

Structure-Dependent Vibrational Lifetimes of Hydrogen in Silicon

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The lifetimes of the Si-H vibrational stretch modes of the H_2^* (2062 cm^{-1}) and $HV \cdot VH_{(110)}$ (2072.5 cm^{-1}) defects in crystalline Si are measured directly by transient bleaching spectroscopy from 10 K to room temperature. The interstitial-type defect H_2^* has a lifetime of 4.2 ps at 10 K, whereas the lifetime of the vacancy-type complex $HV \cdot VH_{(110)}$ is 2 orders of magnitude longer, 295 ps. The temperature dependence of the lifetime of H_2^* is governed by TA phonons, while $HV \cdot VH_{(110)}$ is governed by LA phonons. This behavior is attributed to the distinctly different local structure of these defects and the accompanying local vibrational modes.

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Relaxation and delocalization of vibrational energy in the condensed phase entails the energy redistribution into low-frequency vibrational degrees of freedom that are anharmonically coupled to the initially excited local mode [1]. These energy relaxation times are typically hundreds of femtoseconds to hundreds of picoseconds. Low-mass impurities in crystalline solids provide unique opportunities to explore these dynamical processes. Impurities lighter than the host atoms give rise to localized vibrational modes (LVMs) with frequencies above the phonon bands of the solid [2]. Direct (time-domain) determination of the lifetime of LVMs is made possible by recent advances in tunable, ultrafast, high-intensity infrared (IR) light sources [3].

Recently, we have undertaken a systematic study of the vibrational lifetime of hydrogen (H) embedded in bulk silicon (Si) [4,5], a classic example of well-studied local vibrational modes. The low-temperature lifetime of H at the bond-center site in crystalline Si and other interstitial-like configurations is of the order of 10 ps, while the lifetime of vacancy-H configurations are 1–2 orders of magnitude greater [4,5]. This disparity in measured lifetimes is unexpected based on simple theories and is as yet unexplained [1]. Experimentally, the most straightforward way to characterize a multiphonon relaxation rate from a given vibrational level is from the temperature dependence of its lifetime. In this paper, we report a detailed comparison of the temperature dependence of the vibrational lifetime of two structurally distinct point defects in crystalline Si, H_2^* , an interstitial defect, and $HV \cdot VH_{(110)}$, a vacancy complex. The very different temperature dependences show that these vibrationally excited defects decay into markedly different accepting vibrational modes, giving new insights into the origin of the observed large difference in lifetimes.

In addition to the fundamental interest in understanding energy relaxation in solids, the actual lifetime of LVMs plays a unique role in determining impurity stability, transformation, and migration of impurities in solids under dynamical conditions. For example, Persson, Avouris,

Lyding, and their co-workers have reported intriguing data on the different behavior of the desorption of deuterium (D) and H bonded to Si [6–9]. Although the chemical binding of these species is essentially the same, the difference in desorption behavior was attributed to differences in their vibrational lifetimes [10].

Hydrogen in Si gives rise to localized vibrational modes with frequencies above the Si phonon bands [11,12]. Here we are interested in the decay channels of the 2062- and 2072- cm^{-1} modes of the H defects H_2^* and $HV \cdot VH_{(110)}$. The structures of H_2^* and $HV \cdot VH_{(110)}$ are shown in Fig. 1. The H_2^* defect has C_{3v} symmetry with one H close to the bond-center (BC) site and the other near the antibonding (AB) site [13]. It gives rise to two IR active Si-H stretch modes: one at 1838 cm^{-1} corresponding to vibration of H at the AB site, and one at 2062 cm^{-1} due to H at the BC site. The divacancy binding two H atoms may exist in several variants. The one illustrated in Fig. 1 is denoted $HV \cdot VH_{(110)}$ to emphasize that the Si-H bonds are located in the same (110) plane, in separate halves of the divacancy. As discussed in Ref. [5], the two Si-H bonds of $HV \cdot VH_{(110)}$ are antiparallel, and the defect therefore has only one IR active stretch mode, which has been assigned to the absorption line at 2072 cm^{-1} [5,14].

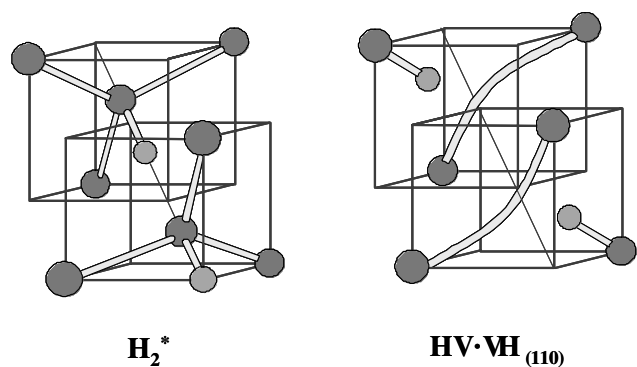


FIG. 1. Structure of the H_2^* complex and the divacancy binding two H atoms, $HV \cdot VH_{(110)}$. The large spheres are Si, whereas the small spheres are H.

The lifetime of high-frequency vibrational modes decaying into a bath of low-frequency phonon modes has been studied theoretically by Nitzan and co-workers [1], and by Egorov and Skinner [15]. The total decay rate (inverse lifetime) is given as the sum of the rates of all of the decay channels:

$$\frac{1}{T_1} = 2\pi \sum_{\{\nu\}} |G_{\{\nu\}}|^2 n_{\{\nu\}} \rho_{\{\nu\}}, \quad (1)$$

where each channel $\{\nu\}$ is characterized by the set $\{\omega_1^{(\nu)}, \omega_2^{(\nu)}, \dots, \omega_{N_\nu}^{(\nu)}\}$ of accepting mode frequencies. Energy is conserved in the decay process, $\hbar\omega = \sum_{j=1}^{N_\nu} \hbar\omega_j^{(\nu)}$, where ω is the frequency of the LVM. The decay rate of each channel is given by the temperature-independent coupling strength $G_{\{\nu\}}$ of the channel, the function $n_{\{\nu\}}$ describing the temperature dependent population of the receiving modes:

$$n_{\{\nu\}} = \frac{\exp(\hbar\omega/k_B T) - 1}{\prod_{j=1}^{N_\nu} [\exp(\hbar\omega_j^{(\nu)}/k_B T) - 1]}, \quad (2)$$

and the compound spectral density of accepting states $\rho_{\{\nu\}}$ which can be expressed in terms of a convolution of single spectral densities of states,

$$\rho_{\{\nu\}} = \int d\omega_1^{(\nu)} \dots \int d\omega_{(N_\nu-1)}^{(\nu)} \rho_1^{(\nu)}(\omega_1^{(\nu)}) \dots \rho_{N_\nu}^{(\nu)}(\omega_{N_\nu}^{(\nu)}). \quad (3)$$

In the low-temperature limit ($k_B T \ll \hbar\omega_j^{(\nu)}$, for all j), the decay rate reflects spontaneous decay into N_ν accepting modes and $n_{\{\nu\}} \cong 1$. At higher temperatures the decay rate increases due to stimulated emission in a fashion determined by the frequencies of the accepting modes [1,15].

To investigate the vibrational relaxation channels of the 2062- and 2072-cm⁻¹ modes of H₂^{*} and HV · VH₍₁₁₀₎ in Si, we measured the lifetime T_1 of these modes as a function of temperature by time-resolved transient bleaching spectroscopy. The sample consists of a 2-mm thick disk cut from single crystalline high-resistivity Si. The sample was polished on both sides, and coated with a mid-IR antireflection coating on one side to prevent spurious signals arising from multiple internal reflections. A uniform H concentration of 1.7×10^2 ppm was formed from the surface to a depth of 47 μm by variable-energy implantation of the uncoated side of the sample at 80 K. After warming to room temperature, IR absorbance measurements from the implanted sample revealed a series of strong absorption lines in the Si-H stretch region, including lines at 2062.1, 2068, and 2072.5 cm⁻¹. Figure 2 shows an absorbance spectrum taken with 0.15-cm⁻¹ resolution at 10 K from a Si-H sample with a low H concentration (~7 ppm) to clearly resolve the different absorption lines. The 2068-cm⁻¹ line has been assigned to the divacancy binding one H atom HV · V [16], and was ~3 times smaller than the 2072.5-cm⁻¹ line of HV · VH₍₁₁₀₎ in the

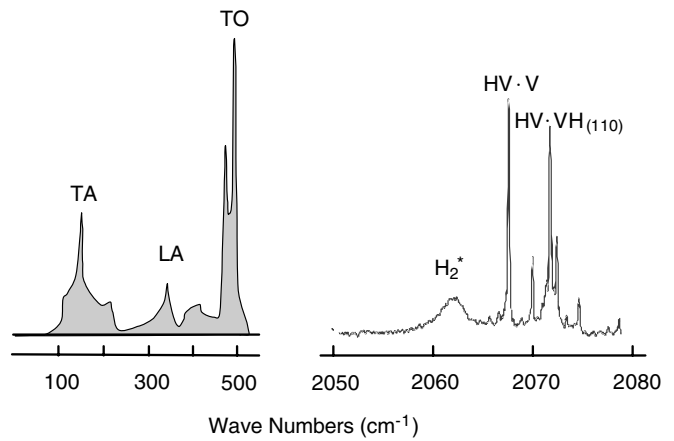


FIG. 2. Left: Phonon spectrum of Si adapted from Ref. [19]. Right: Absorbance spectrum of proton-implanted Si showing the 2062.1-, 2068-, and 2072.5-cm⁻¹ lines of H₂^{*}, HV · V, and HV · VH₍₁₁₀₎.

sample with the high H concentration. Since the linewidth is inversely related to the lifetime, it is immediately apparent that H₂^{*} and the vacancy complexes have very different excited state lifetimes. However, a direct determination of the lifetime from the width may be uncertain due to inhomogeneous broadening, instrumental resolution, and dephasing at elevated temperatures. Therefore, a transient bleaching (pump-probe) technique was used for time-domain measurements of the lifetimes.

The transient bleaching signal S_b was measured as a function of time delay between the pump and probe pulses, as described in Ref. [4]. The experiments were performed using the high-power, IR free-electron laser (FEL) at the Thomas Jefferson National Accelerator Facility (TJNAF) [3]. The FEL delivered pulses with a time duration of ~1 ps, spectral width of 12 cm⁻¹, and pulse energy of ~1 J at a pulse repetition rate of 18.6 MHz.

Figure 3 shows the transient bleaching signal versus time delay measured at a temperature of 10 K with the laser frequency centered either on the 2062-cm⁻¹ (left) or

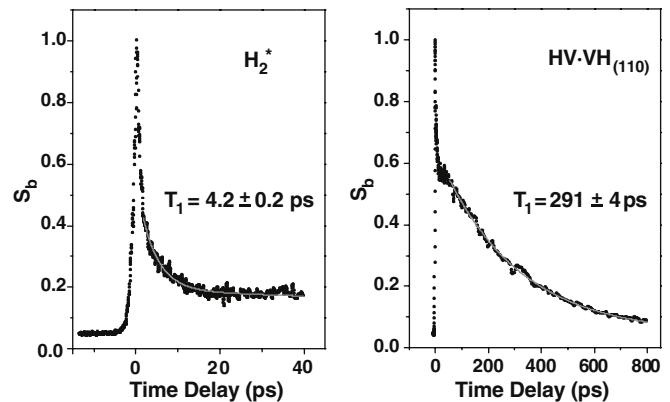


FIG. 3. Transient bleaching signal from the 2062-cm⁻¹ (left side) and the 2072-cm⁻¹ mode (right side) measured at a temperature of 10 K.

the 2072-cm⁻¹ line (right). The signal of the former decreases with a time constant $T_1 = 4.2 \pm 0.2$ ps (left side of Fig. 3) [17]. In addition, a long-lived tail is clearly present in the decay of S_b . Since the laser spectrum has a FWHM of ~ 12 cm⁻¹, we expect that S_b also exhibits a response from the 2068- and 2072-cm⁻¹ modes. Indeed, by centering the laser frequency on the 2072-cm⁻¹ mode, the long-lived component of S_b is enhanced; i.e., it corresponds to the stretch mode of $HV \cdot VH_{(110)}$, possibly with a small contribution from $HV \cdot V$ (right side of Fig. 3) [18]. The lifetime of the $HV \cdot VH_{(110)}$ stretch mode is constant within experimental error up to 60 K, with a mean value of $T_1 = 295 \pm 6$ ps. Both signals in Fig. 3 exhibit a fast transient, which coincides with the pump pulse. This instantaneous response results from the nonresonant excitation of the bulk crystal.

Figure 4 shows T_1 versus temperature for H_2^* (left side) and $HV \cdot VH_{(110)}$ (right side). In the case of the 2062-cm⁻¹ mode, T_1 is nearly constant up to ~ 60 K, where it starts to decrease, reaching half of its low-temperature value at 130 K. The solid lines in Fig. 4 are fits using Eq. (1) with the vibrational relaxation channel of the 2062-cm⁻¹ mode represented by a set of six accepting modes $\{165, 165, 165, 522, 522, 522\}$ cm⁻¹. This set of accepting modes is very similar to that of the 1998-cm⁻¹ mode of bond-center H in Si [4], which is well described by decays into six accepting modes, $\{150, 150, 150, 516, 516, 516\}$ cm⁻¹. In contrast, the lifetime of the 2072-cm⁻¹ mode starts to decrease at ~ 120 K reaching half of its low-temperature value at 250 K. The decay channel of the 2072-cm⁻¹ mode is well represented by five accepting modes with frequencies $\{343, 343, 343, 521, 521\}$ cm⁻¹. We note that the vibrational relaxation channels are not uniquely determined by the temperature dependence of the lifetimes. In particular, the high-frequency phonon modes of the decay channels do not have a strong influence on

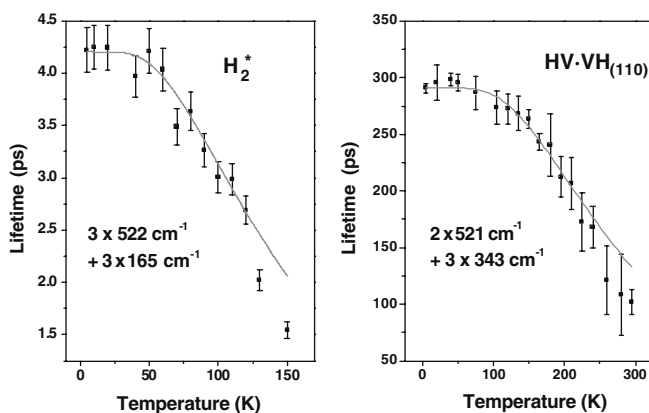


FIG. 4. Temperature dependence of T_1 of the 2062-cm⁻¹ mode of H_2^* (left side) and the 2072-cm⁻¹ mode of $HV \cdot VH_{(110)}$ (right side). The solid lines are fits from Eqs. (1) and (2) for decays into the sets of accepting modes $\{165, 165, 165, 522, 522, 522\}$ cm⁻¹ and $\{343, 343, 343, 521, 521\}$ cm⁻¹ of the 2062- and 2072-cm⁻¹ modes.

the temperature dependence of the lifetimes. For example, the temperature dependence of the 2072-cm⁻¹ mode is equally well represented by a set of accepting modes of $\{343, 343, 343, 343, 700\}$ cm⁻¹. However, the wave number of the accepting mode with the lowest frequency is quite well determined by the onset of the temperature dependence of T_1 , for example, ~ 60 K for H_2^* and ~ 120 K for $HV \cdot VH_{(110)}$. Figure 4 also shows that in both cases the calculations using Eq. (1) deviate from the measured T_1 's at elevated temperatures, indicating that additional relaxation channels may increase the decay rate at higher temperatures. We note that the low-frequency accepting modes of 165 cm⁻¹ for H_2^* (and 150 cm⁻¹ for bond-center hydrogen) nearly coincide with transverse acoustic phonons of the undistorted Si crystal (Fig. 2), which have been calculated in Ref. [19]. Likewise, the 343-cm⁻¹ modes involved in the decay of the stretch mode of $HV \cdot VH_{(110)}$ nearly coincide with the peak in the longitudinal acoustic phonon density (Fig. 2).

The most significant result obtained from our transient bleaching experiments is the large difference in the temperature dependence of the lifetimes of H_2^* and $HV \cdot VH_{(110)}$. We believe that this may be an important clue in explaining the 2-orders-of-magnitude difference in the absolute lifetimes. Indeed, the fact that these modes have very different lifetimes is surprising at first glance considering that both Si-H stretch modes have nearly the same frequency and symmetry, and the compound density of accepting phonon states of the unperturbed lattice $\rho_{\{v\}}$ is almost identical. The critical difference between these defects is their local structure, interstitial- or vacancy-like, which gives rise to a very different local vibrational mode structure, referred to as pseudolocalized modes (PLMs). Evidently it is these local modes that govern the lifetimes, and are responsible for the observed preferential couplings to characteristic bulk phonons. Furthermore, to explain the large difference in lifetimes, one should also consider the anharmonic coupling strength between the stretch mode and the low-frequency modes. In the $HV \cdot VH_{(110)}$ center, it certainly seems plausible that the relatively large open volume of the vacancies would lead to a small interaction between the hydrogen and the surrounding silicon atoms. This small interaction would lead to a longer vibrational lifetime.

These results have great significance in excitation processes which involve the dynamics of energy dissipation in solids. A specific example is the desorption of H at the silicon/silicon dioxide interface [8–10]. The rate of H loss is a sensitive function of the excitation to vibrational states of the Si-H bond and the lifetimes of these states. The results presented here indicate that the relevant lifetime is a strong function of the local defect configuration. Thus quantitative models of these processes require detailed knowledge of the local structure and the associated local phonons.

In conclusion, we have measured the vibrational lifetime of the Si-H stretch mode of two structurally distinct

point defects in Si, H_2^* , and $HV \cdot VH_{(110)}$, as a function of temperature. We have shown that the dominating decay channels of these defects are significantly different, involving low-frequency accepting modes (165 and 343 cm^{-1}) of very different symmetry. It is suggested that this highly selective behavior is due to the nature of the local distortions and the associated pseudolocalized phonon modes. A more detailed understanding of the nature of these PLMs is required to fully elucidate the vibrational energy relaxation and transfer channels in solids.

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- [1] A. Nitzan and J. Jortner, *Mol. Phys.* **25**, 713 (1973); A. Nitzan, S. Mukamel, and J. Jortner, *J. Chem. Phys.* **60**, 3929 (1974).
- [2] A. S. Barker, Jr. and A. J. Sievers, *Rev. Mod. Phys.* **47**, Suppl. No. 2, S1 (1975).
- [3] G. R. Neil, C. L. Bohn, S. V. Benson, G. Biallas, D. Douglas, H. F. Dylla, R. Evans, J. Fugitt, A. Grippo, J. Gubeli, R. Hill, K. Jordan, R. Li, L. Meringa, P. Piot, J. Preble, M. Shinn, T. Siggins, R. Walker, and B. Yunn, *Phys. Rev. Lett.* **84**, 662 (2000).
- [4] M. Budde, G. Lüpke, C. Parks Cheney, N. H. Tolk, and L. C. Feldman, *Phys. Rev. Lett.* **85**, 1452 (2000).
- [5] M. Budde, G. Lüpke, E. Chen, X. Zhang, N. H. Tolk, L. C. Feldman, E. Tarhan, A. K. Ramdas, and M. Stavola, *Phys. Rev. Lett.* **87**, 145501 (2001).
- [6] T.-C. Shen, C. Wang, G. C. Abeln, J. R. Tucker, J. W. Lyding, Ph. Avouris, and R. E. Walkup, *Science* **268**, 1590 (1995).
- [7] K. Hess, L. F. Register, B. Tuttle, J. Lyding, and I. C. Kizilyalli, *Physica (Amsterdam)* **3E**, 1 (1998).
- [8] B. N. J. Persson and Ph. Avouris, *Surf. Sci.* **390**, 45 (1997).
- [9] E. T. Foley, A. F. Kam, J. W. Lyding, and Ph. Avouris, *Phys. Rev. Lett.* **80**, 1336 (1998).
- [10] C. G. Van de Walle and W. B. Jackson, *Appl. Phys. Lett.* **68**, 2526 (1996).
- [11] S. J. Pearton, J. W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors* (Springer-Verlag, Berlin, 1992), and references therein.
- [12] *Hydrogen in Semiconductors II: Semiconductors and Semimetals*, edited by N. H. Nickel (Academic Press, New York, 1999), Vol. 61, and references therein.
- [13] J. D. Holbeck, B. Bech Nielsen, R. Jones, P. Sitch, and S. Öberg, *Phys. Rev. Lett.* **71**, 875 (1993).
- [14] M. Suezawa, *Phys. Rev. B* **63**, 035201 (2001).
- [15] S. A. Egorov and J. L. Skinner, *J. Chem. Phys.* **103**, 1533 (1995).
- [16] P. Stallinga, P. Johannesen, and S. Herstrøm, B. Bech Nielsen, and J. R. Byberg, *Phys. Rev. B* **58**, 3842 (1998).
- [17] The lifetime of 4.2 ± 0.2 ps obtained directly from the transient bleaching experiment is significantly longer than the $T_1 = 1.9$ ps estimated from the width of the 2062.1-cm^{-1} line [5], indicating that the low-temperature linewidth is still broadened by intrinsic (homogeneous) dephasing processes which can be investigated by photon-echo measurements of T_2^* .
- [18] The contribution of the 2068-cm^{-1} line to S_b is expected to be very small since the transient bleaching signal is a non-linear function of the laser intensity. In addition, the $HV \cdot VH_{(110)}$ and $HV \cdot V$ defects are structurally very similar, and we therefore expect them to have similar lifetimes.
- [19] C. Flensburg and R. F. Stewart, *Phys. Rev. B* **60**, 284 (1999).