Infrared spectroscopy of impurities in silicon

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Abstract

Infrared (IR) spectroscopy has yielded fundamental information about the vibrational and electronic properties of impurities in silicon. This paper briefly discusses local vibrational modes of oxygen, hydrogen, and substitutional dopants. Electronic spectra yield acceptor or hole binding energy with high accuracy. The old question of copper in silicon is revisited in the context of a "universal acceptor level."

Introduction

The characterization of impurities in single-crystal silicon has been an essential part of the development of modern electronic devices. IR spectroscopy provides two glimpses into the properties of beneficial or detrimental foreign atoms. First, and most important technologically, acceptors and donors introduce electronic levels into the gap. If these electrically active impurities are shallow (e.g., substitutional dopants such as boron or phosphorus), then the levels lie close to the valence band or conduction band, respectively. The electron or hole orbits around the impurity atom, analogous to a hydrogen atom. The "hydrogenic" impurity gives rise to 1s-to-2p transition peaks in the absorption spectrum. From the energies of these peaks, we can accurately determine the ionization energy.

Along with electronic properties, impurities also affect the vibrational properties of a semiconductor. Fundamentally, the translational symmetry of the crystal is broken. If an impurity with a light mass replaces a heavier host atom, then a local vibrational mode (LVM) will appear. This LVM has a frequency that is higher than the highest phonon frequency of the pure crystal. Hydrogen is extreme in this regard, due to its low mass of only 1 amu. When hydrogen binds to a silicon atom, it has a frequency of ~2000 cm^{-1}, which is ~4 times the maximum phonon frequency for crystalline silicon.

This paper briefly reviews several examples of impurities in crystalline silicon. For more information, the reader is referred to Wronski *et al.* [1] for amorphous silicon, Newman [2] for a review of defects and impurities in silicon crystals, and McCluskey and Haller's textbook [3] for a comprehensive treatment of dopants and defects in semiconductors.

Oxygen

Silicon crystals grown by the Czochralski technique contain a fairly large concentration (>10^{17} cm^{-3}) of oxygen impurities. Interstitial oxygen (O_i) is bonded to two neighboring silicon atoms, forming a kind of Si-O-Si molecule [4]. This molecule has several LVMs that are observed in IR spectroscopy [5]. The *asymmetric* mode involves the Si atoms oscillating out of phase with the O atom and has a high frequency (1136 cm^{-1}). If the oxygen oscillates *transverse* to the Si-O-Si axis, then its frequency is very low (~30 cm^{-1}). The coupling between the asymmetric and transverse modes has been the subject of beautiful work by Yamada-Kaneta *et al* [6]. The *resonant* mode is an extended mode, involving the oscillation of many Si atoms, with a frequency of ~520 cm^{-1}.

In our work, we used O_i in Si is a model system for studying the interaction between local and extended vibrational modes [7]. We used hydrostatic pressure to bring the asymmetric 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 asymmetric stretch mode decreased abruptly as it entered the two-phonon density of states, causing the line to broaden. Second, we observed a novel anti-crossing between the two vibrational modes. A theoretical model of this interaction produced excellent agreement with the experimentally observed frequencies and linewidths. This study showed that, in addition to being a technologically relevant defect, oxygen in silicon is a model system for probing fundamental semiconductor physics.

When a Czochralski-grown silicon crystal is heated, the O_i impurities diffuse and form clusters called thermal donors. 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 a <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 [8,9]. 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}. A comprehensive review of oxygen precipitation and diffusion of oxygen in silicon is given by Newman [10]. In many cases, precipitates are desirable because they getter transition-metal impurities.

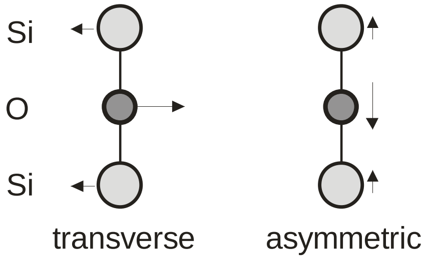

Fig. 1. Transverse and asymmetric vibrational modes of interstitial oxygen in silicon.

Donors and acceptors

IR spectra from donors and acceptors show sharp lines corresponding to 1s-to-2p transitions. See, for example, the books by Pajot [11], Yu and Cardona [12], and McCluskey and Haller [3]. LVMs arising from isolated substitutional impurities in silicon have been observed extensively [13]. IR absorption spectra have been reported for phosphorus donors, boron acceptors, and isoelectronic carbon impurities. In addition, LVMs from acceptor-lithium pairs have been observed. Frequency shifts due to different isotopes (e.g., ^{10}B and ^{11}B) provided a powerful way to establish assignments unambiguously. In general, one should always have an isotope shift to ensure that an IR peak originates from a given impurity.

Hydrogen passivation

Hydrogen has the special property that it can bind to dangling bonds, removing the energy level from the gap. It is this property, *passivation*, which makes hydrogenated silicon such a high-quality electronic material. In addition to passivating dangling bonds on the surface or in vacancies, hydrogen can also form pairs with acceptors or donors, rendering them electrically inactive. Numerous LVMs from such hydrogen complexes have been observed, not only in silicon but also in a variety of compound semiconductors. In the case of hydrogen, the isotope effect is especially dramatic when one compares the mass of hydrogen (1 amu) with that of its heavy isotope deuterium (2 amu). Pioneering IR spectroscopy experiments on acceptor-hydrogen pairs in silicon were performed by Stavola *et al.* [14] and Pajot *et al* [15]. Reviews of hydrogen in semiconductors are given in Refs. 16-18.

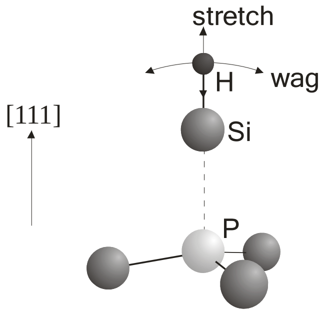

Fig. 2. Stretch and wag (or bending) vibrational modes of the phosphorus-hydrogen complex in silicon.

Copper

Copper is a fast-diffusing interstitial impurity. In its interstitial form, it acts as a shallow donor and, like hydrogen, can passivate acceptors. Unlike hydrogen, it cannot passivate donors. A small fraction of the copper impurities in a sample assume substitutional sites, where they act as acceptors. Hall-effect and IR photoconductivity measurements performed in the 1950s [19] proposed a donor level at 0.24 eV and an acceptor level at 0.49 eV. However, a careful reading of their paper suggests that the 0.24 eV level may actually be the (0/-) acceptor level (first ionization energy). To put this into context, the band lineups are plotted for numerous semiconductors (Fig. 3). The valence band maxima were determined by first-principles calculations [20], the conduction band minima are from experimental data, and the vacuum level was taken from Ref. 21. In our "universal acceptor model," the copper acceptor level is assumed to be constant relative to vacuum. IR spectroscopy would be an ideal method to measure the acceptor binding energy for copper in silicon, resolving this old question and providing evidence for the universal model.

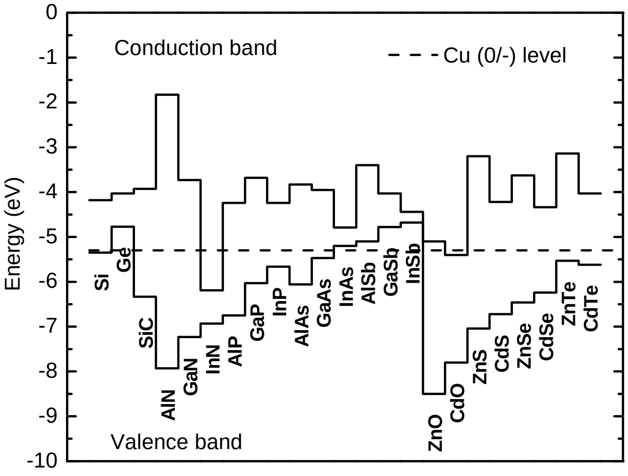

Fig. 3. Proposed “universal acceptor model” for copper in semiconductors. The dashed line indicates the Cu (0/-) acceptor level. When this level is in the valence band, Cu is a shallow (hydrogenic) acceptor. When it is in the gap, it is a deep acceptor. If the level lies in the conduction band, then the acceptor level is inactive.

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