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

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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 ($\sim 0.1\ \mathrm{cm}^{-1}$) 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. [S0163-1829(96)50434-0]

Silicon crystals grown by the Czochralski (CZ) method contain grown-in bonded interstitial oxygen impurity atoms at concentrations $[\mathrm{O}_i]$ close to $10^{18}\ \mathrm{cm}^{-3}$. During annealing at temperatures in the range $350\ ^\circ\mathrm{C} < T < 500\ ^\circ\mathrm{C}$, the O_i atoms diffuse and form agglomerates that act as donor defects. Infrared (IR) absorption[1–3] measurements then show electronic transitions associated with two distinct types of donors called thermal donors TD(N) and shallow thermal donors STD(N). Two distinct electron paramagnetic resonance (EPR)[4,5] spectra are also present: the NL8 spectrum relates to singly ionized thermal donor centers $\mathrm{TD(N)}^+$ and the NL10 spectrum relates to centers with a more highly delocalized unpaired electron.

The TD(N) centers comprise a family of helium-like donors that give rise to sharp electronic IR absorption lines in the spectral regions 350–533 cm^{-1} and 580–1170 cm^{-1} from $\mathrm{TD(N)}^0$ and $\mathrm{TD(N)}^+$, respectively. There is an unambiguous correlation of these centers with the EPR spectrum labeled NL8, established from studies of the stress alignment of the defects.[6] Measured values of the EPR g tensor change progressively with anneal time caused by overlapping spectra from donors with decreasing localization (increasing values of N),[5] consistent with the IR data. Electron nuclear double resonance (ENDOR) measurements confirm the incorporation of oxygen in TD(N) defects in samples containing $^{17}\mathrm{O}$ with nuclear spin $I=5/2$,[4,5] but no microscopic evidence has been presented for the incorporation of any other impurity, e.g., carbon ($^{13}\mathrm{C}$, $I=1/2$) or nitrogen ($^{14}\mathrm{N}$, $I=1$), and there is still no such evidence.[7,8]

The STD(N) centers comprise a family of single donors that give rise to absorption in the spectral range 150–300 cm^{-1}. These centers were first detected by photothermal ionization and absorption spectroscopy in CZ Si preannealed in nitrogen[9] or oxygen[10] gas and then heated at $\sim 450\ ^\circ\mathrm{C}$. Silicon grown from a melt containing silicon nitride[11,12] also showed the presence of donors (without annealing) that were not eliminated unless samples were heated to $T>1100\,^{\circ}\mathrm{C}$. Based on the conditions for their formation, these lines were attributed to complexes incorporating both oxygen and nitrogen impurities, but again no microscopic evidence was presented for the incorporation of nitrogen. Nevertheless, it has been implied that N-O complexes give rise to the STD(N) centers and the NL10 EPR spectrum.[13–16] An alternative view is that the N-O defects are distinct from STD(N)s and nitrogen acts only as a catalytic agent, enhancing the rate of formation of the latter centers.[17] It also has been proposed that the presence of aluminum in a crystal accelerates STD formation,[18] following suggestions that the NL10 EPR center should be identified with the STD absorption.[15,19] However, the IR spectrum (labeled K lines) obtained from aluminum-doped Si does not fit into the accepted STD generation scheme.[20] There are, in addition, reports that donors with low ionization energies are formed by (a) annealing neutron transmutation-doped Si grown in a hydrogen atmosphere[21] or (b) exposing neutron irradiated float zone (FZ)Si (essentially oxygen-free) to a hydrogen plasma.[22] It is important to note that the incorporation of hydrogen in the donor centers produced by the latter process was indicated by small reductions in the frequencies of the IR lines by up to $\sim 0.1\ \mathrm{cm}^{-1}$, when a deuterium plasma was used instead of a hydrogen plasma. Yet another series of shallow centers in the same spectral region has been found in CZ Si after heat treatment in hydrogen gas at 1300 °C, followed by a quench to room temperature, prior to short anneals at 350 °C.[23] The frequencies of the IR lines again were reduced slightly when deuterium was introduced instead of hydrogen, but, as expected, no shifts were found for the $\mathrm{TD(N)}^0$ defects. An important suggestion of this particular work was that the STD(N) centers were partially passivated TD(N) centers that incorporated a single hydrogen atom. These measurements followed earlier work in which a high concentration of STD(N) defects was produced in CZ Si annealed for extended periods in a hydrogen plasma.[2] It is clear that various types of complexes behave as shallow donors, but there is still no consensus about the identity of the STDs found in annealed as-grown undoped CZ silicon.

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 $[\mathrm{In}]=1.2\times10^{15}$ cm^{-3} (boron acceptors were also present with $[\mathrm{B}]=1.3\times10^{14}\ \mathrm{cm}^{-3}$) or phosphorus ($[\mathrm{P}]=2\times10^{15}\ \mathrm{cm}^{-3}$) 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) centers[25] (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.

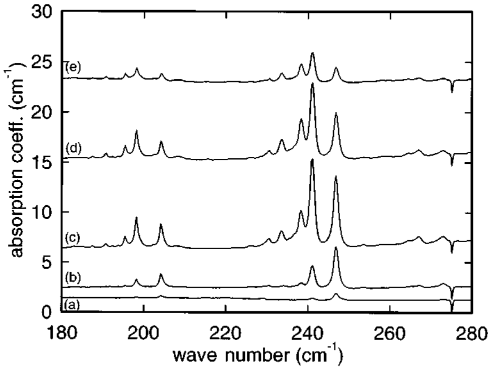

FIG. 1. The IR absorption spectra from STD centers in B-doped ($2\times10^{14}\ \mathrm{cm}^{-3}$) samples annealed at 470 °C in a hydrogen plasma for (a) 5 h, (b) 10 h, (c) 20 h, (d) 40 h, and (e) 70 h. Spectra (a)–(e) are displaced progressively for clarity of presentation. Absorption lines usually ascribed to $1s\rightarrow 3p_{\pm}$ transitions were very weak or absent.

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 $\sim 2\times10^{14}\ \mathrm{cm}^{-3}$. The oxygen concentration was $[\mathrm{O}_i]=1.0\times10^{18}\ \mathrm{cm}^{-3}$ and the carbon concentration was smaller than the detection limit of $3\times10^{15}\ \mathrm{cm}^{-3}$. 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 $\mathrm{H}_2(\mathrm{D}_2)$ 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 $0.25\ \mathrm{cm}^{-1}$ with the samples held at a temperature of ~ 10 K.

Infrared measurements indicate that the highest concentration of STD(N) centers are produced by anneals at $\sim 470\,^{\circ}\mathrm{C}$. 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 $1s\rightarrow 3p_{\pm}$ 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

TABLE I. The IR absorption line positions of the main transitions at ~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.

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

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 $\mathrm{cm}^{-1}\,\mathrm{K}^{-1}$ [Fig. 2(a)], which is greater than the rate for STDs of 0.012–0.013 $\mathrm{cm}^{-1}\,\mathrm{K}^{-1}$ [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-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-type), the shifts in the frequencies of the STD(N) lines were *significantly* smaller (~0.04 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 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 (~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 ~2 cm in length and 1.4×1.4 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 (~10 K). Nevertheless, there is a correspondence

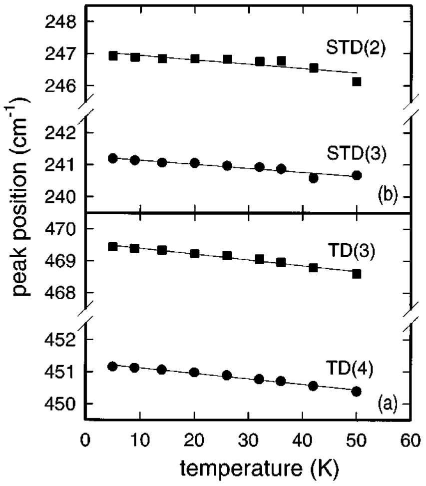

FIG. 2. The peak position of the absorption line corresponding to the transition $1s \rightarrow 2p_{\pm}$ of (a) TD(3), TD(4), and (b) STD(2), STD(3), as a function of sample temperature in the range 5–50 K.

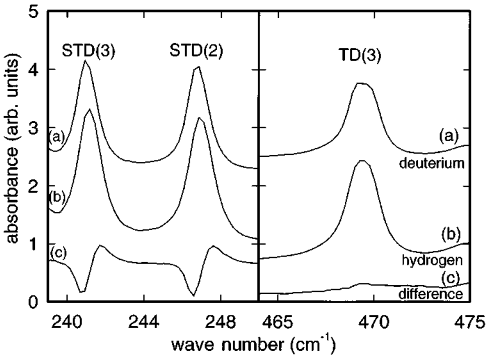

FIG. 3. $1s \rightarrow 2p_{\pm}$ transitions of the two strongest STDs: STD(2) and STD(3) (left) and TD(3) (right) in the spectra of a pair of n-type phosphorus doped samples which had been heated (a) in a deuterium plasma for 34 h, and (b) in hydrogen plasma for 17 h. After normalizing the strengths 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.

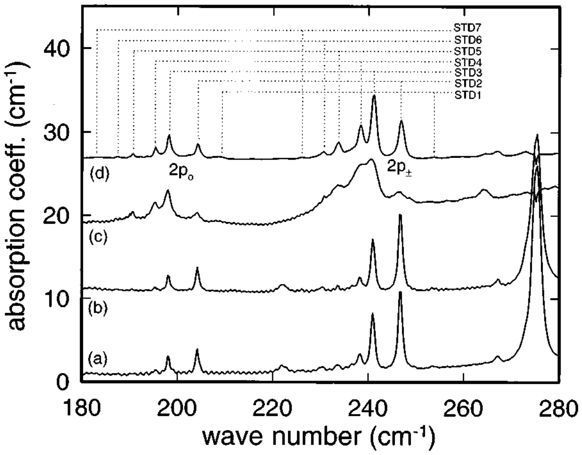

FIG. 4. The IR absorption spectra of samples pretreated in water vapor at 1250 °C and then annealed at 470 °C for (a) 20 h (P doped) (b) 30 h (P doped) and (c) 70 h (In doped). Spectrum (d) is for the B-doped sample annealed at 470 °C in a hydrogen plasma for 40 h (see Fig. 1). The strengths of the NL10 EPR spectrum were measured for samples (a), (b), and (c) (see text). Spectra have been displaced upwards for clarity. Lines at 275 and 222 cm^{-1} [(a) and (b)] are caused by phosphorus.

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 $1s\rightarrow 2p_{\pm}$ 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 3×10^{15} cm^{-3}, respectively. Using the IR calibration for the 315 cm^{-1} line ($1s\rightarrow 2p_{\pm}$) caused by phosphorus,[29] for which IA=1 cm^{-2} corresponds to [P]=1.01×10^{13} cm^{-3}, we obtain estimates of the STD(N) concentrations of 2.7, 2.5, and 5.3×10^{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 γ-ray irradiation[30]: 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 $\sim$0.1 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.

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