

Silicon incorporation in a shallow donor center in hydrogenated Czochralski-grown Si crystals: An EPR study

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An electron paramagnetic resonance (EPR) signal, labeled TU1, has been found in hydrogenated Czochralski-grown Si crystals after irradiation with fast electrons and annealing at 300–400 °C. An isotropic g factor of 1.9987 indicates the shallow donor nature of the defect giving rise to the signal. Unusual for shallow donor centers in silicon, well-resolved lines due to the hyperfine interaction of unpaired electrons with ^{29}Si nuclei are detected in the TU1 spectrum. The observed features are expected if a wave function of the unpaired electron is localized around a central Si atom of the defect. From a comparison of the EPR data with the results of optical and electrical measurements on identical crystals, it has been established that the TU1 signal is related to the shallow donor state of a hydrogen-oxygen-related center with negative- U properties.

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Hydrogen behavior in semiconductors has been studied extensively^{1,2} since hydrogen significantly influences the properties of semiconductor materials and devices. The most common effect of hydrogen is known to be the passivation of various electrically active dopants and defects. Beside the passivation, hydrogen is also the origin of formation of a number of electrically active centers. In crystalline silicon, such hydrogen-related defects have been observed both in Czochralski-grown (Cz) and float-zone-grown samples.^{1–5} Recently, by means of electrical (Hall effect, deep-level transient spectroscopy) and optical [Fourier transform (FT)-IR] measurements, we have found three hydrogen-related defects, labeled $D1$ – $D3$, in n -type Cz-Si crystals doped with hydrogen.^{6–9} These defects were observed in the Si:O,H crystals after irradiation with fast electrons and subsequent annealing at 300–500 °C. It was shown in Refs. 6, 7, and 9 that one of the defects, $D1$, has properties of a negative- U system, i.e., a system with inverted order of location of energy levels in the band gap. Some details of the electronic structure of the $D1$ defect were reported earlier.^{9,10} It should be pointed out here that only singly negatively and singly positively charged states of the center are stable under thermal equilibrium conditions. A neutral charge state is thermodynamically unstable. However, there is an energy barrier that prevents the transition from the metastable neutral state to the stable singly negatively charged state in n -type crystals at low temperatures (≤ 40 – 60 K). Hence, it is possible “to freeze” the center in the metastable neutral charge state and to study the properties of the defect in this state. For this “frozen” state we observed a series of infrared absorption bands related to electronic transitions from the ground $1s$ to various excited states.^{7,8} The transitions were characteristic for an effective-mass-like shallow donor in the neutral charge state.

From the study of the formation process of the $D1$ center, it has been inferred^{6,8} that hydrogen atoms and an oxygen-related radiation-induced defect, the A center (vacancy-oxygen)¹¹ or interstitial-carbon–interstitial-oxygen ($C_i\text{-}O_i$) complex,¹² form the core of the center. The micro-

scopic model of the $D1$ defect, however, is absent and the origin of its peculiar electronic properties is unclear.

Magnetic-resonance techniques are powerful tools for the identification of the microscopic structure of defects in semiconductors. To obtain further information about the structure of the $D1$ center, electron paramagnetic resonance (EPR) study of the defect was performed. An X-band spectrometer ($\nu_{\text{EPR}} \approx 9$ MHz), equipped with a continuous-flow-type liquid-helium cryostat, was used. Samples were prepared from an n -type phosphorus-doped Cz-Si crystal ($\rho \approx 1 \Omega \text{ cm}$). Concentration of oxygen in the crystal, determined by means of FT-IR absorption technique, was about $9.5 \times 10^{17} \text{ cm}^{-3}$. Carbon was under the detection limit of optical-absorption method ($\leq 1 \times 10^{16} \text{ cm}^{-3}$). Hydrogen (deuterium) was introduced into the samples by annealing in a H_2 (D_2) gas ambient at 1200 °C for 2 h, terminated by quenching.¹³ We will refer to these samples as hydrogenated (deuterated) ones in the following. Irradiation with fast electrons (3 MeV in energy, $5 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ in electron-beam intensity) was performed at room temperature. Fluence of irradiation was $1.6 \times 10^{16} \text{ cm}^{-2}$. Isochronal annealing was carried out in an argon atmosphere in temperature increments of 50 °C over the range 100–400 °C, for 30 min at each temperature. Before EPR measurements, the surface layer (about 100 μm) of the samples was removed by etching in a 1 HF+5 HNO_3 mixture. Final size of the samples was $3 \times 3 \times 15 \text{ mm}^3$, with the edges parallel to the $\langle 100 \rangle$, $\langle 011 \rangle$, and $\langle 011 \rangle$ directions.

We have not observed any features, which could be associated with the presence of hydrogen, in samples subjected to hydrogenation procedure only. EPR spectra for irradiated Si:O,H crystals will be reported elsewhere as well as the results of the study of annealing behavior of radiation-induced defects in such crystals.¹⁴

A characteristic feature of the irradiated Si:O,H samples is the appearance of an intense EPR signal with $S = \frac{1}{2}$ and nearly isotropic g factor of 1.9987 upon annealings at temperatures higher than 300 °C. As it will be seen later, there are some prominent properties of this signal, so we have labeled it as TU1.

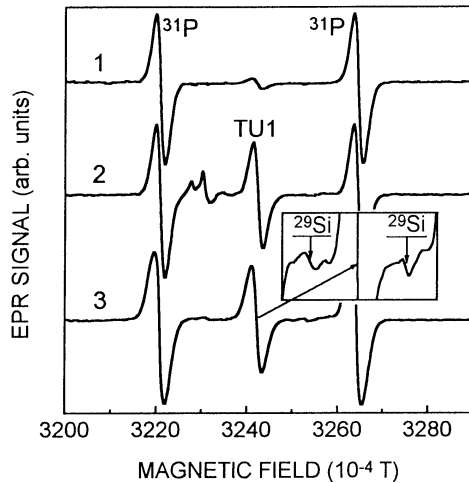


FIG. 1. EPR spectra of a hydrogenated Cz-Si sample, irradiated with fast electrons and annealed at 350 °C for 30 min. The spectra were measured at $T=10$ K for $\mathbf{B}||[011]$ ($\nu_{\text{EPR}}=9.07$ GHz, magnetic-field modulation amplitude was 0.2 G). Other details of the measurement procedure are described in the text. An inset shows the central part of spectrum 3 but recorded with higher amplitude gain.

Figure 1 shows EPR spectra for a hydrogenated sample after irradiation and annealing at 350 °C. All the spectra were recorded at 10 K under the following experimental conditions. When the sample has been cooled down to the measurement temperature in the dark and measured immediately (to minimize the effect of room-temperature irradiation from the walls of microwave cavity on the intensity of EPR signals), only a very weak line between two phosphorus-related lines is observed (spectrum 1). But an intense new line between two phosphorus-related ones has been developed under white-light illumination of the sample (spectrum 2). This line keeps the similar intensity when the illumination has been turned off (spectrum 3). The signal can be suppressed only by heating the sample up to 50–60 K, followed by cooling to the measurement temperature in the dark. Such changes in the intensity of the line are fully consistent with those we have observed earlier for the electronic-transition-related bands due to the $D1$ center in FT-IR measurements.⁷ The comparison of the results of EPR and FT-IR measurements indicates that the TU1 signal is related to the metastable shallow donor state of the $D1$ center. If the sample is cooled down to the measurement temperature in the dark, the center is transformed into the singly negatively charged stable state. Hence, both the electronic-transition-related bands in FT-IR spectra and the TU1 line in EPR spectra disappear. However, it is possible to induce the FT-IR bands and EPR signal by illumination of the sample at measurement temperature (6–10 K). The threshold of the photoionization was found to be about 0.40 eV.⁹ We have not observed the appearance of any new EPR signals in the spectra of the sample cooled down in the dark. Apparently, the electrons at the $(D1)^-$ state are paired, becoming non-paramagnetic. A weak EPR signal at $H \approx 323$ mT, in the spectrum recorded under illumination (Fig. 1, spectrum 2), is a fingerprint of the excited state of a radiation-induced defect.

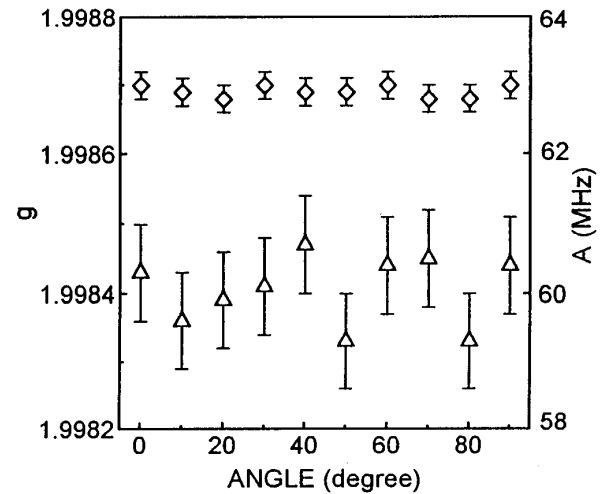


FIG. 2. Angular dependence of g factor (diamonds) and the value of hf interaction tensor A (triangles) for a hydrogenated Cz-Si sample, which was irradiated with fast electrons and annealed at 350 °C for 30 min. Rotation axis was $[0\bar{1}1]$, 0 angle corresponds to $\mathbf{B}||[100]$.

Well-resolved lines due to hyperfine (hf) interaction of the unpaired electron with ^{29}Si nuclei are observed for the TU1 signal. Two satellite lines around the central line are clearly seen in an inset in Fig. 1. The ratio of integrated area under these satellite lines to the total integrated area of all three lines is 0.043 ± 0.006 . This agrees well with the natural abundance of ^{29}Si atoms (4.7%) and indicates that the origin of satellite lines is the hf interaction of unpaired electron with ^{29}Si nuclei. The tensor of the hf interaction is isotropic as we will show later. Its value is estimated as 60.0 ± 0.7 MHz. It should be emphasized that the hf interactions with ^{29}Si nuclei are usually very small in EPR spectra for shallow donor centers in Si. Generally they are not resolved in EPR at all but are the origin of inhomogeneous line broadening.¹⁵

We have not found any changes in the EPR spectra of deuterated samples compared with those of hydrogenated ones. However, in accordance with the previous results,^{6–8} hydrogen atoms should be the constituents of the center. Probably hf interactions with hydrogen(deuterium) atoms are rather small and nonresolved in EPR spectra. A similar situation has been shown to take place for H-related NL10 EPR spectra in Si.^{4,16}

No splitting or visible shift of all the lines in the TU1 spectrum is detected upon the rotation of sample in the (110) plane with respect to the static magnetic field. Figure 2 shows the angular dependencies of the values of both the g and A tensors. Under the measurement conditions we have used, both values are constant in the frame of experimental error. This result indicates that the symmetry of the wave function of the unpaired electron of the TU1 center is close to T_d . The value of the g tensor is 1.99870 ± 0.00002 . This value is very close to that of electrons in the conduction band of Si ($g_{\text{ce}}=1.99875$). In accordance with the commonly used classification scheme of the defects in Si after their g values,¹⁵ the observed center should be identified as an effective-mass-like shallow donor. Again, this is fully consistent with the results of optical-absorption study of the $D1$

center.⁷ In an effective-mass approximation, the effective g value of an electron is obtained as an appropriate average over all the conduction-band minima.¹⁷ The isotropic g tensor for the TU1 signal indicates that the wave function of the unpaired electron of the center is probably constituted from all six conduction-band minima of Si.

From the value of the tensor of the hyperfine interaction for the TU1 center, the probability density of the unpaired electron $[|\psi(0)|^2]$ at the site of magnetic ^{29}Si nucleus has been estimated in accordance with the Fermi-Segre formula.¹⁸

$$A = \frac{8}{3} \pi \beta \beta_n g_n |\psi(0)|^2,$$

where β and β_n are the Bohr and nuclear magnetons and g_n is the nuclear g factor. $|\psi(0)|^2$ is found to be $0.46 \times 10^{24} \text{ cm}^{-3}$. This value is very close to that for phosphorus donor in silicon, $|\psi(0)|_{\text{P}}^2 = 0.44 \times 10^{24} \text{ cm}^{-3}$.¹⁷ This indicates that the character of distribution of the wave function of the unpaired electron at the ^{29}Si site for the TU1 center is similar to that at the substitutional phosphorus site in silicon.

The results obtained lead us to the conclusion that the wave function of the unpaired electron is localized around a central Si atom of the defect. Strong ^{29}Si -related hyperfine interaction should occur only when this central atom is a ^{29}Si isotope. Hence, it is possible to say that Si atom acts as a shallow donor in the considered case.

In accordance with theoretical calculations,^{19,20} $\text{C}_i\text{-H-2O}_i$ center can possess the shallow donor level. The level is dif-

fusively localized on the dangling bond of the central three-coordinated Si atom, which shares the lattice site with a carbon atom (split $\text{C}_i\text{-Si}_i$ configuration). The hydrogen atom is attached to the carbon atom and the structure is surrounded by two $\text{Si-O}_i\text{-Si}$ units in the (110) plane. The real symmetry of the center is C_{2v} . However, delocalization of the wave function of the unpaired electron (we should keep in mind that the center is a shallow donor) can result in misinterpretation of the real symmetry of the defect from EPR measurements. Formation of $\text{C}_i\text{-H-2O}_i$ centers on the basis of $\text{C}_i\text{-O}_i$ complexes is quite possible in our irradiated Si:O,H samples. Hence, $\text{C}_i\text{-H-2O}_i$ structure can be considered as the possible structure of the TU1 center, but at present we cannot exclude other possibilities. Following experimental efforts (electron-nuclear double resonance measurements) should be made to prove the presence of H, O, and C atoms in the defect.

Finally, an EPR signal (TU1) has been observed in hydrogenated (deuterated) Cz-Si crystals. The value of the g factor indicates the shallow donor nature of the defect responsible for the signal. Unusual for shallow donor centers in Si, well-resolved hyperfine interaction with ^{29}Si nuclei is detected in the TU1 spectrum. The observed features are expected if unpaired electrons giving rise to the TU1 signal originates from the central Si atom of the defect. From the comparison of the results of EPR, FT-IR, and electrical measurements on identical crystals, it is inferred that the discovered EPR signal is related to the shallow donor state of the D1 defect, which possesses negative- U properties.

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