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Intrinsic defects in high-purity SiC

E. Janzén [a,*], N.T. Son [a], B. Magnusson [a,b], A. Ellison [b]

[a] Department of Physics, Chemistry and Biology, Linköpings Universitet, SE-581 83 Linköping, Sweden
[b] Norstel AB, P.O. Box 15002, SE-580 15 Linköping, Sweden

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Abstract

Intrinsic defects are of importance for different applications of SiC such as: the semi-insulating (SI) properties of SI substrates, the carrier lifetime of high-voltage, bipolar power devices and the colour of gemstones (Moissanites). In order to tailor the properties of the material, we need to understand the properties of the intrinsic defects, their energy positions in the bandgap, their ability to capture carriers from the bands, their formation and annealing as well as their interplay with other defects.

High-purity SiC materials (doping less than 10^{16} cm^{-3}) grown by high temperature chemical vapour deposition (HTCVD), physical vapour transport (PVT) and chemical vapour deposition (CVD) have been investigated by electron paramagnetic resonance (EPR), photoluminescence (PL), absorption and electrical techniques. Vacancies (V_C^+, V_{Si}^0), divacancies and antisite-related defects are found to be common. The present knowledge of intrinsic defects in SiC based on both experiments and on calculations will be presented as well as their influence on mainly the semi-insulating properties.

Keywords: SiC; Intrinsic defect; Semi-insulating

1. Introduction

Due to the large bandgap of SiC, intrinsic defects often have their ground states and in many cases also excited states within the bandgap and can be electrically and/or optically active. Among these, many are deep levels, which may act as efficient recombination centers and have a strong influence on the carrier lifetime in the material. Depending on their charge states, they can also be carrier traps, which can be used for compensating shallow dopants in order to create semi-insulating (SI) material. In recent years, high-purity semi-insulating (HPSI) SiC substrates grown by high-temperature chemical vapour deposition (HTCVD) and physical vapour transport (PVT) have become commercially available. In HPSI substrates grown by HTCVD and PVT, intrinsic defects have been suggested to be responsible for the SI-properties. There are several different activation energies as determined from the temperature dependence of the resistivity: $E_a \sim 0.85$ eV and $\sim$1.4 eV in HTCVD substrates [1], and $E_a \sim 1.19$, 1.33 and 1.53 eV in PVT material [2]. Different defects have been observed by electron paramagnetic resonance (EPR) and suggested to play an important role in carrier compensation processes [3–6]. Among these the carbon vacancy in the positive charge state [7–9], V_C^+, and the silicon vacancy in the neutral charge state [10], V_{Si}^0, have been identified. The origin of other defects remains unclear.

In this work, we used photoluminescence (PL) and EPR to study defects in HPSI 4H-SiC substrates. New data on vacancies and other important defects, such the SI-5 [6] and P6/P7 centers [4–6,11], are presented and the compensation mechanisms that shall be responsible for different activation energies in HPSI substrates are discussed.

2. Defects in HPSI 4H-SiC substrates

Samples used in this study are high-purity, 4H-SiC HPSI substrates grown by HTCVD and PVT. Typical concentrations of residual impurities, such as nitrogen (N),

* Corresponding author. Fax: +46 13 142337.
E-mail address: erj@ifm.liu.se (E. Janzén).

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boron (B), aluminium (Al), and transition metals are given in Refs. [1,2]. Substrates grown recently by HTCVD and PVT are even purer with the considerably lower concentration of the shallow N donors [12,13]. The secondary ion mass spectroscopy (SIMS) measurements show an average N concentration $\sim 4 \times 10^{15}$ cm^{-3} in HTCVD-grown HPSI wafers, with min value below 1×10^{15} cm^{-3}, while the B concentration is typically around 10^{15} cm^{-3}. Fig. 1 shows a near-band-edge photoluminescence (PL) spectrum in a HPSI 4H-SiC substrate grown by HTCVD with the presence of the free exciton recombination which can be fitted to lower N concentrations (~ 2–5×10^{14} cm^{-3} depending on spots) than that determined by SIMS (~ 1–3×10^{15} cm^{-3} from the edge to the center of the wafer). The result obtained from PL fitting should be taken with precaution since the PL model and calibration are made from uncompensated material.

Defects in HPSI substrates were studied by electron paramagnetic resonance (EPR) at X-band (~9.47 GHz) and W-band (~95 GHz) frequencies. Fig. 2(a) shows the EPR spectrum of the SI-1 center [6] measured in complete darkness in HPSI substrates with an activation energy in the range $E_a \sim 0.6$–0.8 eV. The SI-1 spectrum consists of only one broad and isotropic line with a g-value of 2.0026. In some substrates, the SI-2 spectrum [6], was detected (Fig. 2(b)). A set of hyperfine (HF) lines was also detected for some angles of the magnetic field **B**, but they were too weak to be identified. In some other HPSI substrates, the EPR signals of the SI-3 and SI-4 centers [6] were observed (Fig. 2(c)). The SI-1 signal is very thermally stable. The unusual broad line width of the signal and its annealing behaviour suggest that the signal may be related to the extended defect like vacancy-related clusters. Indeed, in the positron annihilation spectroscopy (PAS) experiments performed in similar samples [14], the positron lifetimes corresponding to vacancy clusters of sizes from 4 to 8 atoms (2–4 Si–C molecules removed) were detected.

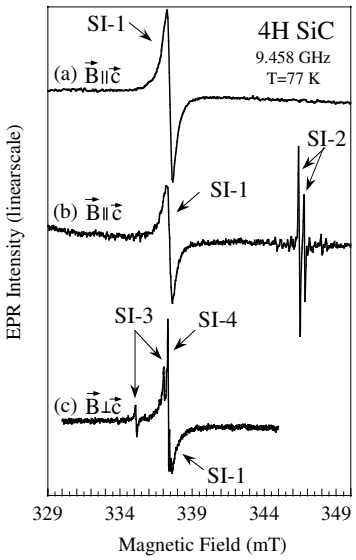

Fig. 2. Typical EPR spectra observed in HPSI 4H-SiC.

Recent ab initio calculations [15] suggested that the isotropic SI-1 and strongly anisotropic SI-2 centers may be related to the metastable configurations $V_C C_{Si} V_C^+$ of the divacancy. Such defects could be formed when the V_{Si} component of the divacancy transformed into the carbon vacancy–carbon antisite pair, $V_C C_{Si}$. However, the SI-2 center was detected only in certain set of samples and their hyperfine structures can not be explained by the interaction with any number of neither ^{29}Si nor ^{13}C nuclei. We therefore believe that the SI-1 and SI-2 centers are not related to each other and the latter is likely related to impurity.

EPR measurements, performed under illumination with either near-infrared or visible light show in this kind of HPSI substrates, strong signals of the SI-5 center [6] and the T_{V2a} center, which was assigned to V_{Si}^0 [10] (Fig. 3) were also detected. As can be seen in the figure, in addition to these defects, weak signals of V_C^+ [7–9] and the SI-6 [6]

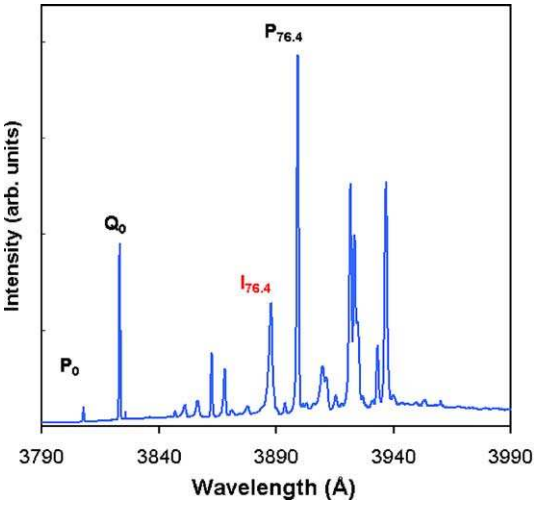

Fig. 1. Near band edge PL spectrum in HPSI 4H-SiC showing strong emissions of N-bound excitons and free-excitons.

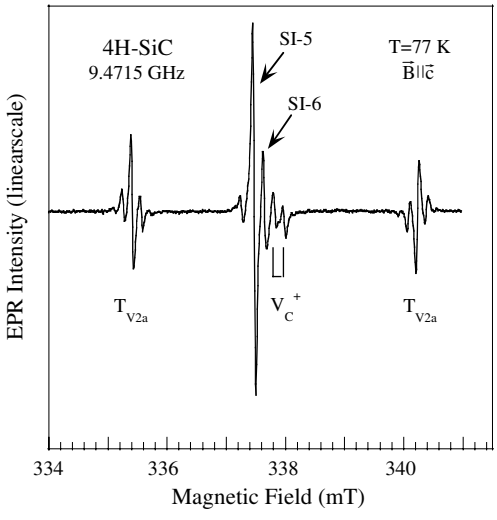

Fig. 3. EPR spectra in HPSI 4H-SiC measured under illumination with light of wavelength $\lambda \geqslant 840$ nm.

center were also observed. The SI-5 and SI-6 signals appear to be stronger in the samples with the Fermi level located in the upper half of the bandgap or in the slightly n-type samples. The photo-excitation EPR (photo-EPR) experiments were performed at W-band frequency in a PVT sample with the concentration of N donor in the low $10^{16}\,cm^{-3}$ ranges. The spectra observed under illumination with light of different photon energies are shown in Fig. 4. The spectral dependence of the intensities of these signals is shown in the inset of Fig. 4. In this PVT sample, the SI-5 signal appears when the photon energy reaches ~1.75 eV, whereas in slightly n-type material grown with different processes for research purposes its observation requires illumination with light of lower photon energies. This indicates that the SI-5 level locates in the upper half of the bandgap. As can be seen in the inset of Fig. 4, the intensities of SI-5 and B centers increase similarly in the range 1.75–3.0 eV. It indicates that the energy threshold of 1.75 eV may correspond to the transition which pumps electrons from the shallow B acceptor level (0.27 eV above the valence band (VB) maximum E_V) as determined from our experiments and from [16] to SI-5 level, leading to the increase of both signals. If the optical excitation to SI-5 level involves the charge transfer via B, the SI-5 level may be located at $\sim E_V + 2.02$ eV or about 1.24 eV below the conduction band (CB) minimum E_C (with assuming that the Franck–Condon shift is negligible). It seems that the energy threshold 1.89 eV also corresponds to the transition from the shallow B. This places the SI-6 level at $\sim E_V + 2.16$ eV or at $\sim E_C - 1.1$ eV (most probably the SI-6 level is the same as the V_C^- level, see Section 3 below). The energy level of V_C^+ is at $\sim E_V + 1.47$ eV in agreement with the previous photo-EPR experiments in irradiated 4H-SiC [17].

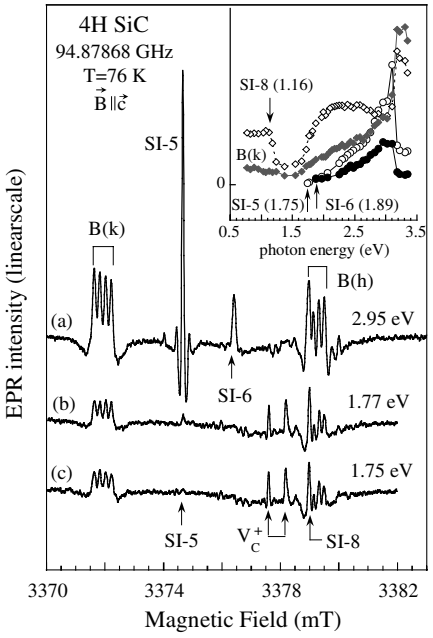

Fig. 4. EPR spectra in HPSI 4H-SiC measured under light illumination. The spectral dependencies of some EPR signals are shown in the inset.

In our previous study [6], we tentatively assigned the SI-5 center to the divacancy in the negative charge state, $V_{Si}V_C^-$, based on the observed hyperfine interactions with neighbouring atoms. Recent calculations [15] also support the divacancy model for the SI-5 center. However, our new experiments show that at temperature below 40 K the SI-5 center lowers its symmetry from C_{3v} to C_{1h} and the hyperfine structure changes dramatically. The new observation does not support the divacancy model. The SI-5 center is probably a complex involving a carbon vacancy in the negative charge state.

In the HTCVD and PVT samples with the activation energy about 1.4–1.5 eV, a strong EPR signal of V_C^+ was always detected in dark. Under light illumination, the P6/P7 [4–6,11] spectra were also observed together with the V_C^+ signal as can be seen in Fig. 5. Using the on-axis samples, the misorientation could be reduced and we obtained more accurate fine structure parameters D and E for the P6/P7 centers as compared to our previous data [6]. We relabelled the spectra in accordance with the recent data obtained for the P6/P7 centers in 6H-SiC [18]. All the P6/P7 centers have an isotropic g-value of 2.003. The D-value of the P6b and P6'b centers is 447 and 436 (in the unit of $10^{-4}\,cm^{-1}$), respectively. For the P7′b center, $D = 447 \times 10^{-4}\,cm^{-1}$ and $E = 10 \times 10^{-4}\,cm^{-1}$. Recent EPR studies of irradiated n-type 4H-SiC [19] show that the P6/P7 centers can be detected in complete dark in the whole temperature range 8–293 K. The hyperfine coupling constants of Si and C neighbours obtained by EPR [19] are in good agreement with the calculated values [20] for the neutral divacancy, $V_CV_{Si}^0$, suggesting that the P6/P7 centers, which were previously assigned to the photo-excited triplet states of the carbon vacancy–antisite pairs in the double positive charge state ($V_CC_{Si}^{2+}$) [21], are related to the triplet ground states of the C_{3v}/C_{1h} configurations of $V_CV_{Si}^0$.

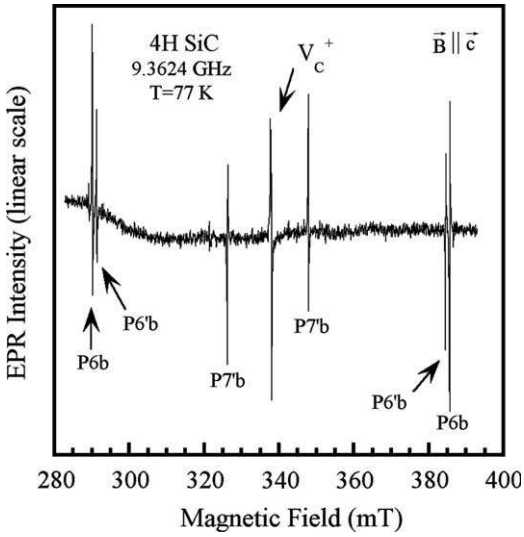

Fig. 5. EPR spectra of the V_C^+ and P6/P7 centers in HPSI 4H-SiC measured under illumination with light of wavelength $\lambda \geqslant 840$ nm.

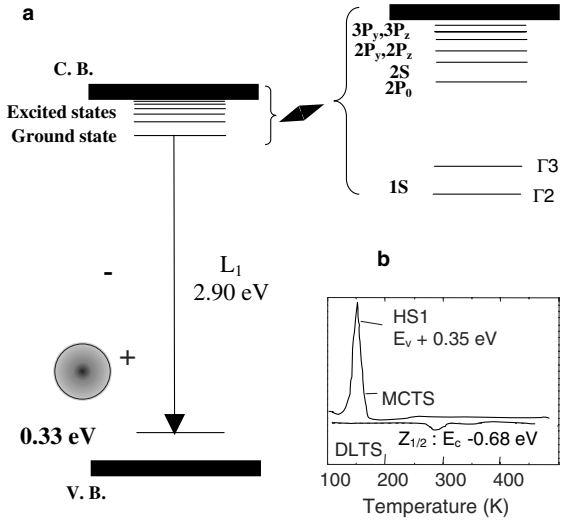

Fig. 6. (a) Schematic representation of the recombination for a pseudodonor isoelectronic center applied for the D_I-bound excitons in 4H-SiC. (b) DLTS and MCTS spectra showing the presence of the hole trap HS1 associated to the D_I center.

In HTCVD and PVT samples, strong PL signal of the D_I center is frequently detected. This center is known to be very thermally stable. The data obtained from PL and photoluminescence excitation (PLE) for the D_I center can be well explained by the pseudodonor model. The energy level scheme of the pseudodonor model for D_I is illustrated in Fig. 6(a). This model predicts that the D_I defect should have a ground state level, acting as a hole trap. By adding the energy of the series limits A to the recombination energy (2901 meV), the ground state of the pseudodonor can be estimated to be located at about 0.33 eV above the valence band ($E_V + 33$ eV) [22]. Using minority carrier transient spectroscopy (MCTS) Storasta et al. [23] have observed a hole trap lying at $\sim E_V + 0.35$ eV, labelled HS1, in 4H-SiC samples containing strong PL signals of the D_I center (see Fig. 6(b)). In theoretical calculations by Gali et al. [24], the model of antisite pairs, $Si_C C_{Si}$, is proposed to explain the electronic structure of the D_I center. In 4H-SiC, the calculated highest one electron defect level is found to be at $E_V + 0.38$ eV, which is very close to the HS1 level or the hole trap level predicted by the pseudodonor model. In recent calculations [18], the detailed phonon spectrum of the D_I luminescence could be well explained by the model of antisite complexes, $Si_C(C_{Si})_2$. The model also predicted a (+/0) level locating less than 0.4 eV above the valence band.

3. The role of important intrinsic defects in HPSI 4H-SiC substrates

After high temperature annealing (up to 1600 °C) the V_C^+ and V_{Si}^0(T_{V2a} center) signals are considerably reduced, whereas the SI-1, SI-5 and P6 signals decrease only slightly. In our previous studies [6], we could not detect the P6/P7 centers after annealing at 1600 °C. We believe that the missing of the P6/P7 centers is due to difficulties in activating the neutral charge state of the divacancy for a certain range of the Fermi level in the samples. It is noticed that the P7 center is always more difficult to detect than the P6 signal.

The concentrations of the intrinsic defects are estimated to be in the low 10^{15} cm^{-3} ranges (except in annealed samples, where the concentration of SI1 can be an order of magnitude higher). The concentrations of the P6/P7 centers can be higher (the absolute concentrations are difficult to be estimated since the signals are strongly dependent on the excitation). The EPR studies by Carlos et al [4,5] also suggested that the P6/P7 centers are dominant defects which have the concentration comparable to that of the residual impurities. Our studies indicate that both the vacancies and their associated defects play an important role in carrier compensation processes. In V_{Si}-rich samples, the acceptor levels (0/–) of V_{Si} ($\sim E_V + 0.6$ eV [25]) and divacancies ($\sim E_V + 0.5$–0.9 eV [26]) together with the shallow B acceptor may be enough to over compensate the N donors to pin the Fermi level at less than 1 eV above the valence band. If the concentration of V_C is also relatively high, its donor level (+/0) may then compensate the acceptors to pin the Fermi level at $\sim E_V + 1.4$–1.5 eV. In the case of higher concentrations of N, the (–/– –) levels of V_{Si} ($\sim E_V + 1.6$ eV [25]) and divacancy ($\sim E_V + 1.76$–1.84 eV [26]), the (0/–) level of the SI-5 center ($\sim E_V + 2.02$ eV) and the (–/– –) level of V_C ($\sim E_C - 1.08$ eV [27]) may be also filled. Consequently, the Fermi level may be pinned at ~1.2–1.6 eV below the conduction band. It seems that in many samples the (–/– –) level of the SI-5 center is also filled (since light illumination with energy about 1 eV is required to activate the (0/–) state). Since the concentrations of intrinsic defects in HPSI substrates are relatively low (10^{15} cm^{-3} ranges), the concentration of the N is required to be below 10^{16} cm^{-3} range for achieving the stable SI properties.

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