Lifetimes of Hydrogen and Deuterium Related Vibrational Modes in Silicon

M. Budde,[1,*] G. Lüpke,[2] E Chen,[3] X. Zhang,[2] N. H. Tolk,[1] L. C. Feldman,[1] E. Tarhan,[4] A. K. Ramdas,[4] and M. Stavola[3]

[1]*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235*
[2]*Department of Applied Science, The College of William and Mary, Williamsburg, Virginia 23187*
[3]*Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015*
[4]*Department of Physics, Purdue University, West Lafayette, Indiana 47907*

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Lifetimes of hydrogen and deuterium related stretch modes in Si are measured by high-resolution infrared absorption spectroscopy and transient bleaching spectroscopy. The lifetimes are found to be extremely dependent on the defect structure, ranging from 2 to 295 ps. Against conventional wisdom, we find that lifetimes of Si-D modes typically are longer than for the corresponding Si-H modes. The potential implications of the results on the physics of electronic device degradation are discussed.

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Hydrogen passivation of defects is a standard processing step in the production of metal-oxide-semiconductor (MOS) electronic devices. This process reduces the density of P_b centers, the most abundant electrically active defect at the Si/SiO_2 interface, by 3 orders of magnitude (see, e.g., Ref. [1] and references therein). The passivation takes place by H atoms forming covalent bonds with the Si dangling bond of the P_b centers, which removes their electronic states from the band gap. Although H passivation solves the immediate problem by dramatically reducing the density of electronic band-gap states at the interface, it is a potential source for device degradation because reactivation of just a small fraction of the passivated P_b centers may alter the device characteristics and thus cause device failure. Lyding *et al.* demonstrated that H plays an active role in the degradation process by showing that devices treated with deuterium (D) have transconductance lifetimes 10–50 times longer than H-passivated devices [2]. Similar "giant isotope effects" have been observed in other contexts [3–5].

Dissociation of Si-H and Si-D bonds is believed to be caused by inelastic electron scattering, which excites the bonds to either a dissociative electronic state or to excited vibrational states [3,6–8]. In this paper we shall focus on the vibrational excitation mechanism, which has been described by the truncated harmonic oscillator (THO) model [3,6–8]. This model describes the Si-H and Si-D bonds as harmonic oscillators, and assumes that the bonds dissociate at a rate given by the rate of excitation from the highest bound vibrational state $|N_{\max}\rangle$ to the lowest unbound state $|N_{\max} + 1\rangle$. Within this model, the dissociation rate is approximately given by

$$R \sim \frac{N_{\max} + 1}{T_1}\left(\frac{\Gamma_{\text{exc}}}{\Gamma_{\text{exc}} + 1/T_1}\right)^{N_{\max}+1}, \qquad (1)$$

where T_1 is the lifetime of the vibrational state $|1\rangle$ and Γ_{exc} is the excitation rate of the $|0\rangle \rightarrow |1\rangle$ transition [3,6–8]. The THO model is in qualitative agreement with H desorption experiments [7,8]. However, this agreement may be fortuitous: For instance, it is well known that Si-H and Si-D bonds are anharmonic, which causes the level spacing to decrease with increasing N. This will affect the value of $N_{\max}$ in (1), and hence also the dissociation rate predicted by the model. Moreover, the assumption of a single normal mode may not be justified, since both the stretching and the bending modes may play a role in the dissociation process [9]. Despite these potentially unjustified assumptions, we believe that the THO model provides a framework for discussing bond dissociation via vibrational excitation. For instance, it is evident from (1) that Γ_{exc} has to be on the order of the decay rate, $1/T_1$, for bond breaking to proceed via this mechanism. The model also provides a simple explanation for the H/D isotope effect. For instance, $N_{\max}$ for Si-D is $\sim\sqrt{2}$ times greater than for Si-H, which would lead to a great reduction in the dissociation rate. Moreover, Si-D modes are usually believed to have shorter T_1's than the corresponding Si-H modes (see, e.g., [9]), which would make the isotope effect even greater.

The rate given by (1) was found to be in qualitative agreement with the degradation rate of MOS devices [7]. To this end, it was assumed that $T_1 \sim 1000$ ps as measured for the Si-H stretch mode of Si surfaces terminated with a full monolayer of hydrogen [10]. In contrast, we recently showed that the lifetimes of isolated Si-H stretch modes of point defects in Si can be as short as 1–10 ps. Such short T_1's would require unrealistically large excitation rates for (1) to yield dissociation rates in agreement with observations. Since Si-H bonds at the Si/SiO_2 interface are isolated, but may be similar structurally to Si-H bonds on Si surfaces, it is critical to determine the lifetime of the Si-H modes as a function of concentration and configuration and to compare these values to deuterium containing defects.

In this work we extend our previous studies of vibrational lifetimes of H related stretch modes in Si, and report the first measurements of the corresponding D related defects. We use high-resolution IR absorption spectroscopy in combination with samples with very low defect densities

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to measure T_1 for stretch modes of a variety of H related defects in Si. The frequency-domain measurements are supported by direct measurements of the population decay by transient bleaching spectroscopy. We find that the T_1's are extremely dependent on the structure of the defect, ranging from ~2 ps for the H_2^* defect to 295 ps for the divacancy binding two H atoms ($HV \cdot VH_{(110)}$). We also argue that the Si-H bond of the $HV \cdot VH_{(110)}$ defect resembles that of the H-passivated P_b center at the Si/SiO_2 interface, suggesting that the latter also have lifetimes of the order of hundreds of picoseconds. Consequently, P_b:H defects may be particularly susceptible to dissociation by the vibrational excitation mechanism. We also extend the lifetime measurements to Si-D stretch modes. Surprisingly, we find that Si-D modes typically have larger T_1's than the corresponding Si-H modes. However, there are exceptions to this rule, one of which is the stretch mode of $DV \cdot VD_{(110)}$, which has a lifetime 3 times shorter than the Si-H mode. According to the THO model, this should cause the dissociation rate of $HV \cdot VH_{(110)}$ defects, and therefore perhaps P_b:H defects, to exhibit a particularly large H/D isotope dependence.

As discussed in Ref. [11], the lifetime of the state $|1\rangle$ of a local vibrational mode (LVM) is given by

$$T_1 = \frac{1}{2\pi c \Gamma_0}, \qquad (2)$$

where c is the speed of light and Γ_0 is the full width at half maximum (FWHM) of the absorption line, given in cm^{-1}, associated with the fundamental transition of the mode. For (2) to be valid, Γ_0 has to correspond to the natural linewidth, and measured FWHMs may have to be corrected for instrumental and inhomogeneous broadening. To minimize the error in T_1 introduced by such corrections, the present measurements were performed at the highest resolution possible using samples with very low defect concentrations.

The samples were 15 mm thick and consisted of n-type Si ($[As] = 3 \times 10^{14}$ cm^{-3}) grown by the float-zone method. The samples were doped with H (Si:H) or D (Si:D) by annealing at 1250 °C for 30 min in quartz ampules containing H_2 or D_2 gas at 0.66 atm. The anneals were terminated by a rapid quench in water to room temperature (RT). The concentration of H or D was $\sim 1 \times 10^{16}$ cm^{-3}, as determined by IR absorption measurement of the 3618-cm^{-1} line of H_2 in Si [12]. The point defects studied here were created by irradiating the samples with 2.5-MeV electrons at RT to a total dose of 10^{17} cm^{-2}. The samples were irradiated with half the total dose from opposite sides to make the defect concentration nearly uniform. We estimate the defect concentration to be $\sim 10^{16}$ cm^{-3}, ~50 times smaller than in the proton-implanted samples studied in Ref. [11], which results in significantly less inhomogeneous broadening. IR absorbance spectra of the Si:H and Si:D samples were measured with a resolution of 0.025 cm^{-1} using a Bomem DA3.16 Fourier transform infrared (FTIR) spectrometer. The spectrum of the Si:H sample was also measured with a Bomem DA3.36 FTIR spectrometer with a resolution of 0.006 cm^{-1} to minimize instrumental broadening. The samples were cooled to 5–8 K during the absorption measurements. Spectra were also measured at elevated temperatures to insure that line broadening due to pure dephasing [13] is negligible at 8 K.

The spectra revealed a series of absorption lines in the Si-H and Si-D stretch regions, some of which are shown in Fig. 1. The absorption lines have been studied extensively and assigned to the H_2^* defect [14], the hydrogen-saturated self-interstitial IH_2 [15], the monovacancy binding two H (VH_2) or four H (VH_4) [16]. Recently, Suezawa assigned the line at 2072.5 cm^{-1} (see Fig. 1) to the divacancy binding two H atoms [17]. We denote this defect $HV \cdot VH_{(110)}$ to emphasize that the Si-H bonds are located in the same (110) plane, in separate halves of the divacancy [18]. One of the main results of Ref. [11] was that the lifetimes of Si-H stretch modes in Si depend strongly on the bonding configuration of the defect. Both $HV \cdot VH_{(110)}$ and P_b:H consist of H atoms forming a covalent bond with a Si dangling bond, with the H atom well separated from all atoms other than the Si to which it is bonded. Because of these structural similarities we expect the vibrational properties of P_b:H to be very similar to the $HV \cdot VH_{(110)}$ complex.

The lifetimes of the Si-H modes were obtained in the following way: First, the FWHMs of the lines were obtained by fitting Lorentzian line shapes to the measured absorbance profiles. These FWHMs were then corrected for instrumental broadening [19], and the result was entered into (2). As shown in Table I, the lifetimes of Si-H stretch modes are extremely dependent on the defect structure, ranging from 1.9 ps for H_2^* to more than 262 ps for $HV \cdot VH_{(110)}$. We shall not discuss the reasons for this here, but refer the reader to Ref. [11]. However, we note

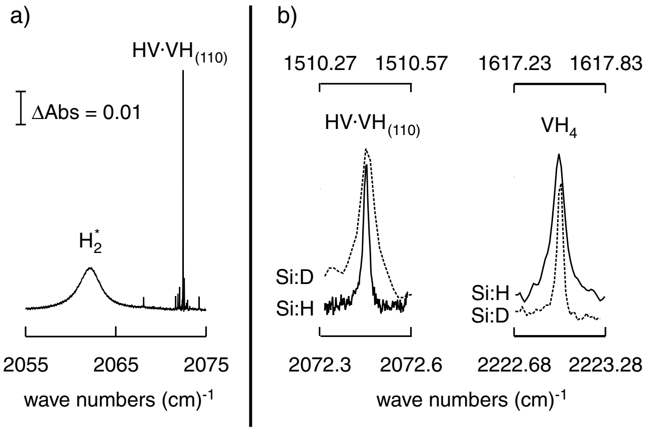

FIG. 1. (a) Section of the IR absorbance spectrum of e-irradiated, H-doped Si, showing the lines of $HV \cdot VH_{(110)}$ and H_2^*. (b) Comparison of the Si-H (full) and Si-D (dashed) absorption lines of $HV \cdot VH_{(110)}$ and VH_4. The instrumental resolution was 0.025 cm^{-1}, except for the 2072.5-cm^{-1} line which was measured with a resolution of 0.006 cm^{-1}.

TABLE I. Lifetimes of H and D related stretch modes in Si. To obtain the lifetimes shown in columns 3 and 4, the linewidths were corrected for instrumental broadening and then entered into (2).

Defect	Si-H ω (cm^{-1})	Si-H T_i (ps)	Si-D T_i (ps)	Si-D ω (cm^{-1})
H_2^*	2062.1	1.9	4.8	1500.1
IH_2	1987.1	12	20	1446.5
IH_2	1990.0	11	18	1448.7
VH_2	2122.3	60	70	1547.9
VH_2	2145.1	42	55	1565.1
VH_4	2223.0	56	143	1617.5
$HV \cdot VH_{(110)}$	2072.5	262 (295 ± 6)[a]	93	1510.4

[a] Measured by transient bleaching spectroscopy.

that the reduction in defect density and higher spectral resolution make the present lifetimes more reliable than our previous data.

The narrowest line in the Si:H spectrum originates from the 2072.5-cm^{-1} mode of $HV \cdot VH_{(110)}$. Having a width of only 0.0203 cm^{-1}, this mode has a lifetime of at least 262 ps. It cannot be ruled out that the width is dominated by inhomogeneous broadening, and hence the lifetime could be significantly longer. To obtain a reliable T_1 for this defect, we measured the lifetime directly with transient bleaching spectroscopy. This technique requires stronger absorption lines than can be obtained by e-irradiation of H-doped Si, and we therefore used a proton-implanted Si sample.

The sample was a 2-mm thick, disk-shaped Si single crystal, coated with a mid-IR antireflection coating on one side. The coating prevented spurious signals due to internally reflected light. A total dose of 2×10^{17} protons/cm^2 was implanted into the uncoated side of the sample at 80 K yielding a 47-μm deep, uniform H concentration profile (see Ref. [11] for details). The absorbance spectrum of the sample revealed a series of strong absorption lines in the Si-H stretch region including the 2062.1-cm^{-1} line of H_2^* and the 2072.5-cm^{-1} line of $HV \cdot VH_{(110)}$ observed in the e-irradiated sample. In addition, a line was observed at 2068 cm^{-1} with $\sim\frac{1}{3}$ the intensity of the 2072.5-cm^{-1} line. This line has been assigned to the divacancy binding one H atom $V \cdot VH$ [20].

The transient bleaching signal S_b was measured as a function of time delay between pump and probe pulses, as described in Ref. [11]. The experiments were performed using picosecond light pulses, centered on the 2072.5-cm^{-1} line, generated by the free-electron laser (FEL) at the Thomas Jefferson National Accelerator Facility (TJNAF). The laser spectrum has a FWHM of $\sim$14 cm^{-1}, and the stretch modes of H_2^* and $V \cdot VH$ at 2062.1 and 2068 cm^{-1} therefore also contribute to S_b. Figure 2 shows a semilog plot of S_b vs time delay measured at $\sim$10 K. The signal decreases exponentially with a time constant of 295 ± 6 ps once two fast decaying transients associated with H_2^* and the bulk crystal have vanished. This time constant corresponds to T_1 of the 2072.5-cm^{-1} mode of $HV \cdot VH_{(110)}$, possibly with a small contribution from $V \cdot VH$ [21]. The extremely long lifetime of $HV \cdot VH_{(110)}$ compared to other defects shows that this bonding configuration is particularly susceptible to dissociation by the vibrational excitation mechanism. Because of the structural similarity of P_b:H and $HV \cdot VH_{(110)}$ centers, this indicates that P_b:H centers could be responsible for degradation of CMOS devices.

Table I also shows the lifetimes of the Si-D stretch modes, and allows for the first time a direct comparison of the lifetimes of H and D related LVM's. Substitution of H with D may affect the lifetime of LVM's in two ways. First, the vibrational amplitude is less for Si-D modes than for Si-H modes, and since the decay of the LVM into other modes is an anharmonic effect, Si-D modes have longer lifetimes than the corresponding Si-H modes. Second, the vibrational energy of the Si-D mode is $\sim\sqrt{2}$ less than that of the Si-H mode. Consequently, the order of the decay process, i.e., the number of modes into which the LVM decays, can be smaller for Si-D than for Si-H. Since the strengths of anharmonic terms are expected to decrease with increasing order, this suggests that Si-D modes

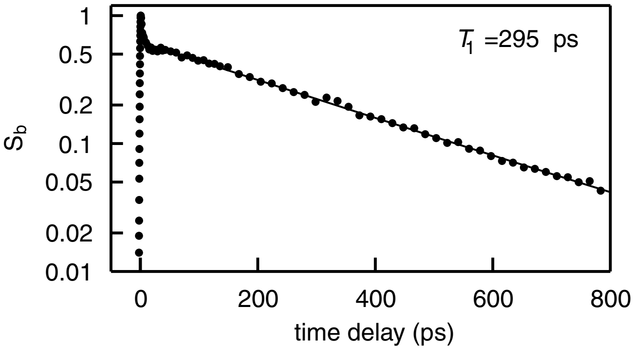

FIG. 2. Normalized transient bleaching signal S_b as a function of the time delay between pump and probe. For delays larger than $\sim$20 ps, S_b decays exponentially with a time constant of $T_1 = 295 \pm 6$ ps, corresponding to the decay of the $|1\rangle$ state of the 2072.5-cm^{-1} mode of $HV \cdot VH_{(110)}$. The peak at short delays originates from the Si crystal and the 2062.1-cm^{-1} mode of H_2^*. The measurements were performed at $\sim$10 K on a proton-implanted Si sample.

have shorter lifetimes than the corresponding Si-H modes. Until now, the second contribution has been assumed to be dominant [9], which is consistent with the experimental results for Si-H and Si-D modes on H-terminated Si surfaces [10]. In contrast, Table I shows that the lifetimes of D related stretch modes are longer than the corresponding Si-H lifetimes for all defects except $\mathrm{HV \cdot VH_{(110)}}$, for which the Si-D lifetime is 3 times shorter than for Si-H [see also Fig. 1(b)]. According to (1), the inverted isotope dependence of T_1 observed for $\mathrm{HV \cdot VH_{(110)}}$ implies that this defect, and perhaps also P_b:H centers, exhibits much larger differences in Si-D and Si-H dissociation rates than most other H related defects.

Before closing, we would like to place the present work in the proper perspective. We have measured the lifetimes of a selection of Si-H and Si-D stretch modes of point defects in Si, which is key to understanding the physics of the giant isotope effect. We showed that H-terminated dangling bonds, exemplified by the $\mathrm{HV \cdot VH_{(110)}}$ defect, have particularly long lifetimes, and that the H/D isotope dependencies of their lifetimes are "inverted." Based on this, we argued that P_b:H centers might be particularly susceptible to dissociation by multiple vibrational excitation, and are likely to exhibit a particularly large isotope effect. No H related centers at the $\mathrm{Si/SiO_2}$ interface, including P_b:H, have ever been observed directly. It is therefore quite likely that the giant isotope effect will have to be explained by theoretical methods. We believe that the present work provides an indispensable benchmark for such theory.

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*Present address: Division of Engineering and Applied Science, Harvard University, Cambridge, MA 02138. Email address: budde@fas.harvard.edu

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[18] The $\mathrm{HV \cdot VH}$ defect might be expected to give rise to two absorption lines in the Si-H stretch region, rather than the single line assigned by Suezawa [17]. The following explanation of the absence of a second line supports the assignment of the 2072.5-cm^{-1} line to $\mathrm{HV \cdot VH}$. There are two ways that a defect with two Si-H bonds can have only one IR active stretch mode: (a) The two Si-H bonds are equivalent and so weakly coupled that the splitting between the two stretch modes is less than the linewidth, or (b) the two Si-H bonds are equivalent and oriented along the same axis. The fact that a new Si-H line appears $\sim 1\ \mathrm{cm}^{-1}$ from the 2072.5-cm^{-1} line in samples co-doped with H and D [17] rules out the first explanation. Consequently, the two Si-H bonds of the 2072.5-cm^{-1} defect must be equivalent and parallel or antiparallel. The simplest vacancy-hydrogen complex consistent with this is $\mathrm{HV \cdot VH_{(110)}}$, i.e., the $\mathrm{HV \cdot VH}$ defect with the two H located in the same (110) plane.

[19] Except for $\mathrm{HV \cdot VH_{(110)}}$, all the T_1's were obtained from spectra measured with 0.025-cm^{-1} resolution, because these spectra had superior signal-to-noise ratios. The instrumental line shape at this resolution was well represented by a sinc function with $\mathrm{FWHM} = 0.025\ \mathrm{cm}^{-1}$, as deduced from the absorption lines of atmospheric $\mathrm{CO_2}$ and $\mathrm{H_2O}$. The natural linewidths of the Si-H and Si-D lines were determined by comparing the experimental FWHMs with the FWHM obtained by fitting a Lorentzian to the convolution of the instrumental sinc function and a Lorentzian function of variable width. The width of $\mathrm{HV \cdot VH_{(110)}}$ was obtained from the spectrum measured with 0.006-cm^{-1} resolution, and was not corrected for instrumental broadening.

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[21] The $\mathrm{HV \cdot VH_{(110)}}$ and $\mathrm{V \cdot VH}$ defects are structurally very similar, and we therefore expect them to have similar T_1's. This is consistent with S_b being well represented by a single exponential for time delays larger than ~ 20 ps.