ELSEVIER

Isotope effects and temperature-dependence studies on vibrational lifetimes of interstitial oxygen in silicon

K.K. Kohli [a,*], Gordon Davies [a], N.Q. Vinh [b], D. West [c], S.K. Estreicher [c], T. Gregorkiewicz [d], I. Izeddin [d], K.M. Itoh [e]

[a] *Department of Physics, King's College London, Strand, London WC2R 2LS, United Kingdom*
[b] *F.O.M. Institute for Plasma Physics 'Rijnhuisen', P.O. Box 1207, NL-3430 BE Nieuwegein, The Netherlands*
[c] *Department of Physics, Texas Tech University, Lubbock, TX 79409-1051, USA*
[d] *Van der Waals-Zeeman Institute, University of Amsterdam, Valckenierstraat 65, NL-1018 XE Amsterdam, The Netherlands*
[e] *Department of Applied Physics and Physico-Informatics, Keio University, Yokohama 223-8522, Japan*

Available online 7 November 2006

Abstract

Vibrational lifetimes of the asymmetric stretch mode ($1136 \, \text{cm}^{-1}$) of oxygen in silicon are measured using pump-probe spectroscopy and calculated by *ab initio* theory. We find that increasing the isotope of the nearest-neighbouring silicon atom increases the lifetime of the vibration. This isotope-dependence establishes the participation of the v_1 ($613 \, \text{cm}^{-1}$) local vibrational mode in the decay of the v_3 ($1136 \, \text{cm}^{-1}$) mode. Temperature-dependence measurements show the low-energy v_2 ($29 \, \text{cm}^{-1}$) mode governs the repopulation rates for the ground state. We also analyze the temperature-dependence of transitions of excited states of the v_2 vibration.
© 2006 Elsevier B.V. All rights reserved.

1. Introduction

The most abundant impurity in Czochralski grown silicon is oxygen and is typically found in concentrations of the order of 10^{18} atoms/cm^3. Oxygen is incorporated in CZ–Si as a result of dissolution of the SiO$_2$ crucible at the growth temperature. The majority of the oxygen atoms occupy bond-centred interstitial sites where they vibrate and can hop between different Si-Si bonds to move through the silicon lattice. The relatively high diffusivity of oxygen makes it an important precipitate-forming defect in CZ–Si.

The structure of interstitial oxygen (O$_i$) in silicon gives rise to local vibrational modes (LVMs) and Fig. 1 illustrates the possible LVMs of the oxygen defect in Si for

the case of a linear molecule [1]. In the v_1 and v_3 modes, the defect vibrates at frequencies that are too high for the energy to travel through the crystal, so it remains trapped until other mechanisms of release are found. The v_3 vibration is almost twice the maximum frequency, $\sim 523 \, \text{cm}^{-1}$ [2], that can be accepted by the silicon lattice. The v_2 mode is a two-dimensional low energy anharmonic excitation of oxygen ($29 \, \text{cm}^{-1}$). In addition, vibrations caused by O$_i$-induced transverse motion of the neighbouring silicon atoms produce the $518 \, \text{cm}^{-1}$ line.

Recently, optical excitation of the v_3 vibration has been shown to enhance the diffusion of oxygen through the lattice at 1173 °C [3] and so the lifetime of the vibration at that temperature is an important factor. Previously, the decay of the v_3 vibration had been attributed to a three lattice-phonon process [4]. We will show that the decay is actually into the v_1 LVM plus one or two lattice modes and we will investigate its temperature dependence.

---
* Corresponding author. Tel.: +44 20 7848 2149; fax: +44 20 7848 2420.
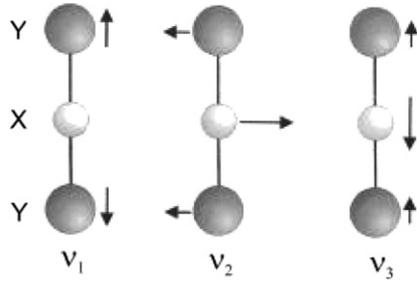*E-mail address:* kriteshwar.kaur@kcl.ac.uk (K.K. Kohli).

Fig. 1. Local vibrational modes of the Si–O–Si defect.

2. Experimental setup

CZ-grown silicon samples of natural isotopic abundanc and of single-isotope ^{30}Si were used. They contained 9×10^{17} cm^{-3} of oxygen. Measurement temperatures between 5 and 100 K were obtained by using a continuous flow helium cryostat.

The lifetime of the 1136 cm^{-1} vibration was measured by the pump-probe technique using a free electron laser. The free electron laser delivers pulses of radiation with FWHM ~5 ps and a repetition rate of 5 Hz. The laser pulse is divided into three pulses by beamsplitters. Most of the intensity is in the pump pulse, which can be absorbed by the oxygen, depopulating the ground state. About 5% of the intensity is split off into a probe beam, which is retarded relative to the pump by a variable time t. Neglecting reflection effects, the fraction of the probe pulse that is transmitted is

$$I_{\text{probe}} = \exp(-\mu' s) \qquad (1)$$

where s is the sample thickness and μ' the absorption coefficient at that time t. Finally, the third (reference) pulse arrives after a sufficiently long time that the population of the ground state has returned to equilibrium. The fraction transmitted is

$$I_{\text{reference}} = \exp(-\mu s) \qquad (2)$$

and the ratio of the intensities is

$$\frac{I_{\text{probe}} - I_{\text{reference}}}{I_{\text{reference}}} = \exp[-(\mu' - \mu)s] - 1 \approx (\mu - \mu')s. \qquad (3)$$

The last step in Eq. (3) requires small changes in the absorption coefficient and is valid here. For a homogeneous sample, the absorption coefficient is proportional to the change in the concentration of oxygen in the ground state from the equilibrium value. Therefore, the evolution with time of the intensity ratio gives the repopulation of the ground state.

3. Analysis

The exponential decay time for the repopulation of the ground state at ~5 K is shown by the dash–dot (red) points on Fig. 2 as a function of the excitation wavelength for silicon with natural isotopic abundances. For reference, the solid (green) line shows the absorption coefficient of the
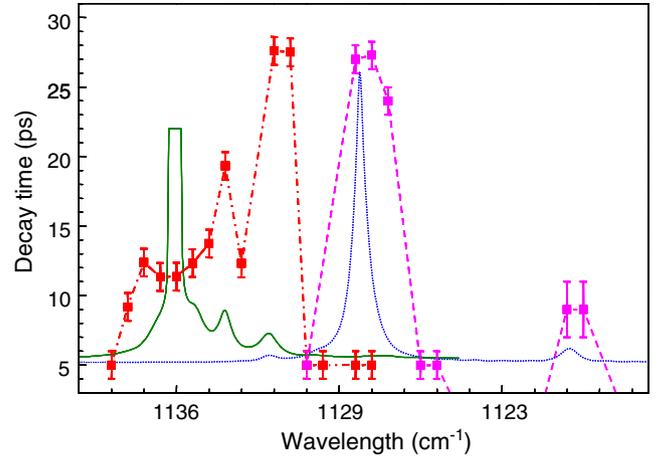

Fig. 2. Wavelength dependence of the decay times of $^{\text{isotope}}$Si–^{16}O. The dash-dot (red) curve is decay time for sample $^{\text{nat}}$Si:O sample and the dashed (pink) curve is decay time for ^{30}Si:O sample. Also discussed in Section 4. (For interpretation of the references to the colour in this figure legend, the reader is referred to the web version of this article.)

sample. The pump-probe spectroscopy shows that the lifetime of the v_3 vibration is dependent on the isotopes of the silicon atoms which immediately neighbour the oxygen atom, increasing as the mass of the neighbour increases. The dash (pink) points show the measured lifetimes at ~15 K for the single-isotope ^{30}Si sample, with the corresponding absorption spectrum (square dot (blue) line).

All the data are consistent with the v_3 (1136 cm^{-1}) vibration decaying through the creation of one v_1 (613 cm^{-1}) mode, with the rest of the energy going into lattice modes that correspond to the difference between the v_3 and v_1 vibrations. The v_3 mode is mainly an oxygen vibration and the v_1 is entirely a Si vibration as discussed below. When the isotopes are changed, v_3 and v_1 are affected by different amounts. The difference between v_3 and v_1 depends on the isotopes. The differences ($\Delta v = v_3 - v_1$) are plotted on the one-phonon density of states (Fig. 3)
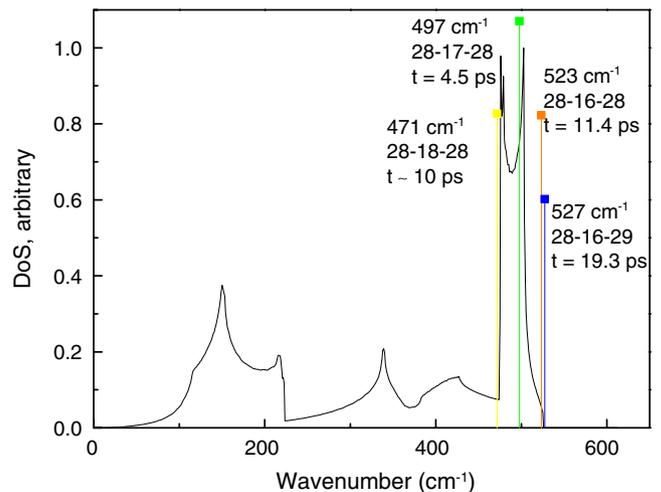

Fig. 3. One-phonon density of states in ^{28}Si. The vertical lines are markers for the different Si–O–Si structures showing the values for Δv and the corresponding lifetimes.
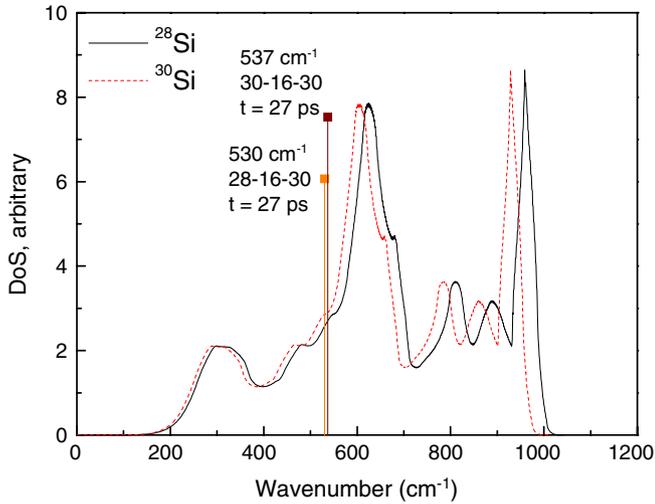
Fig. 4. Two-Phonon density of states for ^{28}Si and ^{30}Si. The vertical lines are markers for the different Si–O–Si structures with values of Δv that lie outside the one-phonon density of states. The density of two-phonon states is similar for the two structures, which have the same lifetimes.

[5]. For Si–O–Si masses of 28-17-28, the lifetime is 4.5 ps [4] and Δv coincides with a high density of states, so the energy can be easily sent into the lattice, explaining the very short lifetime. The lower phonon density results in longer decay times as can be seen for 28-16-28 and the other isotope combinations. For 28-18-28, we can estimate the lifetime $\sim$10 ps from the line width and plotting Δv for this isotope combination shows that it lies on a similar density of states as for 28-16-28 and both have comparable lifetimes.

As the differences increase, they edge towards the maximum phonon frequency of silicon. When Δv falls outside the one-phonon spectrum, as for 30-16-28 and 30-16-30, the measured decay time saturates at 27 ps. The decay here could occur through the emission of one v_1 LVM plus two lattice phonons.

This model, using the v_1 vibration, describes the data well. But, since the transverse bending mode v_2 is at 518 cm^{-1}, we should consider if it could be used instead. However, the v_2 mode is not a possible candidate for the decay process because it is inconsistent with the expected trends. For the combination 28-17-28, $v_3-v_2 = 591$ cm^{-1}, placing it in a lower density of two-phonon states than $v_3-v_2 = 618$ cm^{-1} for 28-16-28. However, the lifetimes, at 4.5 ps and 11 ps, respectively, are in the opposite order. A higher density of states should result in a shorter lifetime but this is not the case if v_2 is used instead of v_1 (See Fig. 4).

4. Temperature dependence

The temperature-dependence of the v_3 vibration was measured (Fig. 5) using the single-isotope ^{30}Si sample to avoid the influence on the measurements through isotope effects. We have shown that the v_3 vibration for 30-16-30 decays into v_1 and two other phonons totalling $\sim$537 cm^{-1}. From the density of states they are likely to be $v_a \sim 335$ cm^{-1} and
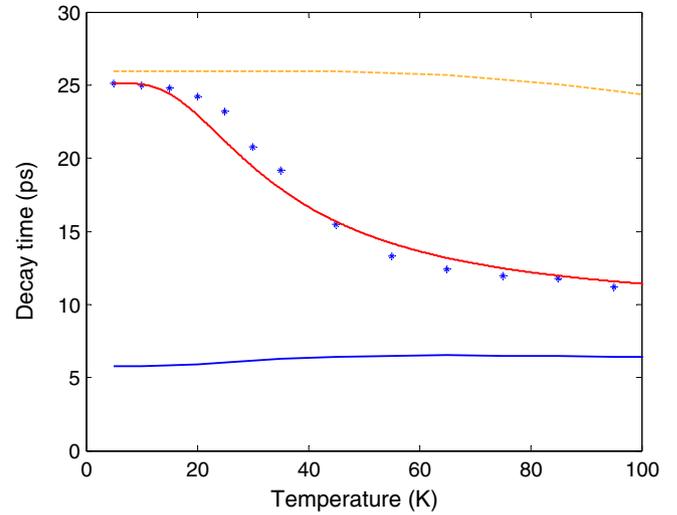

Fig. 5. The decay time as a function of temperature for the v_3 vibration in ^{30}Si is shown by the starred (blue) points fitted to Eq. (6) (red line). The dashed (orange) line gives the expected temperature dependence of the 1129 cm^{-1} vibration (Eq. (4)) and the solid (blue) line gives the temperature dependence of the 1121 cm^{-1} vibration (Eq. (7)). (For interpretation of the references to the colour in this figure legend, the reader is referred to the web version of this article.)

$v_b \sim 200$ cm^{-1}. The temperature-dependence of the decay is then expected to be:

$$\frac{1}{\tau(T)} = \frac{1}{\tau(0)}[(1+n(v_1))(1+n(v_a))(1+n(v_b))] \qquad (4)$$

where

$$n(v) = \frac{1}{e^{\hbar\omega/kT} - 1} \qquad (5)$$

and $\hbar\omega$ is v_1, v_a or v_b. However, Fig. 5 shows that the data does not conform to this equation and other processes must be taken into account.

The pump pulse empties some of the ground state population disturbing the thermal equilibrium. We simplify the energy levels of the 29 cm^{-1} system to a set of two-dimensional harmonic oscillators. The energy separation of the levels is $\hbar\omega = 49$ cm^{-1} from the Bosomworth model [6]. At $T > 0$ K, the higher vibrational levels decay back to the ground state, restoring the equilibrium. The rate of repopulating the ground state depends on the rate of decay for the v_3 vibration and the fraction of empty states. For a two-dimensional harmonic oscillator, the fraction of the ground state that is empty at temperature T is given by the term in braces in Eq. (6). The fitted data in Fig. 5 shows that the higher levels of the v_2 state govern the temperature dependence. The parameter s determines the transition rate in the v_2 manifold and is found to be $s \sim 74$ GHz.

$$\frac{1}{\tau(T)} = \frac{1}{\tau(0)}[(1+n(v_1))(1+n(v_a))(1+n(v_b))]$$
$$+ s\left\{1 - (1 - e^{-\hbar\omega/kT})^2\right\} \qquad (6)$$

In Fig. 2, the data for 1121 cm^{-1}, which is a transition due to the excitation of the v_3 vibration while the system is in the first excited state of v_2, shows a measured repopulation time of 9 ± 2 ps measured at 10–15 K. This is significantly shorter than the lifetime of the basic 1129 cm^{-1} v_3 vibration, of 27 ps. Applying the same argument as used to obtain Eq. (6) to the doubly-degenerate $n = 1$ level of energy $2\hbar\omega$, we can estimate the rate of repopulation of the initial state of the 1121 cm^{-1} transition as

$$\frac{1}{\tau(T)} = \frac{1}{\tau(0)} + s\left\{2 - 2\,e^{-\hbar\omega/kT}(1 - e^{-\hbar\omega/kT})^2\right\} \qquad (7)$$

where $\tau(0) = 27$ ps. Using $s \sim 74$ GHz, Eq. (7) estimates the repopulation time of the 1121 cm^{-1} initial state as 13.5 ps, compared to the measured 9 ps. The solid (green) line on Fig. 5 shows that this repopulation time is only weakly dependent on temperature.

5. Theoretical calculations

Insight into the de-excitation processes comes from *ab initio* calculations. We have used the SIESTA implementation of molecular-dynamics simulations in 64 host-atoms periodic supercells. Fig. 6 shows the contribution (the square of the eigenvector) to each mode of vibration for the Si and O atoms in the Si–O–Si cluster. The v_3 vibration, calculated at 1153 cm^{-1} and the v_1 vibration, calculated at 607 cm^{-1}, are both highly localized on the Si–O–Si cluster: energy transfer between them immediately appears likely.
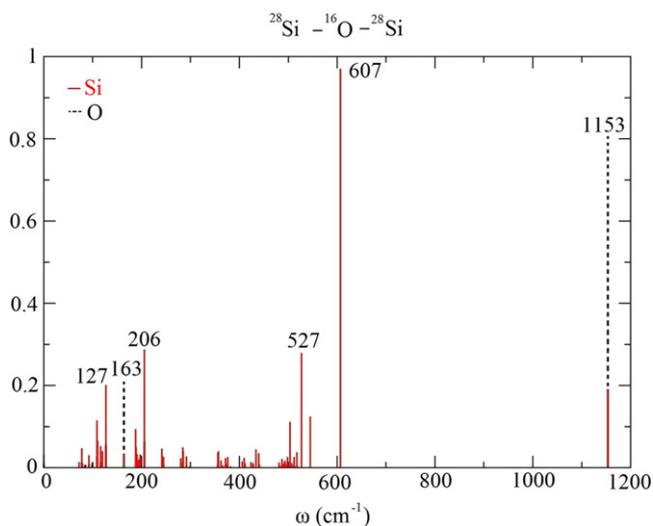

Fig. 6. Plots of the squared eigenvectors of the Si and O atoms in the central Si–O–Si cluster against the frequency of vibration for each mode in a 64 host-atom supercell. The central cluster is specifically the 28-16-28 structure. Dotted (black) lines show the contribution from the O atom, solid (red) from the Si atoms in the central cluster. The v_3 mode is calculated at 1153 cm^{-1} and the v_1 mode at 607 cm^{-1}. (For interpretation of the references to the colour in this figure legend, the reader is referred to the web version of this article.)

To calculate the lifetime of the v_3 vibration, that mode has been excited with one quantum, with the remainder of the cluster in thermal equilibrium and the time-evolution calculated using the method of [7]. The decay of the v_3 vibration is found to coincide with energy transfer to the v_1 vibration, plus other modes. Fitting an exponential decay to the energy in the v_3 mode results in decay times ranging from 10 ps for the 28-16-28 combination (measurement 11 ps) to 22 ps for 30-16-28 (measurement of 27 ps). The *ab initio* calculations agree with the importance of the v_1 mode in the de-excitation process and agree closely with the measured decay times.

6. Optically-enhanced diffusion

Recently, optical excitation in the v_3 band has been shown to enhance the diffusion of oxygen by a factor of 3 at a temperature of 1173 °C [3]. The lifetime of the first v_3 level has been shown to be described by Eq. (4). Evaluation at 1173 °C gives a lifetime ~ 0.5 ps, in which time the oxygen atom would vibrate ~ 3 times in the v_3 mode, implying an efficient increase in the diffusion rate. However, we note that in thermal equilibrium at 1173 °C, about 30% of the oxygen atoms are in the first excited v_3 vibrational level already and $\sim 10\%$ in the next level. Optical excitation may be occurring from these higher levels. To understand the enhanced diffusion will require further optical and lifetime measurements at higher temperatures.

7. Summary

Pump-probe measurements have shown that the decay time of the v_3 vibration of O in Si depends strongly on the isotopes of the Si atoms immediately neighbouring the O atom. Empirical and *ab initio* modelling has established that the v_3 mode decays into one v_1 mode plus lattice modes. Pump-probe measurements of the temperature dependence of the v_3 decay time are dominated by repopulation within the low-frequency v_2 manifold. We estimate that at the temperature used in recent optically-enhanced diffusion studies [3], the lifetime of the first excited state of v_3 is ~ 0.5 ps.

References

[1] M.D. McCluskey, J. Appl. Phys. 87 (2000) 3593.
[2] J.P. Russell, Appl. Phys. Lett. 6 (1965) 223.
[3] H. Yamada-Kaneta, K. Tanahashi, Physica B 376&377 (2006) 66.
[4] B. Sun, G.A. Shi, S.V.S. Nageswara Rao, M. Stavola, N.H. Tolk, S.K. Dixit, L.C. Feldman, G. Lupke, Phys. Rev. Lett. 92 (2004) 185503.
[5] P. Giannozzi, S. DeGironcoli, P. Pavone, S. Baroni, Phys. Rev. B 43 (1991) 7231.
[6] D.R. Bosomworth, W. Hayes, A.R.L. Spray, G.D. Watkins, Proc. Roy. Soc. Lond. A 317 (1970) 133.
[7] D. West, S.K. Estreicher, Phys. Rev. Lett. 96 (2006) 115504.