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Optically detected magnetic resonance of a thermally induced deep center in electron-irradiated silicon

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We report the investigation of a thermally induced deep-level center (denoted as Si-*X*) in electron-irradiated silicon by optical detection of magnetic resonance (ODMR). This deep center was created after a heat treatment, at 400 °C for a time longer than 60 min, in irradiated boron-doped silicon single crystals by both Czochralski and float-zone techniques. The symmetry of the Si-*X* center is determined to be trigonal, and the identity of the center is discussed in terms of a Si-related interstitial complex. The energy level for this center is argued to be deep. This work shows that ODMR technique is capable of exploring strong nonradiative recombination channels in silicon, even when defects elude EPR detection due to their low concentrations, nonparamagnetic ground state, or short-lived excited states.

Electron paramagnetic resonance (EPR) of radiation-induced defects, such as lattice vacancies, self-interstitials, impurities, or their aggregates has been extensively studied for electron-irradiated silicon.[1,2] Optical detection of magnetic resonance (ODMR), with the advantage of a higher sensitivity and spectral selectivity as compared to EPR, has been proven to be very useful for studies of defects in both II-VI and III-V compounds.[3] Application of the ODMR techniques for studies of defects in silicon has been very limited so far,[4,5] however.

In this paper we report on ODMR investigation of a deep-level defect (denoted as Si-*X* below) in electron-irradiated silicon. A long heat-treatment time (longer than 1 h) at 400 °C is necessary for the creation of this center. The electronic structure and microscopic identity will be discussed, in relation to additional information gained from a study by deep-level transient spectroscopy (DLTS), and from EPR results reported previously.

A variety of silicon samples were used in this work, grown by float-zone (FZ) or Czochralski techniques, either *p*-type or *n*-type. The samples were irradiated with 2.0 MeV monoenergetic electrons to a total fluence of 1.0×10^{16} e^-/cm^2 at room temperature. Some of them were then sequentially annealed between 200 and 400 °C for 60 or 90 min. The samples studied in this work are listed in Table I, and are obtained from different steps of sample preparation. A description of the experimental setup can be found elsewhere.[6]

For the reference sample, prior to electron irradiation and heat treatment, only shallow boron-related bound-exciton (BE) recombination is seen near the band edge in the photoluminescence (PL) spectrum. Upon electron irradiation, the 0.97-eV luminescence (the *G* line)[7] appears and dominates over the near infrared (IR) spectral region. After 90-min heat treatment at 400 °C, the *G* line has significantly decreased in intensity, whereas a sharp line at 0.935 eV (denoted as the *T* line in the literature[8]) and a broad featureless PL band peaking at 0.8 eV become apparent, as can be seen in Fig. 1.

In Fig. 2 we show ODMR spectra of the Si-*X* center studied in this work, when the external magnetic field is oriented along the main crystallographic axes of the sample. These spectra were only observed in the *p*-type crystals with 90-min heat treatment at 400 °C (samples 4–6); no trace could be detected in other samples. Spectral studies showed that this ODMR signal arises from the 0.8-eV PL band.

The electronic structure of the Si-*X* defect can be simply understood as being in a paramagnetic state ($S=\frac{1}{2}$), as evidenced from the clear donorlike resonance signal. The symmetry of the defect is deduced to belong to point group C_{3v}, from a study of the angular dependence of the

TABLE I. List of samples used in this work.

Sample number	Growth technique	Type	Shallow doping (10^{14} cm^{-3})	e^- irradiation (10^{16} cm^{-2})	Annealing	Resistivity at 300 °C (Ω cm)	ODMR signal
1	FZ	*p*	$[B]\approx3.0$–3.5	0	0	100	no
2	FZ	*p*	$[B]\approx3.0$–3.5	1.0	0	100	no
3	FZ	*p*	$[B]\approx30$	1.0	400 °C/60 min	10	no
4	FZ	*p*	$[B]\approx3.0$–3.5	1.0	400 °C/90 min	100	strong
5	FZ	*p*	$[B]\approx30$	1.0	400 °C/90 min	10	strong
6	Czochralski	*p*	$[B]\approx30$	1.0	400 °C/90 min	10	weak
7	FZ	*n*	$[P]\approx30$	1.0	400 °C/90 min	10	no
8	FZ	*p*	$[B]\approx3.0$–3.5	1.0	200 °C/90 min	100	no

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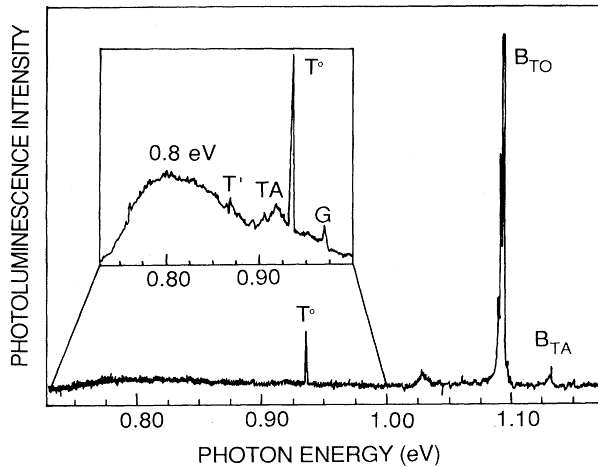

FIG. 1. PL spectrum for sample 4 at 2 K, with a spectral resolution of about 1 meV. Inset: Close-up of the 0.8-eV band is shown with a lower spectral resolution of about 3 meV. B_{TO} and B_{TA} denote the TO- and TA-phonon assisted BE recombination lines related to the shallow boron acceptor. T^0, T^1, and TA follow the notations used in Ref. 8 for the T line.

ODMR spectrum. An analysis of the ODMR spectra, by utilizing a simple spin Hamiltonian[9]

$$H_S = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_j \mathbf{I}_j \cdot \mathbf{A}_j \cdot \mathbf{S}, \quad (1)$$

yields the g factor of the defect: $g_\parallel = g_z = 1.990 \pm 0.001$, $g_\perp = g_x = g_y = 1.999 \pm 0.001$, where z denotes the trigonal axis $\langle 111 \rangle$. Here μ_B is the Bohr magneton. $\mathbf{S}$ ($S = \frac{1}{2}$) represents the effective electronic spin of the paramagnetic center. $\mathbf{g}$ denotes an effective g value, which is different from the free-electron value $g_e = 2.0023$, and will generally be anisotropic given by a tensor induced by spin-orbital interactions.[9] $\mathbf{I}_j$ is the nuclear spin of the defect atom or ligand atoms, and $\mathbf{A}_j$ the hyperfine (HF) interaction tensor.

Though no HF structure could be clearly resolved in the ODMR spectra, appreciable HF interactions are indicated by the side wings of the main ODMR peaks. To reveal quantitatively the possible HF structure, we have carried out a computer-aided deconvolution of the ODMR spectra by subtracting the main electronic transition lines (assuming a Gaussian line shape).[10] The resulting spectra show solely the HF satellites, which originate from a nuclear spin $I = \frac{1}{2}$ with an intensity about 5% of the main ODMR peak, as shown in the lower part of Fig. 2. The only candidate which can account for this observation is then obviously the ^{29}Si isotope ($I = \frac{1}{2}$ with 4.7% natural abundance). The A tensor is nearly isotropic within the experimental errors, with $A = (37 \pm 3) \times 10^{-4}\ \mathrm{cm}^{-1}$.

Although rich spectral information can be gained from an ODMR spectrum, its interpretation is by no means straightforward. It is often complicated by various indirect processes such as energy transfer,[5,11,12] competing recombination process or spin-dependent carrier capture.[3,13] This is particularly true for silicon, where all ODMR signals obtained so far have arisen from indirect processes.[4,5] It is noticed in the present case that despite the fact that the 0.8-eV PL band appears in the same intensity for both samples 3 and 4, the ODMR signal is only observed for sample 4. This observation, together with the negative sign of the ODMR signal (decrease in intensity of the 0.8-eV PL band under magnetic resonance conditions), strongly suggest that the luminescent center giving rise to the 0.8-eV PL band is *not* the same as the Si-X center (where the ODMR actually occurs).

Many mechanisms may be responsible for the present experimental observations, as shown in Figs. 3(a)–3(d).[14] Figure 3(a) shows a competition process between the 0.8-eV center and the Si-X center in the capture of the photoexcited free carriers. Figure 3(b) shows a recombination between the Si-X center and the G state of the 0.8-eV center (or capture of a bound hole by the Si-X center), which competes the recombination between the E and the G state.[14] A spin-dependent carrier capture model is shown in Fig. 3(c). In general, all of these three models belong to recombination competition processes, competing with the 0.8-eV recombination. The microwave-induced

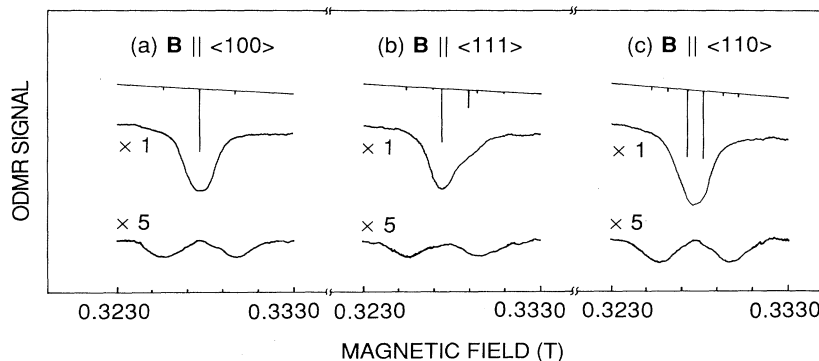

FIG. 2. ODMR spectra of the Si-X center from sample 4 at 4 K and 9.16 GHz, when (a) $\mathbf{B} \parallel \langle 100 \rangle$; (b) $\mathbf{B} \parallel \langle 111 \rangle$; (c) $\mathbf{B} \parallel \langle 110 \rangle$. The curves correspond to the as-obtained experimental spectra or these after subtracting the main transition lines in the upper or lower part of the figure, respectively. The latter cases show solely the HF satellite from the ^{29}Si isotope. Stick diagrams are also shown in the figure, both for the main ODMR lines and for the ^{29}Si HF structure, as a guide for the eye. The overall slope for the ODMR spectra is induced by the Drude-type heating of the free carriers.

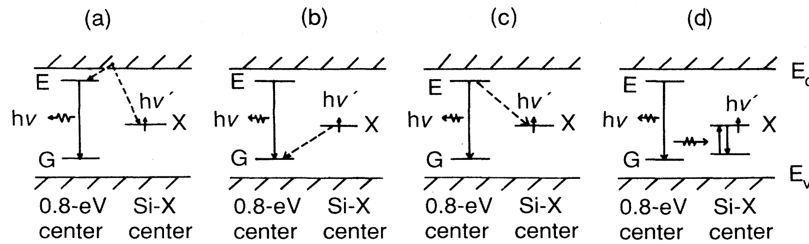

FIG. 3. Possible spin-dependent recombination processes: (a) competition in free-carrier capture; (b) recombination competition (or capture of a bound hole); (c) capture of a bound electron; (d) excitation energy transfer. E, G, and X are defined in Ref. 14. $h\nu$ denotes the emitting photon energy, and $h\nu'$ the energy of the microwave radiation.

enhancement in this competition results in a decrease in the 0.8-eV PL emission. Figure 3(d) illustrates a possible excitation energy transfer from the 0.8-eV center to the Si-X center. A decrease in intensity of the 0.8-eV center then corresponds to either a spin-dependent transfer process, or a spin-dependent recombination of the Si-X center, where the microwave-induced enhancement in the transition of the Si-X center to its ground state provides more "energy acceptors" for the 0.8-eV center. Figure 3 is drawn in such a way that it is more appropriate if the Si-X center is assumed to be an electron trap. A similar discussion holds when a hole trap is assumed.

The models discussed above for the recombination processes, except for the first one, demand a substantial overlap of the wave functions between the 0.8-eV center and the Si-X center which makes the intercenter interaction feasible. The separation between these defects is estimated to be large, however, e.g., about 10^3 lattice sites if a moderate concentration ($\approx 10^{14}$ cm^{-3}) for the defects is assumed. We believe therefore that the first model is most likely. This indirect process we suggest is common in silicon, supported by many experimental ODMR spectra from this material recently obtained in our laboratory.

The strong ODMR signal observed for the Si-X center indicates that this center provides either a strong nonradiative recombination channel in this material or an efficient radiative recombination channel but beyond the spectral range of the Ge detector. The reason why this center has not been observed in EPR is believed to be related to a rather short lifetime for the paramagnetic charge state (where the ODMR occurs) and/or to a low concentration of the Si-X center, given the low irradiation dose employed, which is beyond the sensitivity of EPR. Moreover, the Si-X center may not be paramagnetic in its accessible states in thermal equilibrium, in which case EPR is not applicable.

Although the origin of the previously unreported 0.8-eV PL band is still not clear, a donor-acceptor pair (DAP) recombination can probably be ruled out. This is evidenced from the fact that no shift in the 0.8-eV PL band peak position has been observed with varying the laser power by more than one order, which would otherwise be expected for a DAP recombination. Further confirmation is given by a DLTS study which reveals no donor and acceptor levels in the gap that can correlate with the 0.8-eV PL band. This is consistent with the common observation that DAP transitions are less efficient in this type of material, due to the existence of other much more efficient recombination channels. An internal transition of a deep-level defect is one candidate, where a transition of an electron bound at the defect from its orbitally excited state to the ground state gives rise to the featureless 0.8-eV PL band. A BE recombination at a defect is another candidate where the absence of any feature for the 0.8-eV PL band could be due to strong coupling with the lattice.

For low-energy electron bombardment it is known that the primary damage products include interstitial silicon atoms (Si_i). Earlier studies of electron irradiated p-type silicon have concluded that interstitial silicon atoms, once produced by e^- irradiation, are unstable, migrating even at low temperatures ($\approx$4.2 K) until trapped by impurities such as substitutional boron atoms,[15] or oxygen and carbon at somewhat higher temperature ($\approx$100 K).[16,17] This is clearly demonstrated by the production of the C_s-Si_i-C_s complex,[4] which gives rise to the G line dominating in the PL spectrum. Other Si_i complexes which are stable up to $\approx$500 °C are in fact present upon annealing at about 200 °C in irradiated boron-doped silicon, such as a ⟨100⟩-Si di-interstitial or a ⟨100⟩-Si split di-interstitial.[18,19] The Si-X center studied in this work is different from any of these centers reported previously by EPR, however.

The Si-X center belongs in a similar way to a secondary irradiation damage defect, produced after a subsequent heat treatment at 400 °C for 90 min. In view of the nearly isotropic HF interaction from a single ^{29}Si atom, we feel that the Si atom is situated near the center of the defect rather than being a special nearby lattice atom. The latter case often gives rise to a profound anisotropy in the HF interaction since the spin density is not centered at this lattice atom. In order to obtain more information on the localization of the electron wave function, we have done an analysis of the HF interaction observed for the ^{29}Si isotope with the aid of a simple one-electron linear-combination-of-atomic-orbitals (LCAO) method.[20] In this method the wave function for the unpaired electron is assumed to be constructed as a LCAO centered on the atoms near the defect, i.e., $\Psi = \sum_j \eta_j \psi_j$. At each site j, ψ_j can be constructed as a hybrid ns-np orbital as $\psi_j = \alpha_j(\psi_{ns})_j + \beta_j(\psi_{np})_j$, where $n = 3$ for Si atom. From the knowledge on the localization of electron wave function at a neutral atom calculated by the Hartree wave function,[20] we estimate that only less than 20% of the total wave function is localized within the nearest neighbors, i.e.,

$\sum_j \eta_j^2 < 20\%$ (where j sums over the nearest-neighbor sites). This excludes the possibility of the Si-X center as a vacancy-associated defect, since previous studies revealed that such a defect has a very localized wave function (about 60% of the wave function on the nearest neighbors). In contrast, the Si-X center belongs well to the class of interstitial-associated defects, of which the wave functions are considerably more delocalized.[19] The same conclusion for the Si-X center as an interstitial-related defect can also be drawn from the classification of defects in silicon after their g values.[21]

The necessity for the presence of the boron impurities in the creation of the Si-X center, as given in Table I, indicates that either the boron is directly incorporated in the center or it only enhances the formation of the complex without being a defect constituent. A definite distinction between these cases is, however, not possible at the present stage due to the lack of resolved HF structure from the boron atoms. The involvement of carbon as part of the Si-X center could not be determined, due to the absence of HF structure related to ^{13}C with nonzero nuclear spin $I=\frac{1}{2}$ (only 1.1% naturally abundant). The involvement of oxygen in the Si-X center can, however, be ruled out. This is based on the experimental findings that the ODMR signal actually becomes weaker when the oxygen concentration is increased by about two orders from the FZ-grown to the Czochralski-grown material. Definite identification of the Si-X center requires future study on ^{13}C-rich material, and in addition the aid of optically detected electron-nuclear-double-resonance technique.

Separate DLTS studies of the samples show no strong carrier traps that could be correlated with the center studied here, within the limits of the experimental conditions.[22] This indicates that the electronic level associated with the paramagnetic state of the Si-X center is at a depth ≥ 0.6 eV from the conduction- or valence-band edge depending on whether the state is, respectively, an electron or a hole trap.

In summary, we have presented an ODMR investigation of a new thermally induced deep-level center (the Si-X center) in electron-irradiated silicon doped with boron. A paramagnetic charge state ($S=\frac{1}{2}$) of the defect, which has its energy level deep in the forbidden energy gap, is identified to give rise to the observed ODMR signal. The symmetry of the Si-X defect is determined to be C_{3v}. An interstitial-related complex is suggested as a model for the defect identity, where the involvement of a silicon is implied by a detailed analysis of the ODMR line shapes. This study and similar future work may contribute to a better understanding of fundamental native defects as well as of radiation damage in silicon.

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[14] In Fig. 3, generally E denotes the excited state, and G the ground state of the 0.8-eV center. X represents the paramagnetic charge state of the Si-X center, which gives rise to the ODMR. The PL center in the figure responsible for the 0.8-eV PL band is only a simple notation, which does not necessarily mean to be a single center. A donor-acceptor pair recombination, for an example, involves two centers where E denotes the donor state while G the acceptor state.

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