

A very shallow acceptor in Cu-diffused Si

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Abstract

Copper is a common, fast-diffusing impurity in Si. In addition to its interstitial form (Cu_i), it can also occupy a substitutional site (Cu_s). Previous experimental and theoretical studies indicate that Cu_s introduces deep levels into the band gap. In the present work, Cu was diffused into float-zone silicon. Infrared (IR) spectroscopy provides evidence for a shallow acceptor level, only 27 meV above the valence-band maximum. The spectrum and its temperature dependence, when compared to the well-known boron acceptor, confirm its shallow-acceptor behavior.

Introduction

Cu impurities enter Si, almost always unintentionally, during a variety of processing steps [1]. The interstitial donor Cu_i is a fast diffuser and passivates shallow acceptors such as B, Al, Ga, and In [2,3]. It also forms a four-Cu donor [4,5] and Cu-hydrogen complexes [6]. Theory suggests that substitutional Cu_s may introduce deep levels that affect the operation of devices [7,8].

As summarized by Sze and Ng [9], Cu_s has acceptor levels 0.24, 0.4, and 0.53 eV above the valence-band maximum, mostly determined by deep level transient spectroscopy (DLTS). These assignments are controversial. For example, the 0.24 eV and 0.53 eV levels have been attributed to a Cu-O complex [10] and Cu-C-O complex [11], respectively. Other researchers have also questioned whether the levels are due to Cu [12,13]. The literature often refers to the 0.24 eV DLTS level as a donor level [14], based on Hall-effect measurements by Collins and Carlson [15]. However, those Hall measurements clearly showed *p*-type conductivity, suggesting that the assignment to a *donor* level was a mistake. To address these mysteries, we performed IR spectroscopy on float-zone Si that was deliberately Cu contaminated [16].

Experiment

Float-zone Si single crystals of thickness 0.5 mm and 5 mm were used. The Si crystal was placed in a silica ampoule, along with Cu granules, and evacuated to a rough vacuum (~ 0.1 Torr). Cu diffusion was performed by placing the ampoule in a horizontal tube furnace at 1250°C for 2 h. At that temperature, the solubility is $[\text{Cu}] \sim 10^{18} \text{ cm}^{-3}$, although most atoms are in the form of Cu clusters [17,18]. A control Si sample was heated under the same conditions but without Cu present. After the heat treatment, the Si:Cu sample had a room-temperature hole concentration of $p = 2 \times 10^{14} \text{ cm}^{-3}$. The control sample had a free-electron concentration of $8 \times 10^{12} \text{ cm}^{-3}$. These observations are consistent with Cu acting as an acceptor.

IR transmission and photoconductivity spectra were collected with a Bomem DA8 Fourier transform IR (FTIR) spectrometer with a potassium bromide (KBr) beamsplitter. Low temperatures were provided by a Janis closed-cycle helium cryostat with ZnSe windows. A Ge:Cu photoconducting detector, placed in the cryostat along with the sample, was used for IR transmission measurements (5 mm thick sample). For photoconductivity

measurements, a 0.5 mm thick Si sample was used as an IR detector. An instrumental resolution of 2 cm^{-1} was chosen.

Results

A low-temperature photoconductivity spectrum of Si:Cu is shown in Fig. 1, along with Si:B for comparison. The main features are strong peaks labeled $2p'$, $3p'$, and $4p'$. These peaks correspond to transitions from the $1s$ ground state of the hydrogenic acceptor to excited p' states (Fig. 2). These excited states are derived from the split-off valence band and have been observed for group-III acceptors [19,20]. The spacing between the peaks is always the same, regardless of the particular acceptor. The peaks are uniformly shifted by the central-cell correction of the acceptor, which affects $1s$ state but not the p' states [21]. This well-defined shift provides an accurate method to determine the acceptor binding energy.

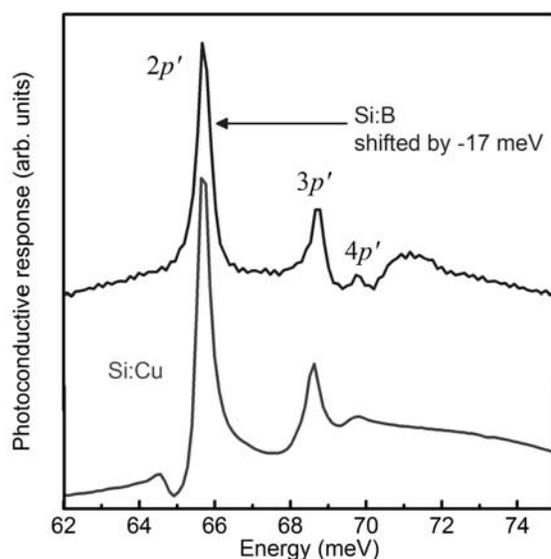


Fig. 1. Photoconductivity spectra of Si:Cu and Si:B, showing the $1s \rightarrow np'$ hole transitions. The Si:B spectrum was shifted 17 meV to lower energy. Thus, the Si:B acceptor is 17 meV deeper than Si:Cu.

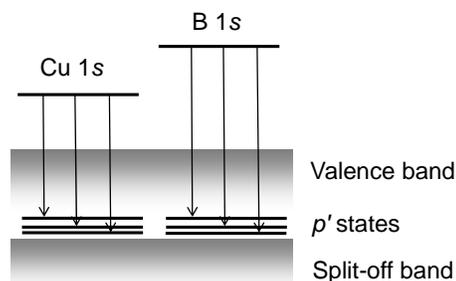


Fig. 2. Energy-level diagram for B and Cu-related acceptors in Si. The p' excited states are derived from the split-off valence band. Hole transitions are indicated by the arrows.

As shown in Fig. 1, the Si:B spectrum is shifted by 17 meV relative to the Si:Cu spectrum. The B acceptor binding energy is known to be 44 meV [21]. Therefore, we estimate the Cu-related acceptor level to be $44 - 17 = 27$ meV. The 27 meV level is consistent with variable-temperature Hall effect measurements [16]. To our knowledge, this is the shallowest acceptor in Si.

To explore the spectroscopy further, IR transmission spectra were taken at several different temperatures. As shown in Fig. 3, the intensity of the Si:Cu $1s \rightarrow 2p'$ peak decreases with increasing temperature. It decreases by 50% at a fairly low temperature, 14 K (Fig. 4). By way of comparison, the intensity of an excited-state peak

($1s \rightarrow 2p$) is plotted for Si:B [22]. This peak also decreases with temperature, but not as fast—it decreases by 50% at 20 K. The authors attributed the decrease in the B peak to thermal ionization of holes from the B acceptors. The observation that this occurs at a higher temperature than Si:Cu is consistent with the notion that B is deeper than the Cu-related acceptor.

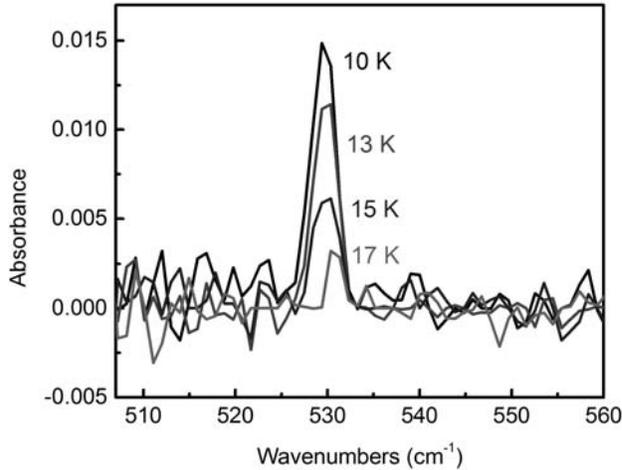


Fig. 3. Plot of the 65.8 meV (530 cm^{-1}) peak in Si:Cu for several temperatures.

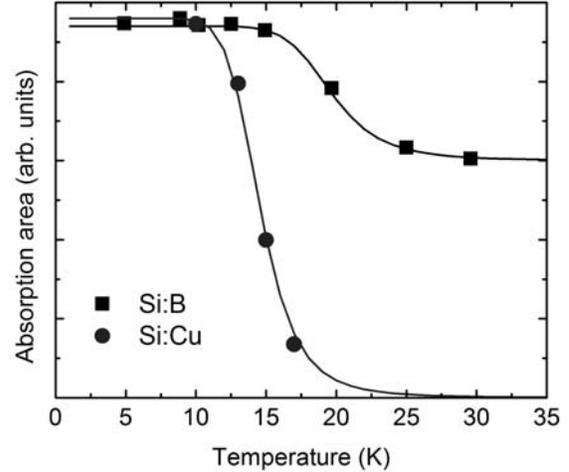


Fig. 4. Plot of the integrated absorbance for excited-state peaks in Si:B [22] and Si:Cu (this work).

Conclusions

Using IR spectroscopy, we have observed a shallow acceptor (27 meV) in Si after Cu diffusion. While it is plausible that this acceptor is Cu-related, we do not have a specific fingerprint (e.g., isotopic) to confirm this. First-principles calculations [7] indicate that Cu is a *deep* acceptor, apparently contradicting our experimental results. Rather than a shallow acceptor level, it is possible that the IR peaks arise from a hole trapped by a neutral Cu-acceptor pair. (The hole would need to come from some other acceptor). Such “overcharged” centers have been observed in Ge:Be [23].

Although a shallow Cu_s acceptor level may seem surprising, it is consistent with a “universal acceptor level” that does not depend on the host crystal [16]. For example, density functional *GW* calculations indicate that the valence band of Si is 0.2 eV higher than that of GaAs [24]. In GaAs, the Cu_s acceptor level is 0.15 eV above the valence-band maximum [25]. Following the universal acceptor level model, the Cu_s acceptor level should be *below* the Si valence band. This implies that Cu_s is a shallow acceptor in Si.

Acknowledgments

MDM would like to thank Anderson Janotti for helpful discussions. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award DE-FG02-07ER46386.

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