore, the extracted exchange modes for Si(100)-2×1:D and Ge(100)-2×1:D should have isotope shifts. The temperature dependence of the line center of the SiD stretch mode at Si(100)-2×1:D is shown in Fig. 4. The fit of the line center shifting for Si(100)-2×1:D yields \( \omega_0 = 293 \pm 113 \text{ cm}^{-1} \) and \( \delta \omega = -11 \pm 6 \text{ cm}^{-1} \). Furthermore, the corresponding one for the GeD stretch at Ge(100)-2×1:D is shown in Fig. 5. The fit of the line center shifting for Ge(100)-2×1:D yields \( \omega_0 = 346 \pm 180 \text{ cm}^{-1} \) and \( \delta \omega = -15 \pm 12 \text{ cm}^{-1} \). In both cases, the extracted exchange modes are appreciably lower than the corresponding ones for hydrogenated surfaces. In contrast, Fig. 6 shows the temperature dependence of the line center of the GeD stretching frequency.

\[ \text{FIG. 4. Temperature dependence of the line center (closed circles) of the SiD stretch at Si(100)-2×1:D. The solid curve was obtained from a fit of the data to the exchange-mode dephasing model.} \]

\[ \text{FIG. 5. Temperature dependence of the line center (closed circles) of the GeD stretch at Ge(100)-2×1:D. The solid curve was obtained from a fit of the data to the exchange-mode dephasing model.} \]
at Ge(111)-1×1:D. The fit of the line center shifting yields \( \omega_0 = 115 \pm 37 \text{ cm}^{-1} \) and \( \delta \omega = -3.7 \pm 1.2 \text{ cm}^{-1} \). In this case, the extracted exchange mode, on the other hand, is identical to that for Ge(111)-1×1:H (128 cm\(^{-1}\)) within the experimental error. The fitted results on the deuterated semiconductor surfaces are also listed in Table V. These experimental results lead to the consistent conclusion that indeed it is the XH/D bending modes causing the vibrational dephasing of the XH/D stretching modes at X(100)-2×1:H/D. The exchange modes for X(111)-1×1:H/D, on the other hand, come from other lower frequency surface vibrations.

V. DISCUSSION

In the consideration of the effects of phonon symmetry on surface vibrational dynamics, several key issues need to be addressed in advance. First, as discussed previously, to ensure a nonzero anharmonic coupling for vibrational dephasing, the symmetric representation of the high-frequency adsorbate mode is required to contain the same irreducible representation of the low-frequency exchange mode. Second, according to Eq. (3), the symmetry-allowed vibrational mode with a very narrow spectral width (small \( \eta_0 \)) is a possible candidate of the exchange mode. Accordingly, the dominant exchange mode must come from one of the isolated surface phonon modes in the surface vibration spectrum. Third, if the adlayer vibrational modes (XH/D stretching and bending modes) are well separated from the projected bulk-phonon spectrum, vibrational modes within a single adsorbate can be considered to be isolated from that of other adsorbates because the dynamical coupling between vibrational dipoles in adjacent unit cells is usually very weak.\(^{40}\) Accordingly, only the vibrations at the zone center need to be considered. On the other hand, if the exchange mode comes from certain surface vibration that involves only substrate atoms, all the phonons within the 2D Brillouin zone have to be considered because its X–X vibrations in adjacent unit cells may be strongly coupled. Fourth, in most cases, the stretching vibration is normally strongly coupled with the bending vibration and is isolated from the PBPS. The bending mode is thus the most possible candidate for the exchange mode.

For X(100)-2×1:H/D (X=Ge and Si), because the XH/D symmetric stretch has an irreducible representation of \( \Gamma_1(z) \), it can only couple with the bending vibrations that have the same irreducible representation, i.e., the symmetric and antisymmetric bending modes [Eq. (12)]. The other two bending modes have different irreducible representations and are thus orthogonal to the symmetric stretch so that no coupling is expected between them. Furthermore, since the two symmetry-allowed bending modes are isolated from the projected bulk phonons, they are thus expected to be the most possible candidates for the exchange mode. For Si(100)-2×1:H, all the bending modes are separated from the rest of surface phonons in energy and have almost the same oscillation frequency,\(^{32}\) leading to a single exchange mode from the experimental results. For C(100)-2×1:H, the bending frequencies are located very close to the maximum of the projected bulk-phonon spectrum.\(^{30}\) Accordingly, the coupling with the motions of atoms lowers the symmetry and results in the splitting in the energy. This energy splitting is, however, too small to be observed in the extraction of the exchange mode. Although no theoretical calculation in the surface phonon spectrum of Ge(100)-2×1:H is available at this moment, the symmetry properties of surface vibrations are presumably very similar to that of Si(100)-2×1:H since the mass difference between hydrogen and germanium atoms is even larger.

As shown in Table V, the exchange modes for both Si(100)-2×1:D and Ge(111)-1×1:D are appreciably lower than the corresponding ones for the corresponding hydrogenated surfaces. Notice that the exchange mode for Ge(100)-2×1:D matches almost exactly with the estimated GeD bending frequency. The one for Si(100)-2×1:D is, on the other hand, considerably lower than the estimated frequency for the SiD bending mode. To explain this behavior, one needs to take a closer look at the surface phonon spectra in both cases. For germanium, since the maximum frequency of the projected bulk-phonon spectrum (PBPS) of Ge(100) is resonant at 304.5 cm\(^{-1}\),\(^{39}\) which is lower than both the bending modes for the hydrogenated and deuterated Ge(100) surfaces, no influence from the projected bulk phonons is expected. In contrast, the maximum frequency of the PBPS of Si is resonant at 524 cm\(^{-1}\),\(^{40}\) which is lower than the SiH bending frequency for the hydrogenated Si(100) surface but is higher than that for the corresponding deuterated surface (Table V). This leads to substantial coupling between the SiD bending mode at Si(100)-2×1:D and the projected bulk phonons. It is thus conceivable that the frequency of the SiD bending mode is away from the estimation made purely based on the mass difference and it is equally possible that the symmetry properties of the bending motion are altered due to this coupling. Similar features can be found in the surface phonon of Si(111)-1×1:D.\(^{51}\)

In the cases of hydrogenated and deuterated semiconductor (111) surfaces, surface atoms preserve an ideal tetrahedral configuration. It is thus expected that the coupling between the XH stretching and bending vibrations of
X(111)-1×1: H is very weak. According to the above-given symmetry analysis [Eq. (9)], the XH stretching mode has an irreducible representation of \( \Gamma_{3}(z) \), while the doubly degenerate bending mode has an irreducible representation of \( \Gamma_{3}(x,y) \). The Kronecker product of the two vector field representations at the \( K \) point is thus given by \( \Gamma_{3}(z) \times \Gamma_{3}(x,y) \). Since these two modes are orthogonal to each other, there is no coupling between them. X(111)-1×1: H is therefore a special case in the consideration of the surface dependence of vibrational dephasing dynamics. Since the XH bending mode is symmetry forbidden for the anharmonic coupling in vibrational dephasing, this allows for another low frequency vibrational mode to become the exchange mode. The coupling strength is therefore expected to be weak. In the studies of Ge(111)-1×1: H and Ge(111)-1×1: D, the extracted exchange modes for both cases are identical within experimental error, leading to the conclusion that because of this mass-independent behavior the motion of this exchange mode apparently does not involve the adlayer.

In the case of Si(111)-1×1: H, the extracted exchange mode resides at \( \sim 210 \text{ cm}^{-1} \). According to the theoretical calculation by Sandfort, Mazur, and Pollmann, there are two possible surface vibrational modes around this frequency range (\( S'_1 \) and \( S_8 \)). The \( S'_1 \) mode is isolated from the PBPS at the \( K \) point and it has a pronounced surface-perpendicular motion. According to Eq. (10), the first-layer Si atom presents the \( K_1(z) \) mode. Because the Kronecker product of the SiH stretching mode at \( \Gamma \) and the \( S_8 \) mode at \( K \) is given by \( \Gamma_1 \times K_1 = K_1 \), the \( S'_1 \) mode should be able to couple with the stretching mode considerably. Its resonant frequency is at \( \sim 180 \text{ cm}^{-1} \). For the \( S_8 \) mode, it couples with substrate phonons at the \( K \) point and is isolated at the \( M \) point. We thus only need to consider the \( S_8 \) mode at the \( M \) point. Since it is a shear vertical motion at the \( M \) point, its irreducible representation is \( M_1(z) \). Because the Kronecker product of the SiH stretching mode at \( \Gamma \) and the \( S_8 \) mode at \( M \) is given by \( \Gamma_1 \times M_1 = M_1 \), the \( S_8 \) mode can thus couple with the SiH stretching mode as well. Experimentally, Guyot-Sionnest used surface photon echo to measure the pure vibrational dephasing time of the SiH stretch on Si(111)-1×1: H directly. He concluded that the \( S'_1 \) mode provides a better match between the measured \( T^0_2 \) and the value predicted from the dephasing model. Based on our symmetry analysis, both surface modes are allowed for pure dephasing on Si(111)-1×1: H, although they come from different points in the 2D Brillouin zone.

In the case of C(111)-1×1: H, Sandfort, Mazur, and Pollmann also calculated its surface phonon spectrum. Because of its coupling with the PBPS, the CH bending vibration is split into three modes: \( B_1 \), \( B_2 \), and \( B_3 \), similar to the case of Si(111)-1×1: D. Furthermore, they found that only at the \( M \) point of the Brillouin zone is the \( B_1 \) mode decoupled with the PBPS. This bending mode, however, has a strong parallel displacement direction on the surface plane. As we discussed previously, this bending mode is not symmetry allowed for anharmonic coupling because it belongs to the \( M_2+M_3 \) irreducible representation. This is consistent with the picture that the exchange mode does not resonate at the bending mode on the (111) surfaces. At around 1200 \( \text{ cm}^{-1} \), the \( R_1 \) mode moves vertically and is isolated at the \( \Gamma \) point. The vibrational field representation of the first-layer carbon atom is given by Eq. (9), yielding only one vertically polarized vibrational mode. Accordingly, the \( R_1 \) mode can be assigned to the \( \Gamma_1(z) \) mode and is symmetry allowed for anharmonic coupling. It is thus the only possible choice for the exchange mode at this frequency range.

### Table V. Comparison of the stretching frequency \( \Omega_e \) observed at room temperature, the bending frequency \( \Omega_b \) from other studies, and dephasing parameters, \( \delta \omega \) and \( \eta_0 \), for GeH, SiH, and CH stretches on germanium, silicon, and diamond surfaces, respectively. (s) the symmetrical mode; (a) the asymmetrical mode. The assignments of several exchange modes are also shown in the fifth column from the right.

<table>
<thead>
<tr>
<th>Surface</th>
<th>( \Omega_e ) (\text{cm}^{-1})</th>
<th>( \Omega_b ) (\text{cm}^{-1})</th>
<th>( \omega_0 ) (\text{cm}^{-1})</th>
<th>Mode</th>
<th>( \delta \omega ) (\text{cm}^{-1})</th>
<th>( \eta_0 ) (\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge(111)-1×1: H</td>
<td>1973$^b$</td>
<td>...</td>
<td>128±93$^b$</td>
<td>N/A</td>
<td>-3.3±2.6$^b$</td>
<td>...</td>
</tr>
<tr>
<td>Ge(111)-1×1: D</td>
<td>1412$^a$</td>
<td>...</td>
<td>115±37$^a$</td>
<td>N/A</td>
<td>-3.7±1.2$^a$</td>
<td>...</td>
</tr>
<tr>
<td>Si(111)-1×1: H</td>
<td>2083.7$^j$</td>
<td>644$^b$</td>
<td>210±25$^b$</td>
<td>( S'_1(K)^h )</td>
<td>-5.03±0.05$^b$</td>
<td>52±2$^j$</td>
</tr>
<tr>
<td>Si(100)-2×1: H</td>
<td>2107.6$^j$</td>
<td>...</td>
<td>647±79$^j$</td>
<td>( B_1^l )</td>
<td>-30±8$^j$</td>
<td>59±3$^j$</td>
</tr>
<tr>
<td>Si(100)-2×1: D</td>
<td>2099$^f$</td>
<td>633$^b$</td>
<td>550±150$^b$</td>
<td>N/A</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>C(111)-1×1: H</td>
<td>2835.5$^k$</td>
<td>1332$^d$</td>
<td>1200±100$^b$</td>
<td>( R_1(\Gamma)^m )</td>
<td>-23±3$^k$</td>
<td>120±30$^k$</td>
</tr>
<tr>
<td>C(100)-2×1: H</td>
<td>2922$^k$</td>
<td>1270$^b$</td>
<td>1300±200$^b$</td>
<td>( B_1^a )</td>
<td>-35±9$^k$</td>
<td>...</td>
</tr>
</tbody>
</table>

$^a$This work.
$^b$Reference 37.
$^c$Reference 38.
$^d$Reference 4.
$^e$Reference 5.
$^f$Reference 34.
Gräschus, Mazur, and Pollmann\textsuperscript{41} also calculated the surface phonons of Si(111)-1×1:D, which are basically identical to that of Si(111)-1×1:H in the energy range of the projected acoustical bulk phonons from 0 to 360 cm\textsuperscript{-1}. The corresponding \(S_4\) and \(S_8\) modes are isolated at \(M\) and \(K\), respectively, and have the same symmetries as that of Si(111)-1×1:H. In the energy above 360 cm\textsuperscript{-1}, i.e., within the projected optical phonons of Si(111) and above, the surface phonon spectrum of Si(111)-1×1:D and that of C(111)-1×1:H are very similar, let alone the fact that the relevant energy scales are different. Similarly, the SiD bending frequencies are close to the maximum of the bulk phonons and are not symmetry allowed for vibrational dephasing. The \(R_1\) mode at \(\Gamma\) is, however, mixed with the projected bulk phonons, which is a lot different from the \(R_1\) mode of C(111)-1×1:H. Based on the discussion in the surface phonon spectrum of Si(111)-1×1:D, the exchange mode of the SiD stretch is expected to resonate at around 200 cm\textsuperscript{-1} as well.

Recently Honke \textit{et al.} have performed an \textit{ab initio} calculation of the temperature dependence of the frequency shift and the intrinsic linewidth of the SiH stretch on the Si(111)-1×1:H surface.\textsuperscript{45} They found that at temperatures greater than 200 K, both line shift and linewidth of the stretching mode are primarily due to strong anharmonic coupling to the bending mode. At low temperatures, direct coupling to various phonon modes of the substrate dominates the temperature dependence of the line shift. They further found that the frequency shift is dominated by thermal expansion. Their results seem to be inconsistent with our experimental observations as well as the earlier studies using infrared absorption\textsuperscript{5} and surface phonon echo.\textsuperscript{35} From their investigation, we notice that the calculation of surface phonon dispersion is comparably deviated from the experimental results, especially the SiH stretching and bending modes. It may be difficult to ensure the validity in the extraction of higher order anharmonic coupling constants based on the calculated interaction potential. Furthermore, if the frequency shift is dominated by thermal expansion, one does not expect to observe the isotope shift in the exchanged mode, which is inconsistent with our observations on the X(100) surfaces. Nor can one explain the absence of the isotope effects on the X(111) surfaces. Finally, in a theoretical discussion of vibrational dephasing at surfaces by Burke \textit{et al.},\textsuperscript{36} the cubic terms in the anharmonic interaction potential were found to be possibly as important as the quartic terms. The former contribution was, however, neglected in the \textit{ab initio} calculation of the vibrational linewidth.

Besides the anharmonic coupling to thermally excited low-frequency modes, Jakob and Persson\textsuperscript{47} pointed out that thermal expansion may also contribute to a line shift, \(\Delta \Omega_{\mathrm{TE}}\), caused by the reduction in the dynamic dipole coupling as the spacing between the interaction oscillators increases with increasing temperature. To the first-order approximation, the frequency shift due to thermal expansion amounts to

\[
\Delta \Omega_{\mathrm{TE}} = -3 \alpha \Delta T \Delta \Omega_{\mathrm{dip}},
\]

with \(\alpha\) denoting the linear thermal expansion coefficient, \(\Delta T\) the temperature variation, and \(\Delta \Omega_{\mathrm{dip}}\) the dynamic dipole shift of the mode under consideration. The frequency shift, \(\Delta \Omega_{\mathrm{dip}}\), caused by the dipole coupling on the hydrogenated semiconductor surfaces can be extracted by the isotope mixture experiments.\textsuperscript{48} Table VI shows the calculated results for C(111)-1×1:H, Si(100)-1×1:H, Ge(111)-1×1:H, and Ge(100)-1×1:H. Apparently, the contribution induced in the dynamical dipole coupling is negligible compared with the observed frequency shift.

Persson, Hoffmann, and Ryberg exploited the exchange model to analyze the IR results on CO/Ru(001) and CO/Ni(111).\textsuperscript{49} In the former case, the exchange mode was assigned to its frustrated translation mode, while, in the latter case, they assigned it to the frustrated rotation mode. The assignment was based on their respective frequency positions. There are, however, several major differences between the CO/metal systems and the hydrogenated semiconductor surfaces. First, the former case is a weakly chemisorbed system such that no major surface reconstruction occurs after adsorption while strong structural relaxation happens in the latter case. Second, since all the vibrational modes of interest (CO stretch, CO–metal stretch, frustrated rotation, and frustrated translation) do not involve major motion in the substrate atoms, these modes are considered to be isolated from other surface phonons. The possible exchange mode therefore comes from vibrational modes within the adlayer. Third, the frustrated translation consists mainly of translational but also some rotational motion.\textsuperscript{110} The same behaviors can also be recognized in the frustrated rotation mode. Thus, no strict symmetry constraint is expected to impose on coupling between these frustrated motions with the CO internal motion.

### VI. CONCLUSIONS

In this study, we have performed a series of surface Raman measurements on hydrogenated and deuterated silicon and germanium surfaces at various temperatures. The dephasing parameters of the SiH/D and GeH/D stretches at these surfaces were extracted. By analyzing the dependence of these dephasing parameters at different surfaces, we deduced the following selection rules for choosing the exchange modes for X(111)-1×1:H/D and X(100)-2×1:H/D (X=Ge, Si, and C). First, the XH/D bending mode is the exchange mode for the XH/D symmetric stretching mode at
X(100)-2×1:H/D. Second, for the hydrogenated and deuterated X(111) surfaces, the exchange mode comes from a surface vibrational mode resonating at a lower frequency. We have also performed a thorough investigation in the symmetry properties of surface vibrational modes at these surfaces. The vibrational field representations of several key surface vibrational modes have been determined. According to the symmetry requirement for anharmonic vibron–phonon coupling, the exchange modes for C(111)-1×1:H and Si(111)-1×1:H have been identified in their respective surface phonon spectra.

From this systematic investigation, we can therefore reach several implications for the vibrational dephasing dynamics at strongly chemisorbed systems. First, for low-symmetry chemisorbed surfaces, vibrational dephasing is mainly caused by the anharmonic coupling between vibrational modes within the adsorbed layer. This principle should apply to most chemisorbed systems, because they usually undergo structural relaxation on surfaces. The resulting surface symmetry may be considerably lower than that in the bulk. This causes significant alteration in the symmetry of surface vibrational modes within the adlayer, which create possible exchange modes. Second, for high-symmetry chemisorbed surfaces, the former coupling channel may be turned off. In the extreme case where no structural relaxation exists on surface atoms, the symmetry properties on surface remain the same as that in the bulk. That is, its 2D space group is the direct projection of the bulk 3D space group onto the surface. This allows a weaker coupling channel from one of other lower-frequency surface phonons. Third, with the help from theoretical calculations on the spectral density of surface phonons in the Brillouin zone, the vibrational field representations of surface phonons can be analyzed and can be used in identifying exchange modes.

ACKNOWLEDGMENTS

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14 S. Marks, P. S. Cornelius, and C. B. Harris, J. Chem. Phys. 73, 3069 (1980), and references therein.


40 The influence of adsorbate–adsorbate interactions on the pure dephasing process at hydrogenated semiconductor surfaces has been investigated [Eqs. (5)–(7) in Ref. 8]. The effect can be neglected when the dipolar frequency shift, $\Delta \omega_{dp}$, is much smaller than the friction parameter, $\gamma$. The experimental values of $\Delta \omega_{dp}$ are on the order of 10 cm$^{-1}$, which is much smaller than the corresponding values of $\gamma$ (Table VI). Accordingly, the dipole interaction is negligible in the discussion of vibrational pure dephasing. This approximation is confirmed by the negligible dispersion of the relevant vibrational modes (such as the XH stretching and bending modes) within the 2D Brillouin zone.


42 B. L. Davies and A. P. Cracknell, Kronnecker Product Tables (Plenum, New York, 1979), Vol. I.


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