Huge isotope effect on the vibrational lifetimes of an $H_2^*(C)$ defect in Si

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The hydrogenation of C-rich Si leads to the formation of two (almost) energetically degenerate $H_2^*(C)$ complexes, each containing one substitutional C (C$_S$) and two interstitial H atoms which are located at a bond-centered (bc) and an antibonding (ab) site, respectively. The two defects are trigonal: C$_S$-H$_{bc}$-$\cdots$-H$_{ab}$ and H$_{ab}$-C$_S$-$\cdots$-H$_{bc}$-Si. Fourier-transform infrared (FTIR) absorption spectra of these two defects should show two C$_S$-H and two Si-H stretch modes, but the H$_{bc}$-C$_S$ mode was absent in earlier studies. The missing line has now been observed by FTIR in especially C rich Si material. The line is unexpectedly broad, suggesting a very short vibrational lifetime. Partial D substitutions result in the formation of a H$_{ab}$-C$_S$-$\cdots$D$_{bc}$-Si center. In this defect, the H$_{ab}$-C$_S$ line shifts by only 0.3 cm$^{-1}$ but becomes very sharp, suggesting a long lifetime. The IR line widths show that the vibrational lifetime of the H$_{ab}$-C$_S$ mode in H$_{ab}$-C$_S$-$\cdots$D$_{bc}$-Si is about 16 times longer than that of the same H$_{bc}$-C$_S$ mode in H$_{ab}$-C$_S$-$\cdots$H$_{bc}$-Si. This paper contains experimental data and first-principles calculations which explain this isotope effect.

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1. INTRODUCTION

Multi- and monocrystalline cast Si are commonly used to fabricate solar cells. These cells are hydrogenated in order to passivate bulk defects. The hydrogenation is achieved by the postdeposition anneal of a H-rich SiN$_x$ to passivate bulk defects. The hydrogenation is achieved by fabricate solar cells. These cells are hydrogenated in order energetically degenerate H$_S$ and Hab-Cs molecules.7–9 In C-rich Si, FTIR studies show that two H atoms facing each other at bc sites: Cs-Hbc-$\cdots$Hab-Cs.10 This configuration is stable up to $\sim$900°C. Finally, VH$_4$ is the fully saturated vacancy. It becomes mobile at $\sim$550°C, traps at Cs, and forms a VH$_4$CH center from which H is released at $\sim$650°C.11,12

The existence of a pair of H$_2^*(C)$ defects was predicted by theory.13 These calculations, performed in small H-saturated clusters, show that the two configurations have energies within 0.02 eV of each other, are electrically inactive, and should exhibit IR-active stretch modes at 3004 and 2135 cm$^{-1}$ (in the case of C$_S$-H$_{bc}$-$\cdots$Si-H$_{ab}$) and 3053 and 2412 cm$^{-1}$ (in the case of H$_{bc}$-C$_S$-$\cdots$H$_{bc}$-Si). The higher frequency corresponds to the H-stretch mode in each case. FTIR studies14 resulted in the observation of the local vibrational modes (LVMs) associated with the C$_S$-H$_{bc}$-$\cdots$Si-H$_{ab}$ defect, with LVMs at 2752 (C$_S$-H$_{bc}$ stretch), 1921.8 (Si-H$_{ab}$ stretch), and 792.0 (Si-H$_{bc}$ wag) cm$^{-1}$.

Joint experimental (FTIR with uniaxial stress and D substitutions) and theoretical (density-functional studies in Si$_{64}$ periodic supercells) studies15 identified the two H$_2^*(C)$ defects, and the theoretical results were later confirmed.16 The C$_S$-H$_{bc}$-$\cdots$Si-H$_{ab}$ and H$_{ab}$-C$_S$-$\cdots$H$_{bc}$-Si structures are trigonal, almost energetically degenerate (within less than 0.1 eV), stable up to $\sim$300°C, electrically inactive, and characterized by three stretch modes and one wag mode. At low temperatures, they are (in cm$^{-1}$) 2752.3 (C$_S$-H$_{bc}$ stretch), 1921.8 (Si-H$_{ab}$ stretch), and 792.0 (Si-H$_{bc}$ wag) cm$^{-1}$.

While it is not uncommon for wag modes to be broad and therefore difficult to see in FTIR spectra, the high-frequency H$_{bc}$-C$_S$ stretch mode should be visible. Yet, it was not observed.

The missing H$_{ab}$-C$_S$ stretch mode has been detected by FTIR in C-rich samples.5 The line is broad, suggesting that its vibrational lifetime ($\tau$) is short. D substitutions lead to the formation of the H$_{bc}$-C$_S$-$\cdots$D$_{bc}$-Si center. Its H$_{bc}$-C$_S$ line shifts by 0.3 cm$^{-1}$ and becomes very narrow, suggesting a much longer $\tau$.

Direct measurements of vibrational lifetimes17 involve transient bleaching spectroscopy and access to a fast-pulse laser. However, $\tau$ can also be estimated from the IR line width. Indeed, the lifetime of a LVM is inversely proportional to the IR line width at low temperatures, in the low defect concentration limit. Since other sources of line broadening are possible, the measured line width only provides a lower limit on $\tau$. In the Si host, the $\tau$’s determined by transient bleaching...
and by low-temperature IR measurements have been consistent for those cases where both strategies could be used.18

The number of phonons involved in the decay can be estimated from the lifetime via the empirical “frequency-gap law.”19 Two-phonon decays correspond to τ’s of the order of 4 to 10 ps, three-phonon decays range from 30 to 90 ps, etc.

The experimental data relevant to the IR line width of Hab-Cs in the Hab-Cs − Hbc-Si and its D/H isotope substitutions are described in Sec. II. The calculations of the vibrational lifetimes and decay channels are described in Sec. III. The key results are discussed in Sec. IV.

II. OBSERVATION OF THE Hab-Cs STRETCH MODE

A. Experimental procedure

Multicrystalline Si samples containing a high C concentration (8 × 1017 cm−3) were used for our FTIR studies. The Si grains are large, ranging from a few millimeters to 1 cm in size. Samples were cut with typical dimensions 6 × 8 × 15 mm3 and viewed with the probing IR light propagating along the long axis of the sample. Hydrogen (or mixtures of H and D) were introduced into our Si samples by annealing in an H2 (or H2 + D2) ambient at 1250°C in sealed quartz ampoules followed by a rapid quench to room temperature.

IR spectra were measured with a Bomem DA3 Fourier transform IR spectrometer. An InSb detector (77 K) was used for measurements of H stretching modes. The highest resolution available with our spectrometer is 0.026 cm−1, a value that was verified by measurements of the rovibrational lines of gas phase CO2 and H2O present in the spectrometer ambient. Samples were cooled to near 4 K with a Helitran, continuous-flow cryostat. Temperature was measured with a Chromel-Au: 0.07 at. % Fe thermocouple placed a few millimeters from the sample.

B. Measured frequencies and line widths

We have measured vibrational spectra for the H stretching lines of the H2(C) defect assigned previously to the trigonal Hab-Cs ··· Hbc-Si structure with sufficiently high resolutions to determine the widths of the IR lines at low temperature. The lines were fitted with Lorentzian line shapes to determine their widths. The frequencies and line widths determined by our measurements are listed in Table I. The Hbc-Si mode has a line width of 0.11 cm−1. However, the Hbc-Cs line at 2688.3 cm−1 has a width of 2.2 cm−1, a value that is sufficiently large to have impeded the observation of this H stretching mode in early studies. The full width at half maximum (FWHM) of the IR line, ΓH, measured at low temperature provides a lower limit for the lifetime of the vibrational mode, given by ΓH = (2πτc)−1. The lifetimes that correspond to the measured line widths are also listed in Table I.

We have also measured the vibrational line widths of the H stretching modes of the partially deuterated Dabc-Cs ··· Hbc-Si and Hab-Cs ··· Dbc-Si structures. Table I shows that the line width of the Hbc-Si mode of the Dabc-Cs ··· Hbc-Si structure is changed dramatically, by only a small factor compared to the fully hydrogenated structure. However, the spectra in Fig. 1 and the line widths listed in Table I show that the width of the Hab-Cs mode of the Hab-Cs ··· Dbc-Si center is changed dramatically, by a factor near 16, even though the mode frequency shifts only slightly.

Why do the C-H stretch modes of the Hab-Cs ··· Hbc-Si and Hab-Cs ··· Dbc-Si have such dramatically different line widths and vibrational lifetimes? The effect of isotopic substitutions on the lifetime of a vibrational mode can provide clues to the mechanism for vibrational relaxation. We turn to theory for an explanation of this surprisingly large isotope effect.

III. CALCULATIONS OF THE VIBRATIONAL LIFETIMES AND DECAY CHANNELS

A. Methodology

The approach used in the calculation of vibrational lifetimes and decay channels has been discussed in detail.20 The key points are as follows. The host crystal is described by Si64 periodic supercells and the k-point sampling is restricted to the Γ point. This relatively small size and k-point sampling has been selected because many nonequilibrium MD runs are required in order to produce the needed averaging over initial mode phases and energies. This approach has been shown to produce accurate short as well as long lifetimes at various temperatures for almost 20 defects.20–22

The electronic structure calculations are based on the SIESTA23,24 method. Norm-conserving pseudopotentials in the Kleinman-Bylander form25 are used to remove the core regions from the calculations. The valence regions are treated self-consistently within local density-functional theory with
the exchange-correlation potential of Ceperley-Alder as parameterized by Perdew-Zunger. The basis sets for the valence states (double zeta for H or D, with polarization functions for Si) are linear combinations of numerical atomic orbitals of the Sankey type. The charge density is projected on a real-space grid with equivalent cutoffs of 250 Ry to calculate the exchange-correlation and Hartree potentials. The dynamical matrices are calculated using the frozen-phonon method.

The eigenvalues of the dynamical matrix are the normal-mode frequencies $\omega_s$. The corresponding orthonormal eigenvectors $e_{s,i}$ (where $i = x,y,z$) give the relative displacements of the nucleus $\alpha$ for each mode $s$. A quantitative measure of the localization of a given mode is on one atom or group of atoms is obtained by assuming that the kinetic energy of the Hab-Cs stretch mode in Hab-Cs averages out to $k_B T = 120 K$. Thus, each MD run begins using the appropriate eigenvector of the dynamical matrix. The simplest relationship, $M \dot{\gamma}_s = -\alpha_s \gamma_s$, gives the relative displacements $\gamma_s = \alpha_s / \sqrt{m_\alpha}$. The index $\alpha$ may be a single atom (e.g., H) or a sum over a group of atoms (e.g., the Si nearest neighbors to H).

The eigenvectors $e_{s,i}$ are used to transform the (harmonic) normal mode coordinates $q_s$ into Cartesian nuclear displacements $u_{\alpha i} = \sum_s q_s e_{s,i} / \sqrt{m_\alpha}$. The simplest relationship, $q_s = A_s(T) \cos(\omega_s t + \phi_s)$, assumes that the normal modes are harmonic. This is of course an approximation but it is needed to calculate the positions and velocities of the nuclei at the time $t = 0$ as well as the amplitudes of the various modes at subsequent times. The MD simulations themselves use forces calculated from first-principles total energies and therefore include all the anharmonic terms. Note that $q_s$ introduces an initial random distribution of mode phases $\phi_s$.

At $t = 0$, the supercell is prepared in thermal equilibrium at $T = 100 K$, and the excited LVM is given $3h \omega_0/2$ potential energy using the appropriate eigenvalue of the dynamical matrix. This background temperature is sufficiently high for the classical MD runs to accurately describe the phonon dynamics. The initial potential energy of the excited mode corresponds to the zero-point energy plus one phonon, which guarantees that the (theoretical) classical and (experimental) quantum oscillators have the same initial amplitude. The added potential energy in this Si$_{64}$ cell results in the net temperature to increase to $\sim 120 K$. Since the IR line widths are measured at low $T$, the calculated $\tau$’s are expected to be somewhat shorter than the low-$T$ ones [measured $\tau(T)$ are in Refs. 17, 18, 29–31].

The amplitudes of all the normal modes in the supercell are obtained by assuming that the average kinetic energy of each mode is $k_BT/2$ which introduces a random distribution of energies that averages out to $k_BT$. Thus, each MD run begins with a random distribution of mode phases and energies. Each calculation involves averaging over 20 to 27 different sets of initial conditions.

B. Vibrational lifetimes and receiving modes

We are interested here in the lifetime and decay channels of the Hab-Cs stretch mode in Hab-Cs with all the possible D substitutions. The localized modes associated with this defect are the two H stretch modes, the corresponding two doubly degenerate H wag modes, as well as the doubly degenerate wag mode of C. Since the defects have trigonal symmetry, the wag modes are not possible receiving modes for the decay of the stretch modes because they are orthogonal and no momentum can be transferred.

The calculated frequencies and localizations of all these modes are given in Table II for $^{12}$C, $^{28}$Si, and the various H/D isotope combinations. In three of the four isotope combinations, the Hab-Cs (or Daa-Cs) stretch mode is the highest-frequency mode. In these three cases, one of the receiving modes is the corresponding Hbc-Si (or Dbc-Si) stretch mode.

![FIG. 2. (Color online) Energy (eV) of the Hab-Cs (or Daa-Cs) stretch (black) and of the Hab-Si (or Daa-Si) stretch (red) vs time (ps), calculated at $T = 120 K$. In three of the four isotope combinations, the Hab-Cs (or Daa-Si) stretch mode is a receiving mode. The missing energy is provided by one (or more) bulk phonon(s). In Hab-Cs, the decay does not fit to one exponential. The two fits shown provide lower and upper limits to the lifetime.](image)
mode, and the missing energy is provided by one (or more) bulk phonon(s). However, in the case of Dab-Cs, the highest-frequency mode is Hbc-Si and the excited Dab-Cs decays slowly directly into a combination of bulk phonons.

Figure 2 shows the calculated decays of the Hab-Cs (or Dab-Cs) mode and of the corresponding receiving Hbc-Si (or Dbc-Si) mode. Figure 3 shows the localization of the two stretch modes, the calculated phonon density of states of Si and, in three cases, the frequency of the bulk phonon required to complete the decay. The calculated lifetimes for the four isotope combinations are compared to the ones estimated from the IR line width in Table III.

IV. DISCUSSION

The excitation of defect-related LVMs leads to the trapping of a phonon by the defect. The trapped energy decays into combinations of lower frequency phonons after a length of time $\tau$, the vibrational lifetime. The value of $\tau$ can depend critically on the existence, symmetry, and frequency of another LVM associated with the defect. When such a second LVM exists, the lifetime of a high-frequency mode can be short and strongly affected by the isotopic composition of the defect.

The defect of interest here has two stretch modes, Hab-Cs (or Dab-Cs) with frequency $\omega_C$ and Hbc-Si (or Dbc-Si) with frequency $\omega_S$. In Dab-Cs, $\omega_C = 1870$ cm$^{-1}$ and $\omega_S = 2190$ cm$^{-1}$ and $\omega_C$ can only decay via multiple bulk phonons with a theoretical lifetime $\tau = 46$ ps. For the other three isotope combinations, $\omega_C > \omega_S$ and the decay is of the type $\omega_C \rightarrow \omega_S + \Delta \omega$.

For Hab-Cs, $\Delta \omega = 384$ cm$^{-1}$ and numerous bulk phonons are available. This decay is a fast two-phonon process with a theoretical lifetime in the range 2.7 $< \tau < 4.8$ ps and the IR line is broad. For Hbc-Si, $\Delta \omega = 996$ cm$^{-1}$, far above the optical phonons of Si, and two bulk phonons are required. The decay becomes much slower three-phonon process, the theoretical lifetime increases to $\tau = 23$ ps, and the IR line becomes very narrow. For Dbc-Si, $\Delta \omega = 310$ cm$^{-1}$ and the predicted 11 ps lifetime is about average for a typical two-phonon decay.

This is not an isolated situation. For example, another unexpected isotope effect has been reported in the case of interstitial oxygen (O$_i$) in Si. The excited asymmetric stretch of O$_i$ ($\omega_O$) decays into the symmetric stretch of its two Si nearest neighbors ($\omega_O$) plus $\Delta \omega$. For the isotope combination $^{28}$Si-^{16}$O-^{28}$Si, $\Delta \omega \sim 530$ cm$^{-1}$, near or at the peak of the Si phonon density of states. Plenty of phonons are available and the decay is a two-phonon process. However, the isotope substitutions $^{29}$Si-^{16}$O-^{28}$Si and $^{30}$Si-^{16}$O-^{28}$Si cause $\omega_O$ to shift to lower frequencies, and then $\Delta \omega$ increases just beyond the edge of the phonon density of states where few (or no) bulk phonons are available. As a result, $\tau$ increases from 11 ps ($^{28}$Si-^{16}$O-^{28}$Si, $\omega_O = 1136$ cm$^{-1}$) to 27 ps ($^{30}$Si-^{16}$O-^{28}$Si, $\omega_O = 1129$ cm$^{-1}$) as the two-phonon process becomes a three-phonon process.

The coupling of an isolated high-frequency LVM to a lower frequency phonon bath has been discussed by Nitzan and Egorov. The theory works as long as none of the receiving modes is a defect-related LVM as well. A well-illustrated example is the failure to fit the temperature dependence of the vibrational lifetimes of two similar H-related stretch modes in Si: a (measured) $\sim 300$ ps lifetime fits nicely to a five-phonon decay while a much shorter $\sim 4$ ps lifetime could only be fitted to a six-phonon decay. The presence of a second LVM in the latter case is the culprit. In the present study, the extreme sensitivity of the vibrational lifetime to the isotopic makeup of the Hab-Cs-Hbc-Si defect betrays the identity of the receiving LVM that plays the critical role in the decay channel.

### ACKNOWLEDGMENTS

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### TABLE III. Vibrational lifetimes $\tau$ (in ps) of the Hab-Cs (or Dab-Cs) stretch mode calculated at $\sim T = 120$ K and extracted from the measured FWHM at 4.2 K.

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