

Local vibrational modes of impurities in silicon

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Abstract

Local vibrational mode (LVM) spectroscopy is a useful technique for determining the structure and stability of defects in crystalline Si. Infrared (IR) absorption peaks arising from impurities such as oxygen, hydrogen, and substitutional dopants provide insight into diffusion as well as a practical “fingerprint” for identification. In this paper, several representative defect systems are reviewed.

Introduction

Silicon-based electronics rely on controlled doping and accurate characterization of impurities and defects. The addition of electrically active impurities introduces energy levels into the band gap. These donor and acceptor energy levels form the basis for modern electronic devices. Along with the *electronic* properties of Si, though, impurities also affect the *vibrational* properties.

Vibrational motion occurs when atoms in a crystalline solid oscillate about their equilibrium lattice positions. Due to quantum mechanics, the resulting vibrational modes are quantized in discrete units called *phonons*. Generally, the term *phonon* is used to denote excitations that have a large spatial extent, involving the motion of many atoms. Phonons are also extended in frequency space, covering a band of frequencies from zero up to a maximum that is typically in the THz range.

When an impurity is placed into an otherwise perfect crystal, the translational symmetry is broken. New vibrational modes may appear due to the defect. If a light-mass defect replaces a heavier host atom, for example, its vibrational frequency will lie above the maximum phonon frequency. Unlike a phonon, the vibrational motion of the defect is *localized* in real space and frequency space. Hence, it is referred to as a *local vibrational mode* (LVM). Hydrogen, for instance, often has LVM frequencies 5-10 times the maximum phonon frequency and has narrow vibrational absorption peaks.

In this paper, several examples of impurities in crystalline Si are given. The review is by no means extensive. Interested readers are referred to Wronski *et al.*¹ for a review of amorphous Si and Newman² for a review of defects and impurities in crystalline Si.

Interstitial oxygen

A common defect in Czochralski-grown crystals, oxygen in Si is probably the most intensively studied semiconductor impurity in human history.³ Oxygen concentration of $\sim 10^{18} \text{ cm}^{-3}$ are incorporated in Czochralski-grown Si crystals, a result of the dissolution of the SiO₂ crucible at the growth temperature.⁴ Oxygen precipitates have a beneficial effect in that they getter transition-metal impurities. Deliberate oxygen implantation is also performed in order to form oxide layers.⁵ A review of the atomic structure of Si:O is given by Pajot.⁶

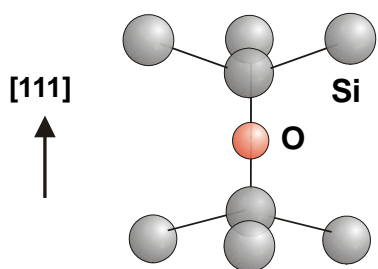


Figure 1. Interstitial oxygen in Si.

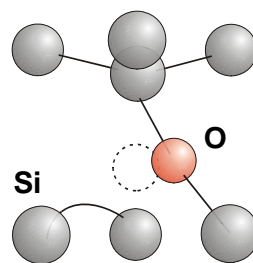


Figure 2. Vacancy-oxygen complex. The dashed circle indicates the substitutional site.

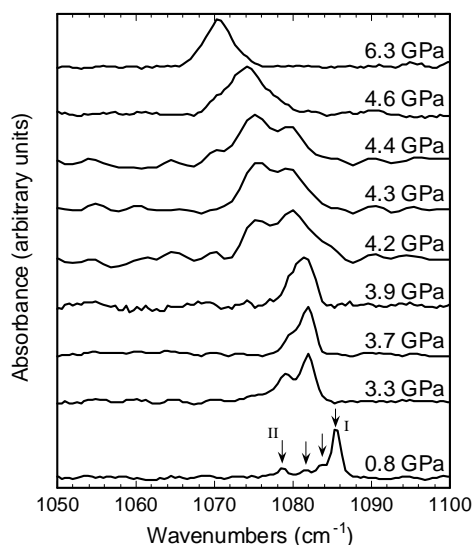


Figure 3. IR spectra of Si:¹⁸O under pressure (Ref. 10).

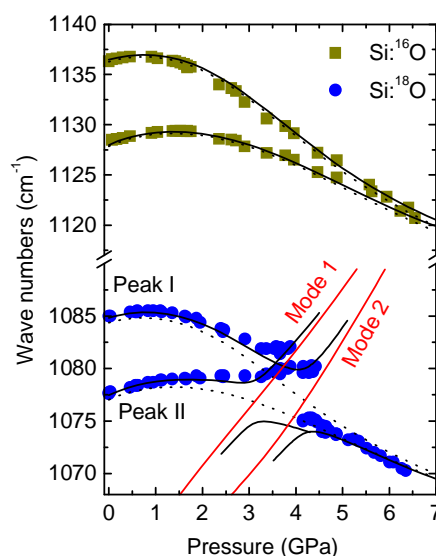


Figure 4. LVM frequencies of Si:¹⁸O and Si:¹⁶O under pressure (Ref. 10).

Intersitial oxygen (O_i) consists of an oxygen atom bonded to two Si atoms (Fig. 1).⁷ With oxygen in the bond-centered position, the Si—O—Si quasimolecule points along the [111] direction. The vibrational frequencies and corresponding normal modes have been studied extensively.⁶ The most famous vibrational mode arises from the oscillation of the oxygen atom along the [111] direction, out of phase with the two attached Si atoms.³ This mode, known as the *antisymmetric* mode, produces an IR absorption peak at 1136 cm⁻¹ for an atom of ¹⁶O bonded to two atoms of ²⁸Si. Studies have identified the LVM frequencies for ¹⁶O, ¹⁷O, and ¹⁸O isotopes bound to different combinations of ²⁸Si, ²⁹Si, and ³⁰Si isotopes. The O_i defect also produces an IR peak at 517 cm⁻¹. This *resonant mode* involves the motion of many Si atoms in the vicinity of the oxygen atom.^{8,9}

In our work, we used O_i in Si as a model system for studying the interaction between local and extended vibrational modes.¹⁰ We used hydrostatic pressure to bring the antisymmetric mode of Si:¹⁸ O_i into resonance with the second harmonic of the ¹⁸ O_i resonant mode. Two things happened. First, the lifetime of the antisymmetric stretch mode decreased abruptly as it entered the two-phonon density of states, causing the line to broaden (Fig. 3). Second, we observed a novel anticrossing between the two vibrational modes (Fig. 4). A theoretical model^{10,11} of this interaction produced excellent agreement with the experimentally observed frequencies and linewidths. This study shows that, in addition to being a technologically relevant defect, oxygen in Si is a model system for probing fundamental semiconductor physics.

Thermal donors

When a Czochralski-grown Si crystal is heated, the O_i impurities diffuse and form clusters called *thermal donors*.^{12,13} Thermal donors are denoted TD(1), TD(2), ... TD(N), where N increases as the number of oxygen atoms in the defect increases. Although the exact structure is not known, it is believed that the defect consists of a row of O_i atoms along the [110] direction. TD(N) defects are double donors, with the ionization of the first and second electron in the range of 350-533 cm⁻¹ and 580-1170 cm⁻¹, respectively.^{14,15} As N increases, the ionization energies decrease. Weak IR absorption peaks arising from TD(N) LVMs were observed in the frequency ranges 975-1015 and 724-748 cm⁻¹.¹⁶ In addition to the TD(N) double donors, single donors also form, denoted STD(N) centers. The STD(N) centers may involve hydrogen. A comprehensive review of oxygen precipitation and diffusion of oxygen in Si is given by Newman.¹⁷

Vacancy-oxygen complexes

Vacancy-oxygen (V-O) complexes are referred to as *A centers*. They are formed by electron or ion-induced damage of Si:O (Ref. 18, 19, 20). The vibrational mode of the oxygen gives rise to an IR absorption peak at 835 cm⁻¹. In V-O complexes, the oxygen is almost substitutional, but it relaxes in an off-center direction and binds preferentially to two neighboring Si atoms (Fig. 2)^{18,21,22}. The other two Si neighbors form a Si-Si bond. The V-O

complex has a deep acceptor level 0.18 eV below the conduction band minimum; hence, it acts as an electron trap. When the acceptor level is occupied, the V-O complex is negatively charged. The additional electron causes the bonds to strengthen, leading to an increase in the LVM frequency (885 cm^{-1}).

Donors and acceptors

LVMs arising from isolated substitutional impurities in Si have been observed extensively.²³ IR absorption spectra have been reported for P donors, B acceptors, and isoelectronic C impurities. In addition, LVMs from acceptor-Li complexes have been observed. Frequency shifts due to different isotopes (e.g., ^{10}B and ^{11}B) provided a powerful way to establish assignments unambiguously.²⁴

Acceptor-hydrogen pairs

Sah *et al.*²⁵ found that hydrogen neutralizes boron acceptors in Si. Hydrogen gives an electron to the acceptor. Johnson *et al.*²⁶ used secondary ion mass spectrometry (SIMS) to measure the concentration profile of deuterium and boron in Si:B exposed to a deuterium plasma. The deuterium and boron concentrations were nearly identical, suggesting the presence of B-D pairs. Proof for B-H complexes came from Pankove *et al.*²⁷, who observed an IR absorption peak at 1870 cm^{-1} in Si:B samples exposed to a hydrogen plasma. Upon substitution of deuterium for hydrogen, the peak shifted to a lower frequency of 1360 cm^{-1} (Ref. 26), due to the heavier mass of D.

First-principles calculations^{28,29} showed that the total energy of a B-H complex is minimized when the hydrogen is oriented along the $[111]$ axis in a bond-centered configuration. The bond-centered model was originally proposed by Pankove *et al.*³⁰ To test this model, Stavola *et al.*³¹ measured the LVMs of several acceptor-hydrogen complexes. At low temperatures, B-H, Al-H, and Ga-H had LVM frequencies of 1907, 2201, and 2171 cm^{-1} , respectively. These vibrational frequencies were reasonably close to the theoretically predicted values^{28,29}. The bond-centered model was essentially proven when Pajot *et al.*³² discovered that the B-H LVM frequency increases by 0.8 cm^{-1} when ^{10}B is substituted for ^{11}B , in qualitative agreement with theoretical calculations³³ that predicted a weak B-H bond.

Donor-hydrogen pairs

Johnson *et al.*³⁴ demonstrated hydrogen passivation of donors in Si. By exposing an *n*-type layer of Si to a hydrogen plasma, they reduced the free carrier concentration and increased the mobility. The increase in the mobility was due to a decrease in ionized impurity scattering. The authors argued that the hydrogen attaches to a Si atom in an *antibonding*, or back-bonded, orientation. In contrast to the bond-centered model, the hydrogen in the antibonding orientation sits opposite to the donor (Fig. 5). Later theoretical calculations confirmed the antibonding model.³⁵

To test this model experimentally, Si samples were implanted with group-V donors (P, As, Sb) and exposed to a hydrogen or deuterium plasma³⁶. Hydrogen stretch modes were observed near 1500 cm^{-1} and transverse (wag) modes were observed at 809 cm^{-1} . The deuterium stretch and wag modes shift downward in frequency, as expected. The observed frequencies were insensitive to the donor species, only shifting by a few cm^{-1} . Such an insensitivity to the donor species provides evidence for the antibonding model (Fig. 6). Unlike the bond-centered configuration, hydrogen is not adjacent to the impurity.

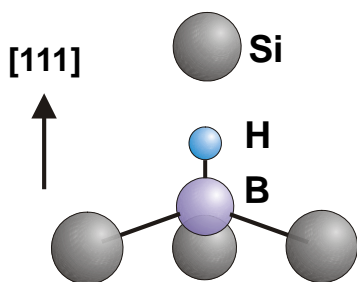


Figure 5. Bond-centered model for B-H complexes in Si.

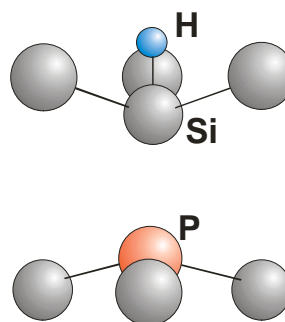


Figure 6. Antibonding model for P-H complexes.

Hydrogen molecules

Although hydrogen molecules had been speculated to exist in Si since the early 1980's, their existence was not established experimentally until the late 1990's.^{37,38} In free space, the H₂ molecule is not IR active, since its vibration does not induce a dipole moment. In the Si lattice, however, the vibration induces a weak dipole moment, allowing it to be observed in the IR absorption spectrum.

H₂ and D₂ dimers in Si exhibit sharp vibrational peaks at 3618.4 cm⁻¹ and 2642.6 cm⁻¹, respectively. In its interstitial location, the hydrogen molecule is free to rotate, where J denotes the rotational quantum number. Owing to the tetrahedral symmetry of the interstitial site, dimers with $J = 0$ are IR inactive. The peaks at 3618.4 cm⁻¹ and 2642.6 cm⁻¹ therefore correspond to vibrational transitions of dimers in the $J = 1$ state. In contrast to the dimers, which must exist in either an *ortho* or *para* state, HD molecules obey different selection rules. The HD absorption line, observed at 3265 cm⁻¹, corresponds to a vibrational transition with $J = 0$ in the ground state and $J = 1$ in the excited state.³⁹ Raman scattering, a complementary technique to IR absorption, confirmed these results.⁴⁰

Acknowledgments

I would like to thank the organizers of the conference, Koichi Kakimoto, Atsushi Ogura, and Kazumi Wada. Collaborators on the high-pressure Si:O work include Eugene Haller, Leonardo Hsu, and Lennart Linstrom. Financial support by the US National Science Foundation (DMR-0704163) and US Department of Energy (DE-FG02-07ER46386) is gratefully acknowledged.

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