Vibrational Lifetime of Bond-Center Hydrogen in Crystalline Silicon

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The lifetime of the stretch mode of bond-center hydrogen in crystalline silicon is measured to be $T_1 = 7.8 \pm 0.2$ ps with time-resolved, transient bleaching spectroscopy. The low-temperature spectral width of the absorption line due to the stretch mode converges towards its natural width for decreasing hydrogen concentration C_H, and nearly coincides with the natural width for $C_H \sim 1$ ppm. The lifetimes of the Si-H stretch modes of selected hydrogen-related defects are estimated from their spectral widths and shown to range from 1.6 to more than 37 ps.

Light impurities in crystalline solids give rise to localized vibrational modes (LVMs) with frequencies above the phonon bands of the solid [1]. LVM spectroscopy has been applied extensively to study isolated impurities and impurity complexes in crystalline solids, including ionic crystals [1] and semiconductors [2]. One of the impurity-material systems studied most extensively is H in semiconductors, which has attracted much interest because of H's ability to interact with virtually any lattice imperfection, including impurities, intrinsic defects, surfaces, and interfaces, thus possibly changing the electronic properties of the material [3,4]. Until now, all spectroscopic studies of H-related LVMs in semiconductors have been carried out in the frequency domain, which probes the time-averaged optical response of the modes. Consequently, very little is known about the dynamics of the modes, i.e., the time scales and mechanisms for population and phase relaxation upon excitation. Such information is crucial since excited vibrational states may be involved in the dissociation of the bond between H and the lattice. For instance, it has been proposed that the degradation of some electronic devices be caused by dissociation of vibrationally excited Si-H bonds [5]. To understand such processes, it is necessary to know the time scale on which excited vibrational states decay, which is given by the lifetime of the states.

In this paper we report the first measurements of the lifetime of a LVM in a crystalline semiconductor. The lifetime of the stretch mode of bond-center H in Si, $H_{BC}^{(+)}$, at 1998 cm^{-1} is measured to be $T_1 = 7.8 \pm 0.2$ ps by transient bleaching spectroscopy. Infrared absorption spectroscopy (IRAS) shows that the spectral width of the stretch mode nearly coincides with its natural linewidth in samples with low H concentrations, indicating that lifetimes of LVMs under such conditions can be estimated from their spectral width. Using this approach, we estimate the Si-H stretch lifetimes of a selection of structurally well-characterized defects. Lifetimes of Si-H stretch modes are found to be strongly dependent on the structure of the defects, ranging from 1.6 to at least 37 ps.

There are several good reasons for studying $H_{BC}^{(+)}$: It is the most fundamental H-related defect in Si, and plays a key role in the reactions of H with defects and impurities. Moreover, it has been studied in great detail experimentally [6–10] and theoretically [11], and is thus well characterized. Finally, $H_{BC}^{(+)}$ gives rise to an intense absorption line at 1998 cm^{-1} due to the excitation of the stretch mode, where the H vibrates parallel to the Si-H-Si bond axis [see Fig. 1(a)] [6–8]. The large absorption cross section of this mode makes it ideal for the experiments reported here.

The samples used in our experiments were cut from high-resistivity Si single crystals. Unless stated otherwise, the samples were implanted with protons at 28 different energies in the range 1.0–1.8 MeV, yielding a constant H concentration C_H of 0.83 to 1.7×10^2 ppm over a range of 24 μm. The samples were cooled to 80 K during implantation and kept below 150 K afterwards to prevent $H_{BC}^{(+)}$ from diffusing. This was accomplished by implanting into a cryostat attached to the end of the accelerator
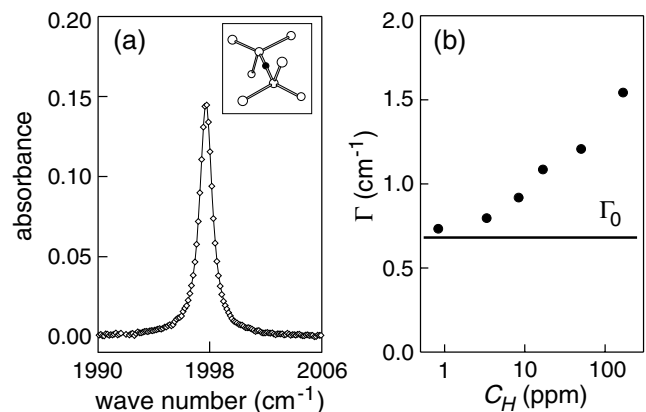

FIG. 1. (a) Absorbance spectrum of proton-implanted Si showing the 1998 cm^{-1} line of $H_{BC}^{(+)}$, shown in the inset. The solid line represents a Lorentzian fit to the data. The spectrum was measured at $\sim$10 K on a sample with $C_H = 17$ ppm. (b) FWHM of the 1998 cm^{-1} line vs C_H. The line represents the natural line width Γ_0 obtained from the lifetime of the mode and Eq. (3).

beam line. After implantation the cryostat was detached from the beam line and moved to the spectroscopic setup. IRAS was performed with a commercial Bruker IFS-66v FTIR spectrometer.

The vibrational lifetime of the 1998 cm^{-1} mode was measured using a standard pump-probe setup. Two different tunable, infrared lasers were used: a Quantronix Optical Parametric Amplifier (OPA) and the Free Electron Laser (FEL) at Thomas Jefferson National Accelerator Facility (TJNAF). The lasers delivered pulses with a time duration ~1 ps, spectral width 14 cm^{-1}, and pulse energy of ~0.5 μJ for the FEL and ~5 μJ for the OPA. The major difference between the lasers is the pulse repetition rate, which is 18.6 MHz for the FEL and 1 kHz for the OPA. The higher repetition rate and better stability of the FEL improves the signal-to-noise ratio of the measurements compared to those with the OPA system. In transient bleaching spectroscopy, the laser beam is split into two parts, pump and probe, carrying 91% and 9% of the power, respectively. The pump excites a fraction of the $H_{BC}^{(+)}$ defects to the first excited state of the 1998 cm^{-1} mode, which causes a transient increase in the transmission coefficient of the sample that decays over time due to the decay of the excited mode. The transient bleaching signal S_b is monitored with the probe beam, delayed in time with respect to the pump.

Figure 2(a) shows S_b as a function of time delay between probe and pump measured at ~20 K with the FEL. The data are well represented by a single-exponential decay with a time constant $T_1 = 7.8 \pm 0.2$ ps. Measurements of S_b vs wavelength showed that S_b originates from the 1998 cm^{-1} mode. Measurements with the OPA system yielded a lifetime in agreement with that obtained at the FEL, showing that the measured lifetime is independent of average laser power.
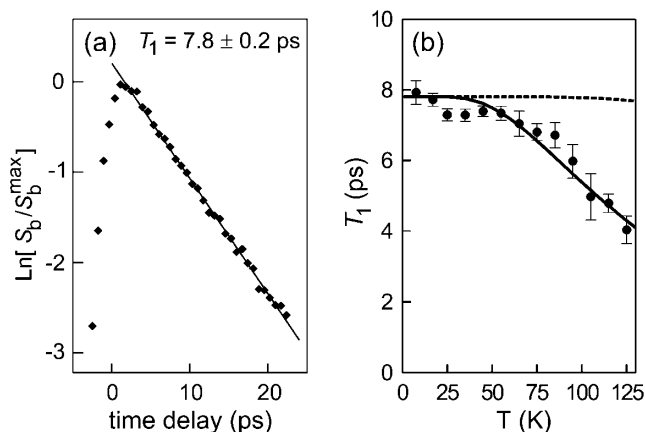

FIG. 2. (a) Decay of the transient bleaching signal from the 1998 cm^{-1} line of $H_{BC}^{(+)}$ measured at ~20 K with the FEL. (b) Temperature dependence of T_1 measured with the OPA. The broken and solid lines are the theoretical predictions from Eqs. (1) and (2) for decays into the set of accepting modes {500, 500, 500, 500} and {150, 150, 150, 516, 516, 516} cm^{-1}.

The excited 1998 cm^{-1} mode can, in principle, decay into photons, electronic degrees of freedom, or other vibrational modes. The radiative lifetime can be estimated to be of the order of milliseconds [12], which rules out radiative decay as the dominating mechanism. Electronic decay can also be ruled out because the positive charge state of H_{BC} studied here has no occupied electronic levels in the band gap. Consequently, only electronic transitions from the valence band to the conduction band or directly to the donor level of H_{BC} are possible, both of which require more energy than the 1998 cm^{-1} available. We therefore conclude that the 1998 cm^{-1} mode decays into vibrational modes of the system consisting of a Si lattice with a H atom located at a bond-center site.

The lifetime of a high-frequency vibrational mode decaying into a bath of low-frequency modes has been studied theoretically by Nitzan et al. [13], who obtained the following expression for the decay rate (inverse lifetime):

$$\frac{1}{T_1} = 2\pi \sum_i |G_i|^2 f_i. \qquad (1)$$

The total decay rate is given as the sum of the rates of all of the decay channels. Each channel is characterized by the set $\{\omega_1, \omega_2, \ldots, \omega_{N_i}\}$ of accepting mode frequencies. Since energy is conserved in the decay process, $\hbar\omega = \sum_{j=1}^{N_i} \hbar\omega_j$, where the sum extends over the frequencies in a given set and ω is the frequency of the LVM. The decay rate of each channel is given by the coupling strength G_i of the channel and the function f_i describing its temperature dependence:

$$f_i = \frac{\exp(\hbar\omega/k_B T) - 1}{\prod_{j=1}^{N_i}[\exp(\hbar\omega_j/k_B T) - 1]}. \qquad (2)$$

In the low-temperature limit ($k_B T \ll \hbar\omega_j, \forall \omega_j$), the decay rate reflects spontaneous decay into the N_i accepting modes and $f_i \cong 1$. At higher temperatures the decay rate increases due to stimulated emission in a fashion determined by the frequencies of the accepting modes [13].

Figure 2(b) shows T_1 vs temperature measured with the OPA. T_1 is nearly constant up to ~60 K, where it starts to decrease, reaching half its low-temperature value at 125 K. The lifetime $T_1 = 7.8 \pm 0.2$ ps thus reflects spontaneous decay. The coupling strengths G_i are proportional to the derivative of the potential energy surface with respect to the normal coordinates of the 1998 cm^{-1} mode and the N_i accepting modes, corresponding to anharmonic terms of order $N_i + 1$. Since the magnitude of the anharmonic terms is believed to fall off rapidly with increasing order, channels with small N_i are likely to dominate the decay. The decay channel of the 1998 cm^{-1} mode with lowest order is the decay into four modes with frequencies at about 500 cm^{-1}, corresponding to optical phonons or possibly Si-related LVMs split off from the phonon bands by the strain fields in the vicinity of $H_{BC}^{(+)}$ [14]. Figure 2(b) shows that the temperature dependence of T_1 is incompatible with the 1998 cm^{-1} mode decaying predominantly

into four modes at about 500 cm^{-1}. Instead, two or three low-frequency modes at about 150 cm^{-1} are required to obtain qualitative agreement with the data [see example in Fig. 2(b)]. The nature of these modes is not known. However, likely candidates are TA phonons and/or pseudolocalized (resonant) modes of H$_{BC}^{(+)}$ [14].

The dynamics of vibrational modes can also be studied in the frequency domain by IRAS. The shape of an absorption line is generally given by the convolution of its homogeneous line shape with a function describing the inhomogeneous broadening [15]. At very low temperatures the homogeneous line shape is Lorentzian with a FWHM (in cm^{-1}) given by

$$\Gamma_0 = \frac{1}{2\pi c T_1}. \tag{3}$$

For LVMs in crystals, the inhomogeneous broadening is determined by the strain fields induced by lattice defects present in the sample. Since the most abundant imperfections in our samples are defects formed during implantation, one would expect the inhomogeneous broadening to decrease with decreasing C_H.

Figure 1(a) shows the absorption line associated with the fundamental transition of the 1998 cm^{-1} mode measured with IRAS at ~10 K, which is well represented by a Lorentzian. The FWHM of the absorption line is shown in Fig. 1(b) as a function of C_H. The width decreases monotonically with decreasing C_H and nearly coincides with the natural linewidth obtained from Eq. (3) for $C_H \sim 1$ ppm. Thus, the results obtained in time and frequency domain are fully consistent. Moreover, the convergence demonstrates that good estimates of the vibrational lifetime can be obtained from IRAS on samples with low concentrations of H and lattice defects.

When Si, implanted with protons at cryogenic temperatures, is heated above ~180 K, the 1998 cm^{-1} line disappears and a series of new lines is formed in the range 1800–2250 cm^{-1}, which have been identified as Si-H stretch modes of distinct H-related defects (see, e.g., Refs. [16–19]). The average absorption cross section of these modes is ~25 times smaller than that of the 1998 cm^{-1} mode [8], which makes direct lifetime measurements on these defects by transient bleaching spectroscopy much more difficult. However, we can estimate the lifetimes of these modes from their spectral widths. In order to do so, IRAS measurements were performed with 0.15-cm^{-1} resolution at ~10 K on a Si sample with $C_H = 7.3$ ppm [20]. Table I gives the spectral widths Γ of the stretch modes of a selection of defects, which are structurally well characterized. The widths vary from 0.15 cm^{-1} for the 2068 cm^{-1} mode of the divacancy binding one H atom (V$_2$H) to 3.4 cm^{-1} for the 2062 cm^{-1} mode of the H$_2^*$ defect. The fact that absorption lines as narrow as 0.15 cm^{-1} are observed shows that the inhomogeneous broadening contribution to the widths is significantly less than for the 1998 cm^{-1} line at the same C_H [see Fig. 1(b)]. This can

TABLE I. Spectral width Γ and minimal lifetime $T_{1,min}$ for a selection of H-related defects. All Γ's were measured at ~10 K with a resolution of 0.15 cm^{-1} on the same sample with $C_H = 7.3$ ppm [20]. The Γ's are not corrected for instrumental broadening. $T_{1,min}$ was obtained from Γ and Eq. (3), except when measured directly. The lifetimes of Si-H modes in a-Si and on Si surfaces are shown for comparison.

Defect	Ref.	ω (cm^{-1})	Γ (cm^{-1})	$T_{1,min}$ (ps)
H$_2^*$	[16]	1839	1.8	2.9
H$_2^*$	[16]	2062	3.4	1.6
IH$_2$	[17]	1987	0.70	7.6
IH$_2$	[17]	1990	0.72	7.4
H$_{BC}^{(+)}$		1998	0.73 (0.68)[a]	7.8 ± 0.2
VH	[18]	2038	0.48	11
VH$_2$	[19]	2122	0.21	25
VH$_2$	[19]	2145	0.26	21
V$_2$H	[18]	2068	0.15	37
a-Si:H	[21,22]	2000		~10, 100[b]
Si(111)/H	[23]	2086		1400 ± 200[c]
Si(100)/H	[24]	2099		>6000[c]

[a]Natural linewidth calculated from $T_1 = 7.8 \pm 0.2$ ps.
[b]Measured at RT.
[c]Measured at ~100 K.

be explained by the annealed sample having a smaller defect concentration because of defect recombination and agglomeration. In addition, the 1998 cm^{-1} mode is more sensitive to strain than the modes observed after annealing at RT [8]. Table I also lists the minimal lifetimes $T_{1,min}$ of the modes obtained from Γ and Eq. (3). $T_{1,min}$ is a good estimate of the vibrational lifetimes for $T_{1,min} < 20$ ps, whereas it may be significantly smaller than the real lifetime for $T_{1,min} > 20$ ps due to instrumental and inhomogeneous broadening. Indeed, we have recently shown by transient bleaching spectroscopy that the 2062 cm^{-1} mode has a lifetime less than 5 ps, consistent with the estimate obtained from IRAS.

Table I shows that the lifetimes of Si-H stretch modes depend strongly on the bonding configuration of the defects. For instance, the interstitial-type defects H$_2^*$, IH$_2$, and H$_{BC}^{(+)}$ have lifetimes of 1.6–8 ps, whereas the lifetimes of vacancy-hydrogen complexes are at least 11–37 ps. The most striking example of the structural dependence is the factor of 20 difference in the lifetime of the 2062 and 2068 cm^{-1} modes of H$_2^*$ and V$_2$H. The strong structural dependence might be explained by either pseudolocalized modes or LVMs being involved in the decay process. Being localized around the defect, such modes have much larger vibrational amplitudes on the atoms close to the Si-H bond than, e.g., lattice phonons, which may cause a strongly enhanced anharmonic coupling to the Si-H stretch mode. However, significant distortions of the Si-Si bonds in the vicinity of the defects are required for pseudolocalized modes or LVMs to form [1], which is consistent with highly distorted interstitial-type defects having shorter lifetimes than vacancy-type defects.

Finally, it is interesting to compare our results with measurements of Si-H modes in different environments. The lifetime of Si-H stretch modes in amorphous Si (a-Si) was recently studied by pump-probe spectroscopy. In this material, the population relaxation is biexponential with a short decay time of $\sim$10 ps and a long decay time of $\sim$100 ps [21,22]. The fast component was initially ascribed to redistribution within the Si-H stretch band and the slow component to decay of the Si-H stretch modes into Si-H bend modes or phonons [21]. However, more recent experiments indicate that the two decay times are due to stretching vibrations at different sites having different lifetimes [22]. The results of this paper support the latest interpretation. It is also interesting to compare our results with measurements of the lifetimes of Si-H stretch phonons on H-terminated Si surfaces. Both the Si(111)/H and the Si(100)/H systems have Si-H lifetimes in excess of 1000 ps at $\sim$100 K [23,24], i.e., 2–3 orders of magnitude longer than we observe for Si-H stretch modes of interstitial-type point defects. This difference may stem from the fact that both the stretch and accepting modes are delocalized in the H-terminated surface case, which may result in an anharmonic coupling strength very different from that between LVMs and the accepting modes in the bulk.

In conclusion, we have measured the vibrational lifetime of the stretch mode of $H_{BC}^{(+)}$ in crystalline Si to be $T_1 = 7.8 \pm 0.2$ ps, and have shown that the dominating decay channel involves modes of $\sim$150 cm^{-1}. Lifetimes of a selection of structurally well-characterized defects were estimated with IRAS. The lifetimes of interstitial-type defects were found to be very short (1.6–8 ps), whereas vacancy-type defects have lifetimes larger than 11–37 ps. The strong dependence of the lifetime on the atomic structure of the defect suggests that pseudolocalized modes or LVMs are involved in the vibrational relaxation of Si-H bonds of point defects in solids.

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