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Mid-infrared pump–probe spectroscopy of Si–H stretch modes in porous silicon

K.W. Jobson [a,*], J.-P.R. Wells [a], N.Q. Vinh [b], P.J. Phillips [b,c], C.R. Pidgeon [c], J.I. Dijkhuis [d]

[a] Department of Physics and Astronomy, University of Sheffield, Sheffield S3 7RH, United Kingdom
[b] FELIX Free Electron Laser Facility, FOM Institute for Plasmaphysics 'Rijnhuizen', P.O. Box 1207, 3430 BE, Nieuwegein, The Netherlands
[c] Department of Physics, Heriot-Watt University, Riccarton, Edinburgh, United Kingdom
[d] Debye Institute, University of Utrecht, P.O. Box 80000, TA 3508 Utrecht, The Netherlands

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Abstract

Using the Dutch free electron laser FELIX, we have investigated vibrational relaxation in free standing porous silicon (p-Si) films. Pump–probe measurements resonant with the SiH, SiH_2 and O_3SiH stretching modes yield temperature dependent measurements of the decay rates which demonstrate that all the modes decay via at least one internal defect mode with the excess vibrational energy distributed among the Si–Si bath phonons in a fourth order decay process.
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1. Introduction

Porous silicon is produced by electrochemically etching a series of pores into a crystalline silicon (c-Si) wafer, in which the wafer is anodized at low current densities whilst immersed in HF solution [1]. The resulting pores have walls that consist of so-called 'dangling' Si- bonds that are then passivated, mostly by hydrogen ions from the HF acid used in the etching process. During the passivation process many hydrogenic bonding configurations are achieved, primarily SiH_x species ($x = 1$, 2 or 3). Further modification of the pore wall structure occurs if the p-Si film is exposed to ambient conditions for a sustained period of time, in which significant oxidation occurs, forming a bridging bond (Si–O–Si) between unpassivated Si bonds and also attacking the weaker Si–Si back-bonds of the SiH_x defects. This results in the production of further SiH bonds which are back-bonded to Si atoms (an O_xSiH species). Porous silicon (p-Si) is an interesting system in which to examine the vibrational relaxation dynamics of SiH bonds because the different bonding configurations of the SiH defects in the passivated pore walls provide multiple vibrational modes to study. In addition, although the SiH defects reside in the locally disordered environment of the pore walls, the majority of the material consists of c-Si and it is therefore, unclear whether the c-Si band modes act as accepting modes for energy stored in the localised vibrations of the Si–H bonds.

2. Results and analysis

Fig. 1 displays the infrared transmission spectrum of our free-standing p-Si sample. The broad absorption peaks at 2114 cm^{-1} and 2262 cm^{-1} are due to the fundamental ($\upsilon = 0 \rightarrow 1$) vibrations of the stretching modes of Si–H and O_3Si–H, respectively, whilst a shoulder at 2083 cm^{-1} is Si–H_2 [2].

Fig. 2 presents three beam pump–probe measurements of the Si–H, Si–H_2 and O_3Si–H vibrations. We have

* Corresponding author. Fax: +44 114 222 3555.
E-mail address: k.jobson@sheffield.ac.uk (K.W. Jobson).

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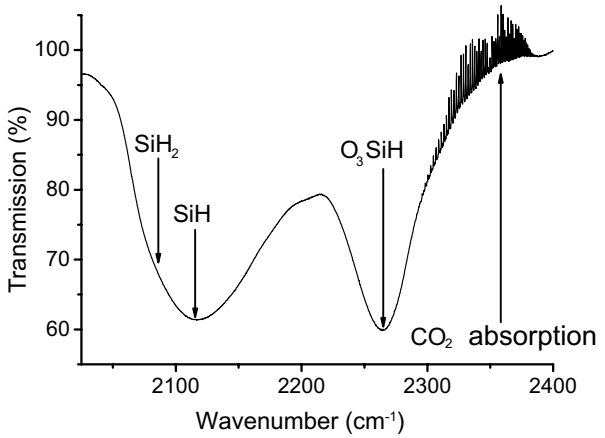

Fig. 1. 10 K infrared transmission spectrum of a free-standing p-Si layer.

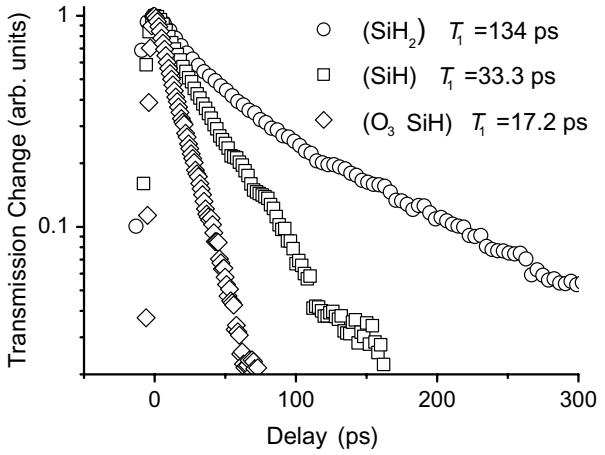

Fig. 2. 10 K pump–probe signals when resonantly exciting at wavelengths of 4.80 μm (Si–H_2 stretch mode-open circles), 4.73 μm (Si–H stretch mode-open squares) and 4.42 μm (O_3Si–H stretch mode-open diamonds).

discussed the three beam pump–probe technique extensively elsewhere [3]. All time resolved measurements were performed using the Dutch free electron laser (FELIX) at Nieuwegein which yields pulses as short as 300 fs. The vibrational transitions were resonantly excited at wavelengths of 4.80 μm (Fig. 2-open circles), 4.73 μm (open squares) and 4.42 μm (open diamonds). The decay of the pump–probe signal when resonantly exciting the Si–H_2 stretch mode is a bi-exponential composed of a very fast component and then a far longer decay. We have established, by making a series of wavelength-dependent measurements of the decay times, that the slowly decaying component is the population relaxation from the Si–H_2 stretching mode and that the short lifetime component is due to the spectral overlap of the FELIX pulse and the low-energy tail of the Si–H stretch mode absorption profile. The lifetime of the Si–H_2 mode was found to be 134 ps. The decay of the pump–probe signal when resonantly exciting the Si–H and oxygen back-bonded Si–H stretch modes are both single exponentials with respective lifetimes of 33.3 ps and 17.2 ps.

Vibrational energy relaxation from a localised mode having frequency ω into a set of lower energy accepting modes having frequency ω_i is described by the expression [4]:

$$[T_1(T)]^{-1} = [T_1(0)]^{-1}\left(\frac{\exp(\hbar\omega/k_BT)-1}{\prod_i[\exp(\hbar\omega_i/k_BT)-1]}\right), \quad (1)$$

where $T_1(0)$ is the vibrational population decay time at a temperature of 0 K (approximated by our 10 K values). Fitting this expression to our temperature dependent measurements of T_1 for the three SiH defect modes determines the appropriate vibrational relaxation pathways. This is presented in Fig. 3a–c.

Fig. 3a shows the temperature dependent decay rate of the Si–H_2 stretch mode at 2083 cm^{-1}. The dashed-dotted curve represents a simplistic assumption of decay into five equal energy (417 cm^{-1}) Si–Si vibrations. This gives poor account of the data as does any other combination of five Si–Si vibrations, pointing to a lower order decay process. The dotted curve assumes decay into two scissor modes (906 cm^{-1}) and a 267 cm^{-1} Si–Si vibration, underestimating the experimental trend. The two 'best-fit' assumptions are shown by the solid and dashed curves, which represent

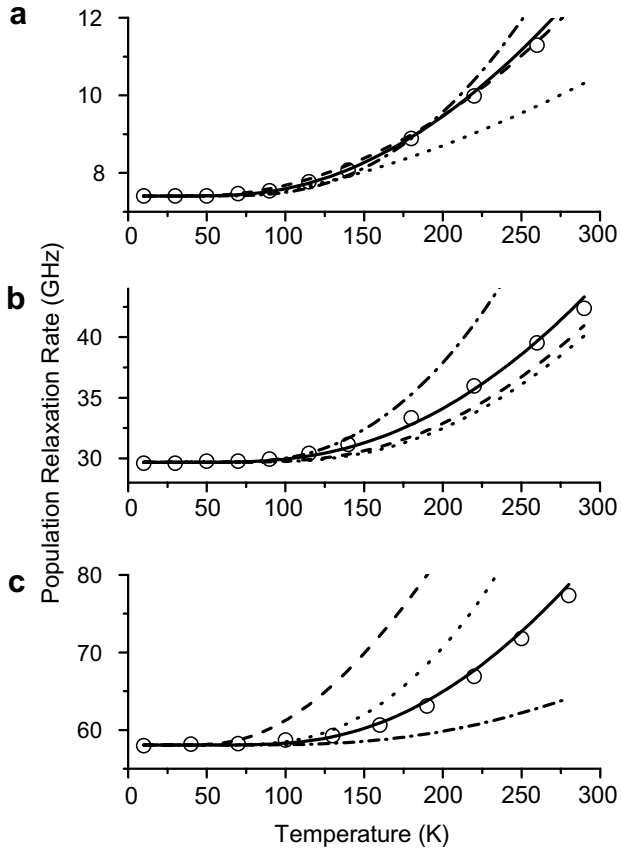

Fig. 3. Temperature dependence of the population relaxation rate $1/T_1$ of (a) the Si–H_2 stretch mode, (b) the Si–H stretch mode and (c) the O_3Si–H mode. The circles are the measured lifetimes whilst the lines are fits of Eq. (1). For details of the fits, see the text.

four phonon anharmonic decay. The solid curve is decay into one scissors mode and three Si–Si vibrations at 530 cm^{-1}, whilst the dashed curve is decay into two bending modes (660 cm^{-1}) and two bulk vibrations at 233 cm^{-1} and 530 cm^{-1}. It is not possible to discriminate between these decay possibilities.

Fig. 3b shows the temperature dependent decay rate of the Si–H stretch mode at 2114 cm^{-1}. The dashed dotted curve represents decay into five equal energy vibrations at 423 cm^{-1} and radically overestimates the data at elevated temperatures. The dotted curve represents decay into four Si–Si vibrations at 529 cm^{-1} which underestimates the increase in decay rate, due to the high activation energy that these modes provide. The dashed curve represents decay into one Si–H bending mode (625 cm^{-1}) and three bulk vibrations, $2 \times 530\ cm^{-1} + 1 \times 429\ cm^{-1}$, again underestimating the data. The closest approximation is shown as a solid curve, which assumes anharmonic decay to two bending modes, and 530 cm^{-1} + 334 cm^{-1} Si–Si vibrations.

Fig. 3c shows the temperature dependent decay rate of the Si–H stretch mode at 2262 cm^{-1}. As expected, fifth order decay processes do not give good account of the data, with the dashed curve illustrating relaxation into five 452 cm^{-1} Si–Si vibrations. Conversely, the dashed-dotted curve, which assumes decay into two bending modes (878 cm^{-1}) and a 506 cm^{-1} Si–Si vibration, underestimates the increase with temperature due to the high energy of the accepting modes. The dotted curve represents decay into two bending modes and two 253 cm^{-1} Si–Si vibrations and significantly overestimates the increase in decay rate. A close approximation is provided by assuming relaxation into four vibrational modes composed of one bending mode and three equal energy 461 cm^{-1} vibration. It is notable that p-Si has a Si–O–Si bending vibration at 460 cm^{-1} [5], suggesting that a resonant coupling to this mode speeds up the relaxation of the O_3SiH stretch mode.

3. Conclusions

Measurements of the vibrational relaxation of Si–H and $Si–H_2$ stretch modes in p-Si reveal that bending and scissors modes play an important role as accepting modes with excess energy taken up by Si–Si TO and LA lattice modes. The vibrational decay channel of the O_3SiH stretch mode is quite efficient, presumably of resonant local character, and governed by bending vibrations. The pump–probe signal is generally single exponential, contrasting strongly with the decay of the Si–H stretch mode in a-Si:H [6], in which the decay curves are non-exponential due to the surrounding amorphous environment of the localised mode causing a distribution of decay times of the ensemble of Si–H oscillators. The essential difference between the Si–H stretch modes in a-Si and p-Si is that in p-Si the SiH defects are surface states, whilst in a-Si:H the SiH defects are uniformly distributed throughout the amorphous network of Si atoms.

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