Materials Science Forum Vols. 600-603 (2009) pp 409-412
online at http://www.scientific.net

Photo-EPR Study of Vacancy-type Defects in Irradiated *n*-type 4*H*-SiC

T. Umeda[1,a], N. Morishita[2,b], T. Ohshima[2,c], H. Itoh[2,d], and J. Isoya[1,e]

[1]Graduate School of Library, Information and Media Studies, University of Tsukuba, Tsukuba, 305-8550, Japan

[2]Japan Atomic Energy Agency, Takasaki, 370-1292, Japan

[a]umeda@slis.tsukuba.ac.jp, [b]morishita.norio@jaea.go.jp, [c]ohshima.takeshi20@jaea.go.jp, [d]itoh.hisayoshi@jaea.go.jp, [e]isoya@slis.tsukuba.ac.jp

Keywords: photo-EPR, energy level, carbon vacancy, silicon vacancy, divacancy, carbon antisite-vacancy pair, 4H-SiC.

Abstract. We report photo-induced electron paramagnetic resonance (photo-EPR) data for irradiated *n*-type 4*H*-SiC. Energy levels and associated photo-induced transitions are discussed for silicon vacancy (V_{Si}), carbon vacancy (V_{C}), carbon antisite-vacancy pair ($\mathrm{C_{Si}}V_{\mathrm{C}}$), and divacancy ($V_{\mathrm{Si}}V_{\mathrm{C}}$).

Introduction

In SiC, vacancy-type defects can be thermally stable and be abundant, having a significant influence on the properties of this material. So far, in 4*H*-SiC, combined studies of electron paramagnetic resonance (EPR) and first principles calculation have identified four fundamental types of such defects, V_{Si} [1,2], V_{C} [3,4], $\mathrm{C_{Si}}V_{\mathrm{C}}$ [5,6], and $V_{\mathrm{Si}}V_{\mathrm{C}}$ [7]. These defects play an important role in high-purity semi-insulating 4*H*-SiC [8]. Furthermore, they are believed to be linked to fundamental defect levels studied by other techniques such as photoluminescence (PL) and deep level transient spectroscopy. However, relationships between the defects and the defect levels are still unclear. The photo-EPR technique [4,5,8-10] is useful for revealing such relationships. Therefore, using this technique, we planed to study a series of irradiated 4*H*-SiC samples that included all or most of the above defects. In such samples, we can obtain photo-EPR data on coexisting defects simultaneously, and can compare one's photo response with others under the same condition, which expectedly give us a hint for unraveling a puzzle of the defect levels.

Photo-EPR experiments

Photo EPR setup is simply consisted of a Bruker Bio-Spin E500 X-band spectrometer and two compact monochromator units (Shimadzu Corp.) combined with a 150-W Xenon lamp. The two monochromators were operated with different sets of concave blazed holographic gratings. Combining them with a set of low-pass optical filters, we can sweep the photon energy from 0.5 to 5.6 eV. A photon energy resolution was estimated to be 0.03 eV or lower, which was primarily determined by an optical slit of a monochromator. The slit width was 1.00 mm and 0.50 mm for lower ($<$1.8 eV) and higher ($\geq$1.8 eV) energy ranges, respectively. The monochromatic light was illuminated to a sample through an optical fiber guide (transparent above approximately 0.5 eV). First, we measured dark EPR spectra after keeping a sample in the darkness for days, and then recorded the spectra for each photon energy (increment step = 0.05 eV) under a steady state after illumination.

Results and discussions

In this study, we present photo-EPR results for three irradiated *n*-type 4*H*-SiC samples, which we call *A*, *B*, and *C* hereafter. They were prepared by high-temperature electron irradiations (3 MeV, 1×10^{18}

e/cm[2]) to nitrogen-doped commercial substrates (room temperature carrier density = 10^{17} /cm[3]) at 350 ºC for *A*, 565 ºC for *B*, and 800 ºC for *C*. With lower temperatures (i.e., for the sample *A*), more V_{Si} defects (V_{Si}^- and T_{V2a}) but less $C_{Si}V_C$ defects (*SI*5) were produced after the irradiation. Figure 1 shows typical EPR spectra in the dark (thermal equilibrium) and under photo excitation.

In the dark, the *HEI*5/6 centers (electron spin $S = 1/2$, C_{1h} symmetry) [5] were commonly observed in the three samples as well as other *n*-type ones. Other centers (*HEI*1 [4], *HEI*2, *HEI*3, *SI*5 [5], etc.) also appeared with increasing the irradiation temperature. The *HEI*5/6 centers were very common and might be related to one of the known vacancy-type defects introduced above. They showed similar sets of four ^{29}Si hyperfine (HF) satellites, implying that they include Si nearest neighbors of V_C. For a conclusive identification, however, full analyses of HF tensors should be necessary. On the other hand, the *HEI*2 and *HEI*3 centers ($S = 1/2$) are believed to be complexes of intrinsic defects, because their formations were enhanced by higher temperatures and higher electron doses.

With photo excitation, the known vacancy-type defects such as V_{Si}^- [1], the T_{V2a} center (V_{Si}^-) [2], the *HEI*1 center (V_C^-) [4], the *EI*5 center (V_C^+) [3], the *SI*5 center ($C_{Si}V_C^-$) [5], and the *P*6/7 centers ($V_{Si}V_C^0$) [7] were strongly observed, as is seen in Fig. 1. The photo responses (EPR signal intensities versus photon energy) of these vacancy-type defects as well as *HEI*5/6 are plotted in Fig. 2. In all examined *n*-type samples, photo-induced changes started weakly at 0.80-0.85 eV and then dramatically at 1.00-1.10 eV. The latter “main” threshold will correspond to a primary transition that an electron is excited from a defect level at the Fermi level (E_F) to the conduction band edge (E_C). At such a threshold, many defects will change their charge states simultaneously. Therefore, we speculate that E_F positions in our samples are E_C – 1.0-1.1 eV. On the other hand, the weak threshold at 0.80-0.85 eV might correspond to photo-induced transitions via intermediate states (e.g., excited states of defects) at around E_C – 0.2 eV. A recent photo-EPR study also reported the presence of such intermediate transitions via energy levels at E_C – 0.2 eV [8]. The other defects, *HEI*2 and *HEI*3, were less sensitive to the photo excitation, and hence no data are shown in Fig. 2. Finally, the main threshold energies for each defect were determined as summarized in Table I. In below, we attempt to interpret the present results in comparison with previous experimental and theoretical studies.

V_{Si}: V_{Si}^- and T_{V2a} exhibited the almost same threshold at 1.05-1.10 eV (Table I). Since both centers are single negative charge states [2], the observed threshold will correspond to a transition from V_{Si}^{3-}

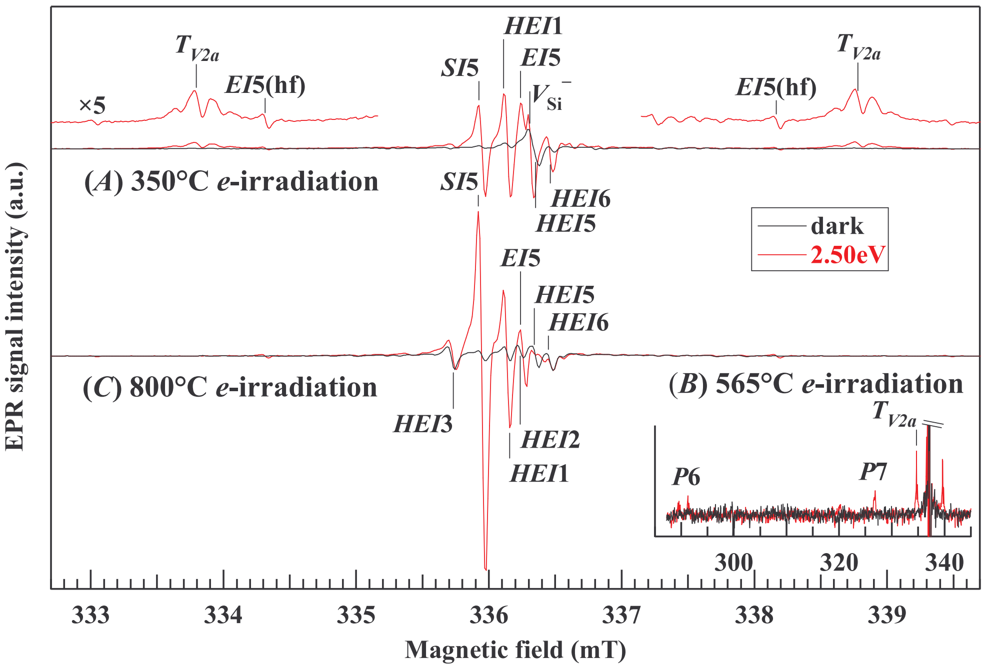

Fig. 1. EPR spectra of irradiated *n*-type 4*H*-SiC samples *A*, *B*, and *C* at 60 K (microwave of 9.428 GHz and 0.2 μW, field modulation of 100 kHz and 0.05-mT width, magnetic field // *c* axis). Assignments of the observed centers have been checked by angular dependence of EPR spectra.

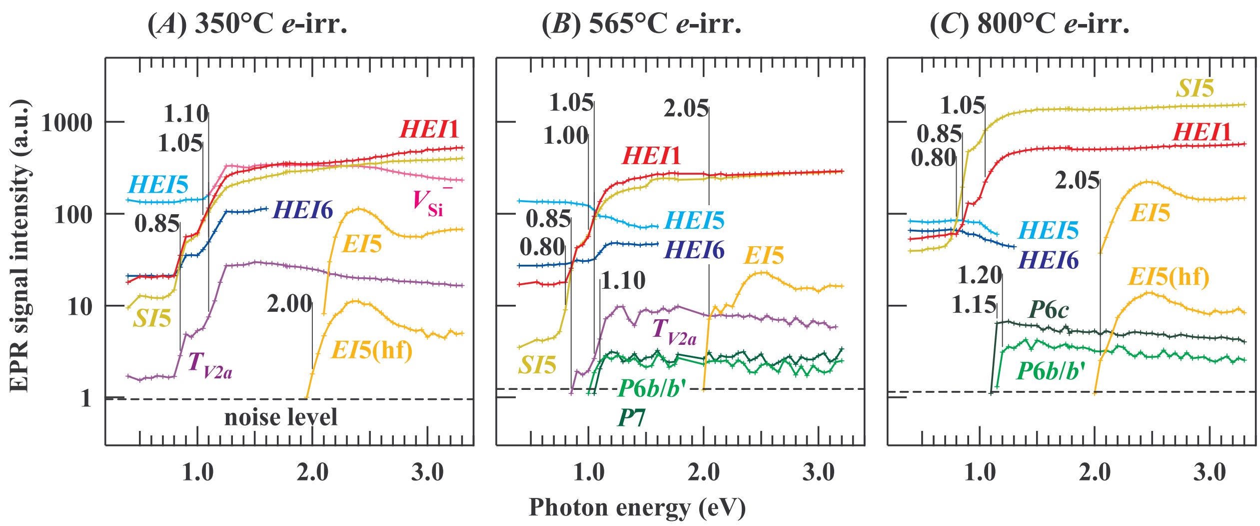

Fig. 2. Photo-EPR data on vacancy-type defects in irradiated n-type 4H-SiC samples A, B, and C at 60 K. First data point of each trace (below 0.5 eV) was measured in the dark. "(hf)" means hyperfine satellite lines.

or V_{Si}^{2-} to V_{Si}^{-}. Since both -3 and -2 charge states are paramagnetic (Table I), we should detect either state by EPR in the dark. Its detection is a future problem. Previously, first principles calculations predicted the ionization levels of V_{Si} at 0.84-0.92 eV for (-3/-2) and 1.50-1.55 eV for (-2/-1) below E_C [11]. The observed threshold energy (1.05-1.10 eV) seems to be enough for converting V_{Si}^{3-} into V_{Si}^{2-} but insufficient for V_{Si}^{2-} into V_{Si}^{-} by a single excitation. Namely, we need an intermediate level of V_{Si} between E_C and the (-2/-1) level which are separated by about 1.1 eV. The observed threshold energy will correspond to this intra-vacancy transition energy. On the other hand, V_{Si} exhibits two sharp $V1/V2$ PL lines (1.438 and 1.352 eV, respectively) owing to two discrete levels of V_{Si} (one level must belong to V_{Si}^{-}) in the band gap [12]. Probably, the photo-EPR data can be correlated with such levels, which also remains a future problem.

V_C: We could detect V_C^{-} from 1.00-1.05 eV and V_C^{+} from 2.00-2.05 eV. The first threshold (1.00-1.05 eV) is almost identical to our previous result (1.08 eV) [4], and we can conclude again that V_C^{2-} are stable when $E_F = E_C - 1.0\text{-}1.1$ eV. For V_C, theoretical calculations predicted the ionization levels at 1.15-1.21 eV for (-2/-1) and at 1.03 eV for (-1/0) below E_C [11] and a negative-U nature [11,13]. Our observation can be consistent with such negative-U model that V_C^{2-} is more stable than V_C^{-}. In other irradiated n-type samples we had prepared, V_C^{2-} were always majority, which is also reasonable supposing the negative-U model. For V_C^{+}, we obtained threshold energies of 2.00-2.05 eV, which are larger than previous results (1.8 eV) [4,9]. To account for this difference, we have to assume the presence of a structural relaxation at least larger than 0.2 eV.

$C_{Si}V_C$: The present data are identical to those of our photo-EPR work on a different n-type sample [5]. Likewise V_C, this defect is stabilized into $C_{Si}V_C^{2-}$ in the dark. We also found that $C_{Si}V_C^{2-}$ were always majority in other n-type samples. However, theories did not expect the negative-U behavior for $C_{Si}V_C^{2-}$ [5,11]. So, we alternatively propose that the (-2/-1) level of $C_{Si}V_C$ is accidentally very close to the (-2/-1) level of V_C, and then $C_{Si}V_C^{2-}$ could accompany V_C^{2-}. It should be also mentioned that no positive charge states ($C_{Si}V_C^{+}$, the *HEI*9/10 centers [6]) were detectable in a higher energy range, in spite of a careful optimization for the detection.

$V_{Si}V_C$: No $V_{Si}V_C^{0}$ signals were detectable in the dark, because $V_{Si}V_C^{2-}$ are most stable according to a theoretical prediction that the ionization level at $E_C - 1.42\text{-}1.50$ eV for (-2/-1) [14]. The observed threshold energies in B (1.05-1.10 eV) are insufficient for exciting an electron from $V_{Si}V_C^{2-}$ to E_C. Moreover, these energies are quite close to 1.10-1.14 eV of the sharp PL lines corresponding to $P6/7$ [10]. Thus, the observed thresholds will correspond to an intra-vacancy transition between lower and upper levels of $V_{Si}V_C$ in the band gap. The observed threshold in C (1.20 eV) is slightly larger, and we do not understand the reason yet.

defect	charge	electron spin (S)[a)]	EPR center	observed threshold energy (eV)			
				sample *A*	sample *B*	sample *C*	previous works
V_{Si}	-3	1/2	Not identified				
	-2	1	Not identified				
	-1	3/2	V_{Si}^{-} [1] T_{V2a} [2]	1.10 1.10	× 1.05	× ×	 1.09[b)] [12]
V_C	-2	0	–				
	-1	1/2	*HEI*1 [4]	1.05	1.00	1.05	1.08 [4]
	0	0	–				
	+1	1/2	*EI*5/6 [3]	2.00	2.05	2.05	1.80[c)] [9], 1.8 [4]
$C_{Si}V_C$	-2	0	–				
	-1	1/2	*SI*5 [5]	1.05	1.00	1.00	1.1 [5,8]
	0	0	–				
	+1	1/2	*HEI*9/10 [6]	×	×	×	~1.9[d)] [6]
$V_{Si}V_C$	-2	0	–				
	-1	1/2	Not identified				
	0	1	*P*6 [7] *P*7 [7]	× ×	1.05 1.10	1.20 ×	1.10[b)] [10] 1.11, 1.14[b)] [10]

Table I. Summary of photo-EPR study and comparison with previous works. a) cited from a theory [13] and experiments [1-7]. b) measured by both PL and EPR; c) measured with respect to valence band edge (E_V); d) deduced relative to V_C^+.

References

[1] T. Wimbauer, B. K. Meyer, A. Hofstaetter, A. Scharmann, H. Overhof, Phys. Rev. B Vol. 56 (1997), p.7384.

[2] N. Mizuochi, S. Yamasaki, H. Takizawa, N. Morishita, T. Ohshima, H. Itoh, T. Umeda, J. Isoya, Phys. Rev. B Vol. 72 (2005), p.235208.

[3] T. Umeda, J. Isoya, N. Morishita, T. Ohshima, T. Kamiya, A. Gali, P. Deák, N. T. Son, E. Janzén, Phys. Rev. B Vol. 70 (2004), p.235212.

[4] T. Umeda, Y. Ishitsuka, J. Isoya, N. T. Son, E. Janzén, N. Morishita, T. Ohshima, H. Itoh, A. Gali, Phys. Rev. B Vol. 71 (2005), p.193202.

[5] T. Umeda, N. T. Son, J. Isoya, E. Janzén, T. Ohshima, N. Morishita, H. Itoh, A. Gali, M. Bockstedte, Phys. Rev. Lett. Vol. 96 (2006), p.145501.

[6] T. Umeda, J. Isoya, T. Ohshima, N. Morishita, H. Itoh, A. Gali, Phys. Rev. B Vol. 75 (2007), p.245202.

[7] N. T. Son, P. Carlsson, J. ul Hassan, E. Janzén, T. Umeda, J. Isoya, A. Gali, M. Bockstedte, N. Morishita, T. Ohshima, H. Itoh, Phys. Rev. Lett. Vol. 96 (2006), p.055501.

[8] N. T. Son, P. Carlsson, J. ul Hassan, B. Magnusson, E. Janzén, Phys. Rev. B Vol. 75 (2007), p.155204.

[9] N. T. Son, B. Magnusson, E. Janzén, Appl. Phys. Lett. Vol. 81 (2002), p.3945.

[10] W. E. Carlos, E. R. Glaser, B. V. Shanabrook, Physica B Vol. 340-342 (2003), p.151.

[11] M. Bockstedte, A. Mattausch, O. Pankratov, Phys. Rev. B Vol. 68 (2003), p.205201.

[12] E. Sörman, N. T. Son, W. M. Chen, O. Kordina, C. Hallin, E. Janzén, Phys. Rev. B Vol. 61 (2000), p.2613.

[13] A. Zywietz, J. Furthmüller, F. Bechstedte, Phys. Rev. B Vol. 59, (1999), p.15166.

[14] L. Torpo, T. E. M. Staab, R. M. Nieminen, Phys. Rev. B Vol. 65 (2002), p.085202.