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

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Abstract

Vibrational lifetimes of the asymmetric stretch mode (1136 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 cm^{-1}) local vibrational mode in the decay of the v_3 (1136 cm^{-1}) mode. Temperature-dependence measurements show the low-energy v_2 (29 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.

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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, ~523 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 cm^{-1}). In addition, vibrations caused by O_i-induced transverse motion of the neighbouring silicon atoms produce the 518 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.

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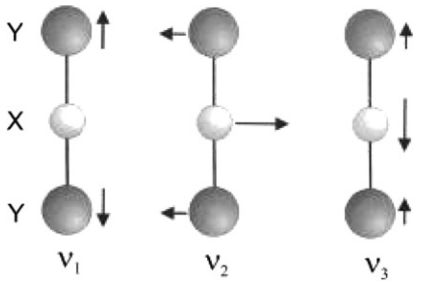

Fig. 1. Local vibrational modes of the Si–O–Si defect.

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

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

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

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

and the ratio of the intensities is

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

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 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).

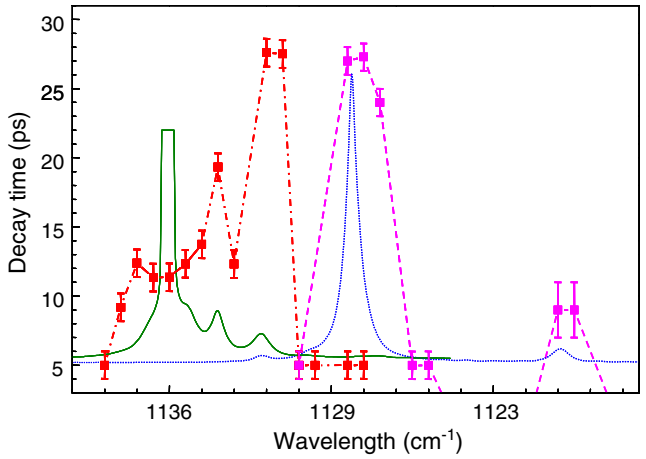

Fig. 2. Wavelength dependence of the decay times of $^{\text{isotope}}$Si–^{16}O. The dash-dot (red) curve is decay time for sample $^{\text{nat}}$Si:O sample and the dashed (pink) curve is decay time for ^{30}Si:O sample. Also discussed in Section 4. (For interpretation of the references to the colour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

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)

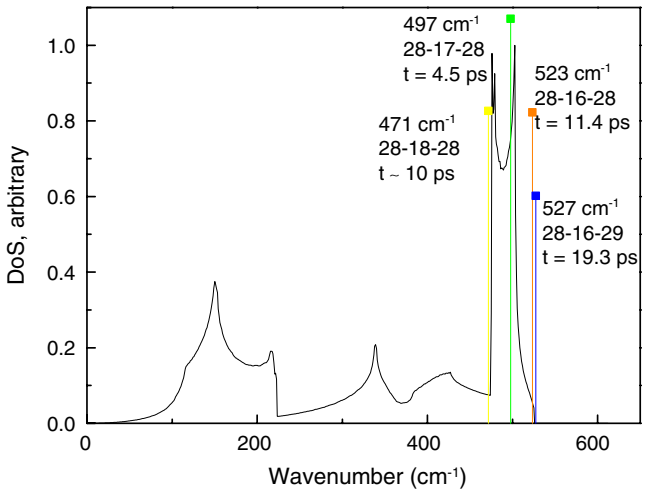

Fig. 3. One-phonon density of states in ^{28}Si. The vertical lines are markers for the different Si–O–Si structures showing the values for Δv and the corresponding lifetimes.