Vibrational Lifetimes and Isotope Effects of Interstitial Oxygen in Silicon and Germanium

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Decay dynamics of local vibrational modes provides unique information about energy relaxation processes to solid-state phonon bath. In this Letter the lifetimes of the asymmetric stretch mode of interstitial ^{16}O and ^{17}O isotopes in Si are measured at 10 K directly by time-resolved, transient bleaching spectroscopy to be 11.5 and 4.5 ps, respectively. A calculation of the three-phonon density of states shows that the ^{17}O mode lies in the highest phonon density resulting in the shortest lifetime. The lifetime of the ^{16}O mode in Ge is measured to be 125 ps, i.e., $\sim$10 times longer than in Si. The interaction between the local modes and the lattice vibrations is discussed according to the activity of phonon combinations.

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Interstitial oxygen (O_i) in silicon (Si) and germanium (Ge) is known to occupy a bridge position between neighboring Si or Ge atoms [1,2]. The well-understood defect is ideal for studying vibrational relaxation mechanisms in semiconductors, which are important to elucidate properties such as diffusion and defect reactions involving oxygen impurities [3]. Recently, McCluskey and co-workers used hydrostatic pressure to bring the asymmetric stretch mode of $^{18}O_i$ in Si into resonance with a spatially extended mode and studied the resonant interaction between these two modes [4]. The authors stated that the transition from a localized to an extended mode might be the first step toward decay into lattice phonons. However, little is known about the actual decay dynamics of the local vibrational mode (LVM) into lattice phonons.

Study of the vibrational lifetime and calculation of multiphonon density of states provides a direct way to elucidate the interaction between silicon (germanium) phonons and oxygen LVMs. In the past, isotope substitution of the oxygen center with ^{16}O, ^{17}O, and ^{18}O has been useful for experimental understanding of oxygen-related LVMs in silicon (germanium). However, the full width at half maximum (FWHM) of the asymmetric stretch mode of $^{17}O_i$ in Si (1109 cm^{-1}) is a factor of 2 larger than for the $^{16}O_i$ (1136 cm^{-1}) and $^{18}O_i$ mode (1085 cm^{-1}), a puzzle that has not been solved since 1995 [5]. The effect may be related to their vibrational lifetimes and to the coupling between the local modes and the lattice phonons.

In this Letter, we report on the first measurements of the vibrational lifetimes of interstitial oxygen in silicon and germanium and their isotope effects. The lifetime of the asymmetric stretch mode of $^{16}O_i$ in Si is measured to be $T_1 = 11.5 \pm 0.5$ ps by transient bleaching spectroscopy, while for $^{17}O_i$ the lifetime is 4.5 ± 0.4 ps. This factor of 2.5 between their lifetimes coincides with the

difference in their absorption linewidths. The combined three-phonon density of states is calculated to explain this isotope effect. The lifetime of the $^{16}O_i$ mode in Ge (861 cm^{-1}) is measured to be 125 ± 10 ps, much longer than in Si. The different vibrational decay channels of O_i isotopes in the two hosts are identified to explain the large difference in lifetimes. Our lifetime measurements show that oxygen absorption line broadening in silicon and germanium are homogeneous at liquid-He temperature.

A float-zone grown silicon sample enriched with oxygen isotopes by diffusion is used for the lifetime experiment. The concentrations of ^{16}O, ^{17}O, and ^{18}O isotopes are 20, 25, and $2.4 \times 10^{16} \text{ cm}^{-3}$, respectively. The germanium sample contains isotopes ^{70}Ge, ^{72}Ge, ^{73}Ge, ^{74}Ge, ^{76}Ge, with relative (natural) abundances of 0.205, 0.274, 0.078, 0.365, and 0.079, respectively. The oxygen concentration of the Ge sample is $4.9 \times 10^{16} \text{ cm}^{-3}$. The lifetime of the asymmetric stretch mode of interstitial oxygen isotopes is measured directly by transient bleaching spectroscopy. We use a low-temperature IR pump-probe setup, as described in Ref. [6]. The traveling-wave optical parametric amplifier of superfluorescence (TOPAS) used in this experiment delivers pulses at 1-kHz repetition rate with a time duration of $\sim$2 ps, spectral width of $15 \sim 20 \text{ cm}^{-1}$, and a pulse energy of 18 µJ at 1136 cm^{-1} and 1109 cm^{-1}, and 9 µJ at 861 cm^{-1}. The TOPAS beam is split into two parts, pump and probe, carrying 91% and 9% of the power, respectively. The pump excites a small fraction of the interstitial oxygen to the first excited state of the asymmetric stretch mode, which causes a transient increase in the transmission coefficient of the sample that decreases with 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 1 shows a semilog plot of S_b vs time delay from the asymmetric stretch mode of $^{16}O_i$ and $^{17}O_i$ in Si at 10 K. Both decay profiles fit well to a single exponential function yielding a decay time $T_1 = 11.5 \pm 1$ ps for $^{16}O_i$, and $T_1 = 4.5 \pm 0.4$ ps for $^{17}O_i$. We could not measure the lifetime of the $^{18}O_i$ mode because of its low concentration. The solid line in Fig. 1(a) is measured at a center frequency of 1123 cm^{-1}, i.e., between the two modes. The curve does not show any decay, but only the laser pulse with 1.7-ps pulse width. The TOPAS spectrum with a FWHM of 15 cm^{-1} is therefore narrow enough to distinguish between the vibrational modes of the oxygen isotopes in Si.

The inset of Fig. 1 shows the infrared absorption spectrum of the asymmetric stretch mode of different oxygen isotopes measured from the Si sample at 7.5 K [5]. The shape of an absorption line is generally given by the convolution of its homogeneous line shape with a function describing the inhomogeneous broadening [7]. The FWHM of the $^{17}O_i$ line is ~1.2 cm^{-1}, while for $^{16}O_i$ and $^{18}O_i$ it is ~0.6 cm^{-1} at 7.5 K [8]. The natural linewidth is given by

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

The natural linewidth deduced from the lifetime is 1.12 cm^{-1} for $^{17}O_i$, and 0.44 cm^{-1} for $^{16}O_i$. Our results measured in the time domain are consistent with those in the frequency domain, which shows that the absorption lines of interstitial oxygen are homogeneously broadened in crystalline silicon at low temperature. We can therefore deduce the lifetime of the $^{18}O_i$ mode from the linewidth according to Eq. (1). The lifetime is ~10 ps, close to that for $^{16}O_i$.

The difference (factor of 2) between the linewidths of $^{17}O_i$ compared with $^{16}O_i$ and $^{18}O_i$ is also observed in their
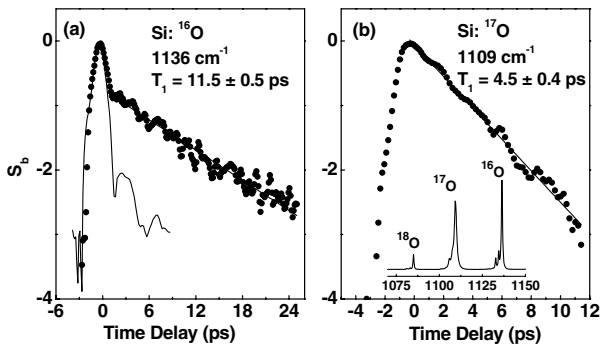

FIG. 1. (a) The transient bleaching signal S_b decays exponentially with a time constant $T_1 = 11.5 \pm 0.5$ ps for the asymmetric stretch mode of $^{16}O_i$ in Si at 10 K; (b) while $T_1 = 4.5 \pm 0.4$ ps for $^{17}O_i$. The solid curve in (a) shows the S_b signal at a center frequency of 1123 cm^{-1}, i.e., between the two modes, decaying with the pulse duration of 1.7 ps. The inset in (b) shows the absorption spectrum of the asymmetric stretch mode of O_i isotopes in Si at 7.5 K.
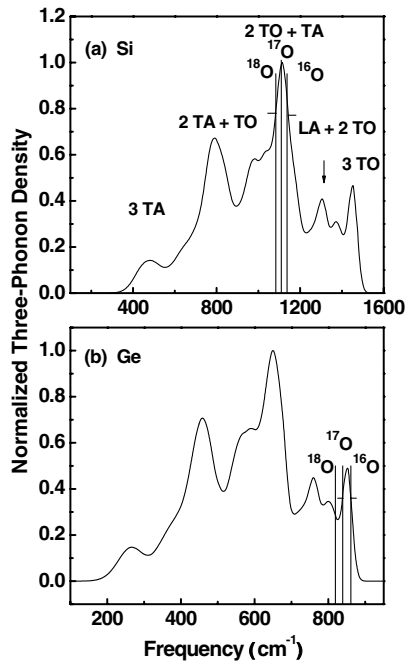
lifetimes. An accidental resonance of the asymmetric stretch mode of $^{17}O_i$ with another excitation was proposed to explain this effect [5]. The asymmetric stretch mode of O_i lies in the three-phonon continuum of Si. The interaction between LVMs and lattice vibrations is crucial to understanding the decay into phonons which has been studied theoretically by Nitzan et al. [9,10]. The decay rate (inverse lifetime) can be expressed as

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

where each channel $\{\nu\}$ is characterized by the set $\{\omega_1, \omega_2, \ldots, \omega_{N\nu}\}$ of accepting mode frequencies. Energy is conserved in the decay process, $\omega = \sum_{j=1}^{N_\nu} \omega_j$, where ω is the frequency of the LVM. The decay rate of each channel is given by the coupling strength $G_{\{\nu\}}$ of the channel, the function $n_{\{\nu\}}$ describing its temperature dependence, and the compound many-phonon density of accepting states $\rho_{\{\nu\}}$. In the low-temperature limit, the decay rate reflects spontaneous decay into N_ν accepting modes and $n_{\{\nu\}} \cong 1$. $\rho_{\{\nu\}}$ can be expressed in terms of a convolution of single phonon densities of states

$$\rho_{\{\nu\}} = \int dE_1 \int dE_2 \ldots \int dE_{N-1} \rho_1(\hbar\omega - E_1) \\ \times \rho_2(E_1 - E_2) \cdots \rho_N(E_{N-1}). \tag{3}$$

Figure 2(a) shows the three-phonon density of states for Si calculated by straightforward convolution of the one-phonon density of states according to Eq. (3). The one-phonon density of states was obtained from ab initio calculations, which are very reliable [11]. The $^{17}O_i$ mode happens to fall right on the peak of the $2TO + 1TA$ phonon combination, whereas the $^{16}O_i$ and $^{18}O_i$ mode are on both sides with smaller combined phonon densities. High phonon density corresponds to a short lifetime. The ratio of the phonon densities at the frequencies of the $^{17}O_i$ and $^{16}O_i$ mode is ~1.3, which is smaller than the ratio of the lifetimes (~ 2.5). The difference of the phonon density provides a satisfactory explanation for the difference of the lifetimes. In a full treatment of vibrational relaxation by anharmonic coupling between LVM and lattice phonon modes, one should consider modifications introduced by the distortion of the lattice because of the impurities, which may affect the phonon density of states locally [12].

Recently, Kato and co-workers reported a surprisingly large effect of Si isotopic mass disorder on the linewidth of the asymmetric stretch mode of $^{16}O_i$, which cannot be explained well by their calculations [13]. The linewidth of this mode in quasi-mono-isotopic (qmi) ^{29}Si and ^{30}Si samples is narrower than those in natural Si and ^{28}Si. This can be explained by the isotopic shift of the phonon frequency rather than the isotopic mass disorder. Passing from ^{28}Si to ^{30}Si, the phonon frequency will shift to a lower wave number, which results in lower phonon densities for ^{29}Si and ^{30}Si than for natural Si at the

FIG. 2. Normalized three-phonon density of states in (a) Si and (b) Ge at 0 K. (a) The asymmetric stretch mode of $^{17}O_i$ coincides with the highest three-phonon density in Si, whereas the $^{16}O_i$ and $^{18}O_i$ modes are on both sides of the $2TO + 1TA$ phonon peak. (b) In germanium, the $^{16}O_i$ and $^{17}O_i$ modes lie on the peak of the 3TO phonon density, whereas the $^{18}O_i$ mode coincides with a $2TO + LO$ phonon process.

FIG. 3. The transient bleaching signal S_b decays exponentially with a time constant $T_1 = 125 \pm 10$ ps for the asymmetric stretch mode of $^{16}O_i$ in Ge at 10 K. The inset shows the corresponding absorption spectrum in Ge at 7.5 K.

frequency of the $^{16}O_i$ mode. Our lifetime measurements indicate that the decrease in phonon density results in longer decay times, which corresponds to narrower linewidths. The isotopic mass disorder contributes little to the broadening of the linewidth, but will affect the phonon spectrum [14].

Further insight into the vibrational dynamics of the O_i defect can be gained by studying the lifetime of the asymmetric stretch mode in germanium. At very low temperature, the $^{16}O_i$ mode at 862-cm^{-1} exhibits a vibration-rotation spectrum with many sharp lines within a 5-cm^{-1} range because of the Ge isotope effect and of the rotational structure (Fig. 3) [15]. The corresponding absorption linewidths are much smaller in Ge (~ 0.04 cm^{-1}) than in Si (~ 0.6 cm^{-1}) [16]. The lifetime of the asymmetric stretch mode is measured to be $T_1 = 125 \pm 10$ ps at 10 K (Fig. 3). Since the absorption lines of the $^{16}O_i$ mode for different Ge isotopes are very close, our laser pulses can measure only an average lifetime. This corresponds to an average linewidth of 0.04 cm^{-1} in good agreement with infrared absorption measurements [17]. This indicates again that at low-temperature and low defect concentration the $^{16}O_i$ mode in Ge is dominated by the natural linewidth, consistent with lifetime studies of hydrogen-related defects in silicon [6,18,19].

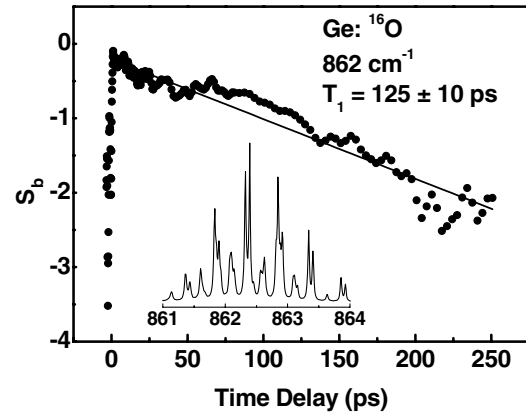To elucidate the long lifetime of the asymmetric stretch mode of $^{16}O_i$ in Ge requires knowledge of

the decay channels and phonon density of states. The 862-cm^{-1} mode falls into the three-phonon continuum since the cutoff frequency of phonons in Ge is 306 cm^{-1}. Figure 2(b) shows the calculated three-phonon density of states in Ge similar to the one of Si. The $^{16}O_i$ mode falls on the $3TO$ phonon peak in Ge while it coincides with $2TO + TA$ phonon processes in Si. The difference in phonon density between the two peaks is only a factor of $2 \sim 3$, which is not enough to explain the large difference in lifetimes. Since the decay channel is different for the two hosts, it is necessary to account for the coupling constant $G_{\{\nu\}}$, representing the strength of the interaction between the local mode and the accepting modes.

The asymmetric stretch mode of interstitial oxygen in Si and Ge has A_{2u} symmetry, which is infrared active in the D_{3d} point group of the O_i defect. The three-phonon combinations must contain A_{2u} symmetry [20], or otherwise the decay channel is not allowed. The infrared dipole operator whose irreducible representation in the O_h group is $\Gamma_{15'}$ can be reduced to $A_{2u} + E_u$ symmetry in the D_{3d} group, since D_{3d} (group of L in the diamond structure) is a subgroup of O_h. So we need to look into the infrared activity of three-phonon processes in the diamond structure. This has been published in Ref. [21]. Table I lists the combinations of $2TO + TA$ phonons in Si and $3TO$ phonons in Ge which are infrared active [21]. Activity (M) is the coefficient of $\Gamma_{15'}$ in the reduction of the direct sum of symmetry elements of three-phonon combinations. Larger M corresponds to a more infrared active three-phonon process [21]. Table I shows that the combinations of $2TO + TA$ phonons are more IR active than $3TO$ phonon processes. The interaction will be stronger between the A_{2u} local mode and the $2TO + TA$ phonons than with $3TO$ phonons. In addition, there are more channels for the A_{2u} mode to decay into $2TO + TA$ phonons, which results in a shorter lifetime of the oxygen mode in Si.

TABLE I. Three-phonon processes in Si and Ge close to the frequency of the asymmetric stretch mode of interstitial oxygen. The infrared activity M is also listed.

Activity (M)	Phonon combinations	Frequency (cm^{-1})
	Silicon	
3	$TO(X) + O(\Gamma) + TA(X)$	1129
6	$TO(L) + O(\Gamma) + TA(L)$	1122
3	$2TO(L) + TA(X)$	1134
6	$TO(L) + TO(X) + TA(L)$	1071
2	$2TO(X) + TA(X)$	1078
	Germanium	
1	$2TO(X) + O(\Gamma)$	856
3	$2TO(L) + O(\Gamma)$	888

The oxygen isotope effect has been investigated also in Ge [22]. A resonant broadening of the $^{17}O_i$ absorption line compared with $^{16}O_i$ and $^{18}O_i$ has not been observed in Ge, but the individual lines of $^{18}O_i$ are broader than those for $^{16}O_i$ and $^{17}O_i$. In Fig. 2(b), we also plot the position of the $^{17}O_i$ and $^{18}O_i$ lines in Ge. The $^{16}O_i$ and $^{17}O_i$ lines coincide with the same peak (3TO phonons), both of them have the same decay channel and their three-phonon density of states is close. So they show the same linewidth in Ge. The $^{18}O_i$ mode in Ge may have different coupling constant since it decays into a different channel ($2TO + LO$ phonons).

In conclusion, we have measured the vibrational lifetimes of the asymmetric stretch mode of oxygen isotopes in silicon and germanium. In silicon, the $^{17}O_i$ mode lies in the highest density of three-phonon states, which gives rise to a shorter lifetime ($T_1 = 4.5$ ps) than for the $^{16}O_i$ and $^{18}O_i$ modes ($T_1 \sim 10$ ps). We also measured the lifetime of $^{16}O_i$ modes in Ge, which show a much longer lifetime, $T_1 = 125$ ps, than in Si. We argue that the oxygen modes in Si decay into $2TO + TA$ phonons, while they decay into $3TO$ phonons in Ge. These phonon combinations have different infrared activities, which result in different coupling strengths and very different lifetimes. A more quantitative understanding of the vibrational energy relaxation and transfer channels in solids requires detailed knowledge of anharmonic coupling between LVM and lattice phonon modes and phonon density of states modified by impurities. The measured lifetimes presented here have great significance in elucidating the stability and diffusivity of impurities in semiconductors as well as complex formation and will generate renewed interest in the dynamics of energy dissipation from local modes into a phonon bath.

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