Infrared absorption in silicon from shallow thermal donors incorporating hydrogen and a link to the NL10 paramagnetic resonance spectrum


DOI
10.1103/PhysRevB.54.R6803

Publication date
1996

Published in
Physical Review. B, Condensed Matter

Citation for published version (APA):
Infrared absorption in silicon from shallow thermal donors incorporating hydrogen and a link to the NL10 paramagnetic resonance spectrum

R. C. Newman, J. H. Tucker, and N. G. Semaltianos
Interdisciplinary Research Centre for Semiconductor Materials, The Blackett Laboratory, Imperial College of Science, Technology and Medicine, Prince Consort Road, London SW7 2BZ, United Kingdom

E. C. Lightowlers
Department of Physics, King’s College London, Strand, London WC2R 2LS, United Kingdom

Van der Waals-Zeeman Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands

Received 14 February 1996; revised manuscript received 22 April 1996

Shallow thermal donors (STDs), generated in Czochralski silicon, annealed at 470 °C in a hydrogen plasma, and detected by their infrared (IR) electronic absorption, have ground states that shift slightly (~0.1 cm⁻¹) to smaller binding energies, when deuterium is introduced instead of hydrogen, demonstrating the presence of a hydrogen atom in the donor core. No other IR spectrum is detected apart from that from neutral double thermal donors (TDs). The same optical transitions are observed in three annealed samples given a preheat treatment in water vapor. These latter samples show the NL10 electron-paramagnetic-resonance (EPR) spectrum, recently attributed to hydrogen passivated TDs. The relative strengths of the EPR NL10 spectra correlate with those of the STD IR spectra, providing a strong indication that both spectra arise from the same defects.
were partially passivated TD...2

It is clear that various types of complexes be-

work in which a high concentration of STD...

been implied that N-O complexes give rise to the STD...

sented for the incorporation of nitrogen. Nevertheless, it has...

attributed to complexes incorporating both oxygen and nitro-

duced by the latter process was indicated by small reductions...

In indium-doped samples...

are pretreated in water vapor at 1200 °C, prior to an anneal...

centrations of these centers are enhanced greatly if samples...

The NL10 EPR spectrum shows g shifts with increasing anneal time of samples (cf. the results for NL8).5 The concentrations of these centers are enhanced greatly if samples are pretreated in water vapor at 1200 °C, prior to an anneal at 470 °C.24 In indium-doped samples [In]=1.2×10^{15} cm^{-3} (boron acceptors were also present with [B]=1.3 ×10^{14} cm^{-3}) or phosphorus ([P]=2×10^{15} cm^{-3}) doped material ENDOR measurements have shown the incorporation of oxygen and a hydrogen (or deuterium) atom in the defects responsible, but no evidence has been found for the presence of either nitrogen or carbon. These results support the proposal that the NL10 spectrum is caused by a family of single donors to be identified with partially passivated double TD(N) centers25 (cf. the conclusions given in Ref. 23).

In the present work, we first study the IR spectrum of STDs in various hydrogenated or deuterated Si samples to investigate whether or not there are small isotopic shifts in the line frequencies. In addition, we investigate line shifts as a function of the sample temperature. Finally, IR measurements are reported for three Si samples that showed a strong NL10 spectrum and a correlation was found between the strength of the IR absorption and the spin concentration of the NL10 spectrum.

Most samples were cut from a CZ Si ingot that had been grown in an argon atmosphere and contained residual boron acceptors at concentrations of ∼2×10^{14} cm^{-3}. The oxygen concentration was [O]=1.0×10^{15} cm^{-3} and the carbon concentration was smaller than the detection limit of 3×10^{15} cm^{-3}. The material had been heated in pure argon and quenched to remove grown-in donors. The samples then were hydrogenated or deuterated either by exposing them to a radio-frequency plasma (13.56 MHz, 2 Torr, 40 W) for various periods or by heating them in H_{2}(D_{2}) gas at 1300 °C and quenching them to room temperature.26 Similar treatments were given to samples cut from other CZ ingots, including phosphorus-doped n-type material. Infrared measurements were made using a Bruker IFS 120HR interferometer at a spectral resolution of 0.25 cm^{-1} with the samples held at a temperature of ∼10 K.

Infrared measurements indicate that the highest concentration of TD(N) centers are produced by anneals at ∼470 °C. Spectra from p-type samples annealed for different times in a H plasma (Fig. 1), indicate clearly the evolution of the family of shallow donor centers (Table I). Spectra from the n-type samples showed additional lines, usually attributed to 1s→3p_{\pm} transitions of STDs at 273 and 267.1 cm^{-1}, together with lines in the same spectral range, presumably caused by the presence of other defects or unknown impurities. In making assignments to STD(N)s (see below), these lines have been ignored. Spectra then were recorded with samples held at different temperatures in the range 5–50 K in a flow cryostat. A monotonic decrease of the strengths of the STD(N) transitions, consistent with an ionization energy of ∼36 meV, demonstrated that none of the transitions originate from excited states of the centers, as found, for example, for phosphorus donor impurities.27 These measurements also yielded data for the temperature dependence of the frequencies of the transitions (Fig. 2), that

FIG. 1. The IR absorption spectra from STD centers in B-doped (2×10^{14} cm^{-3}) samples annealed at 470 °C in a hydrogen plasma for (a) 5 h, (b) 10 h, (c) 20 h, (d) 40 h, and (e) 70 h. Spectra (a)–(e) are displaced progressively for clarity of presentation. Absorption lines usually ascribed to 1s→3p_{\pm} transitions were very weak or absent.
TABLE I. The IR absorption line positions of the main transitions at \( \sim 10 \) K from the ground states of the shallow thermal donors (our labeling) STD(1)–STD(7), together with electron binding energies \( E_i \), determined by assuming that the \( 2p_\pm \) state was 6.4 meV below the conduction band. Reductions in the line frequencies induced by the substitution of deuterium for hydrogen in the \( n \)-type samples are given in the final column.

<table>
<thead>
<tr>
<th>Transition</th>
<th>( 1s \rightarrow 2p_0 ) (cm(^{-1}))</th>
<th>( 1s \rightarrow 2p_\pm ) (cm(^{-1}))</th>
<th>( E_i ) (meV)</th>
<th>H( \rightarrow )D shift for ( 2p_\pm ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>208.7</td>
<td>253.6</td>
<td>37.8</td>
<td>not measured</td>
</tr>
<tr>
<td>2</td>
<td>204.2</td>
<td>246.8</td>
<td>37.0</td>
<td>(-0.15)</td>
</tr>
<tr>
<td>3</td>
<td>198.2</td>
<td>241.1</td>
<td>36.3</td>
<td>(-0.18)</td>
</tr>
<tr>
<td>4</td>
<td>195.4</td>
<td>238.4</td>
<td>35.9</td>
<td>(-0.12)</td>
</tr>
<tr>
<td>5</td>
<td>190.7</td>
<td>233.7</td>
<td>35.4</td>
<td>(&lt;0.05)</td>
</tr>
<tr>
<td>6</td>
<td>187.4</td>
<td>230.6</td>
<td>35.0</td>
<td>(&lt;0.05)</td>
</tr>
<tr>
<td>7</td>
<td>183.0</td>
<td>226.1</td>
<td>34.4</td>
<td>(-0.12)</td>
</tr>
</tbody>
</table>

could be compared with corresponding data for the transitions of TD(N) centers. The rate of shift to lower wave numbers for the latter centers is 0.017–0.018 cm\(^{-1}\) K\(^{-1}\) [Fig. 2(a)], which is greater than the rate for STDs of 0.012–0.013 cm\(^{-1}\) K\(^{-1}\) [Fig. 2(b)]. This means that there would be a shift of \(-0.1\) cm\(^{-1}\) for a change in temperature of \(-8\) K for STDs, so that great care is necessary in comparing line positions in hydrogenated samples with deuterated samples. To demonstrate that an isotopic shift actually occurs, it is necessary to show that there is no corresponding shift in transitions from TD(N) from each pair of samples examined.

We compared the frequencies of the various transitions of STD(N)s and TD(N)s for hydrogenated and deuterated samples; five pairs of samples were measured. For two pairs \((n\text{-type Si})\), there were clear shifts of STD(N) lines to lower frequencies by about 0.1 cm\(^{-1}\) in the deuterated samples compared with hydrogenated samples, but no shifts were observed for the TD(N) transitions (Fig. 3 and Table I). For two of the other pairs of samples, \((p\text{-type})\), the shifts in the frequencies of the STD(N) lines were significantly smaller than 0.1 cm\(^{-1}\), but for a third pair, the shifts were again \(-0.1\) cm\(^{-1}\). The strengths of the absorption from the STD(N) centers in the deuterated samples were smaller than those in the hydrogenated samples (by a factor of 3 and 4.5 for the first two pairs and the second two pairs, respectively), presumably caused by the more limited depth of diffusion of the deuterium atoms.\(^{28}\) The very small shifts observed here are similar in magnitude to those reported for neutron irradiated FZ Si after treatment in a plasma,\(^{22}\) but they are on average smaller than those \((-0.23\) cm\(^{-1}\)) reported previously by us for precursor related oxygen defects present after short anneals of CZ Si preheat treated in \(\text{H}_2\) gas.\(^{23}\) Nevertheless, the shift \((0.16\) cm\(^{-1}\)) reported for line F \((246.9\) cm\(^{-1}\)) (Ref. 23) may be compared with the same value of 0.15 cm\(^{-1}\) found in the present work (Table I). Only small shifts are expected since the donors have small ionization energies \(E_i\), and are, therefore, very delocalized.

The choice of N for labeling the STDs in relation to passivated TD(N) centers is not yet definitive. In our earlier work,\(^{23}\) several donors were observed in the initial stages of the passivation process that were attributed to partially passivated TD(1) centers with different geometries. It was suggested that the \(1s \rightarrow 2p_\pm\) transition of passivated TD(2) should be identified with the line at 246.8 cm\(^{-1}\) (Table I) and we use the same labeling here. This procedure is consistent with measurements of STD(N)s and TD(N)s produced in Si samples containing high concentrations of carbon \((\sim 10^{18}\) cm\(^{-3}\)) so that there is a very slow rate of TD(N) formation: no new absorption lines were detected that could be attributed to donor centers incorporating a carbon atom.

Broadening of the \(1s \rightarrow 2p_\pm\) lines occurred in some samples, when they were given a long anneal in air. This broadening was particularly strong (Fig. 4) for one of the three samples that had been heated in water vapor and made specifically for EPR and ENDOR measurements. These samples, originally \(\sim 2\) cm in length and \(1.4\times1.4\) mm\(^2\) in cross section were cut into three pieces and mounted side by side to obtain their IR spectra and so their temperatures during measurements might have been higher than that normally achieved \((\sim 10\) K). Nevertheless, there is a correspondence

FIG. 2. The peak position of the absorption line corresponding to the transition \(1s \rightarrow 2p_\pm\) of (a) TD(3), TD(4), and (b) STD(2), STD(3), as a function of sample temperature in the range 5–50 K.

FIG. 3. \(1s \rightarrow 2p_\pm\) transitions of the two strongest STDs: STD(2) and STD(3) (left) and TD(3) (right) in the spectra of a pair of \(n\)-type phosphorus doped samples which had been heated (a) in a deuterium plasma for 34 h, and (b) in hydrogen plasma for 17 h. After normalizing the strengths of the absorption (increasing that from the deuterated sample), we obtained the difference spectra shown in (c), demonstrating the isotopic shift of the STD lines.
of all the transitions in these samples with those in the plasma treated samples. The measured integrated absorption coefficient (IA) for the STDs across the range of $1s\rightarrow2p_{\pm}$ transitions from 228.8 to 250.6 cm$^{-1}$ were compared with the relative NL10 spin concentrations. Samples heated for 20 h (P doped), 30 h (P doped), and 70 h (In doped) had IAs of 27, 25, and 53 ($\pm$ 10%) cm$^{-2}$, and spin concentrations of 1.2, 1.4, and $3\times10^{15}$ cm$^{-3}$, respectively. Using the IR calibration for the 315 cm$^{-1}$ line ($1s\rightarrow2p_{\pm}$) caused by phosphorus, for which IA=1 cm$^{-2}$ corresponds to [P]=1.01$\times10^{15}$ cm$^{-3}$, we obtain estimates of the STD(N) concentrations of 2.7, 2.5, and $5.3\times10^{14}$ cm$^{-3}$. The discrepancies with the measured NL10 spin concentrations of approximately 5 are not considered excessive since (a) the absolute concentrations of the NL10 defects could be in error by this factor, although the relative concentrations should be reasonably accurate and, (b) the absolute concentrations of the STD(N)s are not known since we do not have a calibration factor. In spite of these problems, the results overall provide a strong indication that the observed IR absorption lines are caused by the same centers that give rise to the NL10 EPR spectrum since no other IR absorption spectrum was detected in the EPR/ENDOR samples apart from that from TD(N) centers (and phosphorus). There was no evidence that the NL10 spectrum was caused by a relatively deep level, as implied for phosphorus doped samples that had been subjected to $\gamma$-ray irradiation$^{26}$: it is possible that phosphorus donors in these samples formed complexes with the products of the irradiation so that they no longer acted as donors.

In summary, IR absorption spectra from annealed hydrogenated CZ Si samples show the evolution of a family of STD(N) defects. The frequencies of the electronic transitions were found to shift to lower energies by $\sim0.1$ cm$^{-1}$ in five pairs of samples when deuterium was introduced instead of hydrogen. The same STD spectrum was observed for three samples that had been heated in water vapor and showed a strong EPR NL10 spectrum. There were correlations of the relative strengths of the two types of spectra, with the implication that they originate from the same defects. In view of comparisons indicating similarities of the ENDOR spectra of NL8 and NL10$^{31,32}$ it is inferred that the defects giving rise to the STDs and NL10 spectra are partially passivated TD(N) centers. There is no evidence from ENDOR measurements for the presence of nitrogen or carbon in these defects.

We thank MEMC, Philips Components, and Wack- erchloritronic for supplying silicon samples. The work at Imperial College was supported by the Engineering and Physical Sciences Research Council (EPSRC) United Kingdom (Grant No. GR/J 97540), and at King’s College by EPSRC (Grant No. GR/K 30995).

\*Current address: 12 G. Papandreou, 62122 Serres, Greece.

8J-M. Spaeth, private communication.