EPR and pulsed ENDOR study of EI6 and related defects in 4*H*-SiC

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Abstract. The EI5 and EI6 centers are typical intrinsic defects in radiation-damaged and semi-insulating SiC. So far, the origins of EI5 and EI6 have been identified as positively-charged carbon vacancies (V_C^+) and silicon antisites (Si_C^+), respectively. However, our complete set of ^{29}Si hyperfine (HF) data changes these identifications. Our EPR data clearly show that both centers can be well described by V_C^+ but their locations should be different (cubic sites for EI5 and hexagonal sites for EI6), as recently proposed by other groups. It was also found that both defects have similar high thermal stability over 1000 ºC. In addition to EI5 and EI6, we found a new thermally-stable center, labeled HEI1, in *n*-type radiation-damaged 4*H*-SiC.

Introduction

Electron or neutron irradiation to SiC has been widely studied to explore a variety of intrinsic defects (vacancies, antisites, etc.) in this material. These radiation experiments were performed at relatively low temperatures (4 K or room temperature ~ 450 ºC). From a technological point of view, defects that have high thermal stability are of crucial importance. Also, the origin of high thermal stability is of great interest to science. Therefore, we investigate thermally-stable defects in SiC by means of electron irradiation at a high temperature (850 ºC) and identify their atomic structures by using electron paramagnetic resonance (EPR). In our study, 4*H* polytype was selected because of its importance for electronic-device applications.

In our high-temperature radiation experiments, only selected (i.e., thermally-stable) defects were found in a specimen. There were at least three types of thermally-stable defects; EI5, EI6, and a new center (we label it “HEI1”). Although the identification of EI5 and EI6 had been published [1,2], more recent EPR experiment [3] and theoretical calculation [4] suggested an alternative model that both EI5 and EI6 are V_C^+ defects but they are located at cubic and hexagonal sites, respectively [4]. The conclusion has not been obtained yet, because of a lack of HF interaction data. Thus, we here report complete angular dependence of ^{29}Si HF interactions of EI5 and EI6. Then, we show that EI6 is well compatible with a hexagonal V_C^+ rather than a simple Si_C^+. In addition, EPR data of HEI1 are briefly reported.

Experimental

SiC substrates are commercial 4*H*-SiC(0001) wafers supplied by Nippon steel corporation. Dopant concentrations are 1×10^{15} and 1×10^{17} cm^{-3} for the *p*- and *n*-type wafers, respectively. Electron irradiation was performed with an electron energy of 3 MeV and a dose of 4×10^{18} cm^{-2}. During the irradiation, substrates were located in a high vacuum and were heated at a constant temperature of 850 ºC. Then, they were measured by X-band EPR and pulsed-EPR spectrometers (Bruker E500 and E580 systems, respectively). Pulsed-EPR was used to deconvolute HF structures by means of pulsed electron-nuclear-double-resonance (ENDOR) techniques.

Results and Discussions

EI5 and EI6 in *p*-type 4*H*-SiC. Figure 1(b) shows EPR spectrum of a *p*-type sample measured for **B** (magnetic field) || c. As is indicated in the figure, EPR spectrum consists mainly of central lines of EI5 and EI6, and many HF satellites (labeled *a* to *g*). Before starting the analyses of this spectrum, we should mention that EI5 (V_C^+) was stable over 1000 °C, although its anneal-out temperature was known to be much lower (450 ~ 600 °C [1,2,4]) than that of EI6 (> 1000 °C [1]). In our anneal study, both EI5 and EI6 were fully stable at 1000 °C, started to be annihilated at 1200 °C, and almost disappeared at 1500 °C. Thus, we have to change our mind with respect to the thermal stability of EI5.

Figure 1(a) shows an angular-dependence map when **B** was rotated from the c axis ([0001]) to the c-normal direction ([11$\bar{2}$0]). The HF satellites *a*, *b* and *c* were already reported by Son et al. [1,2].

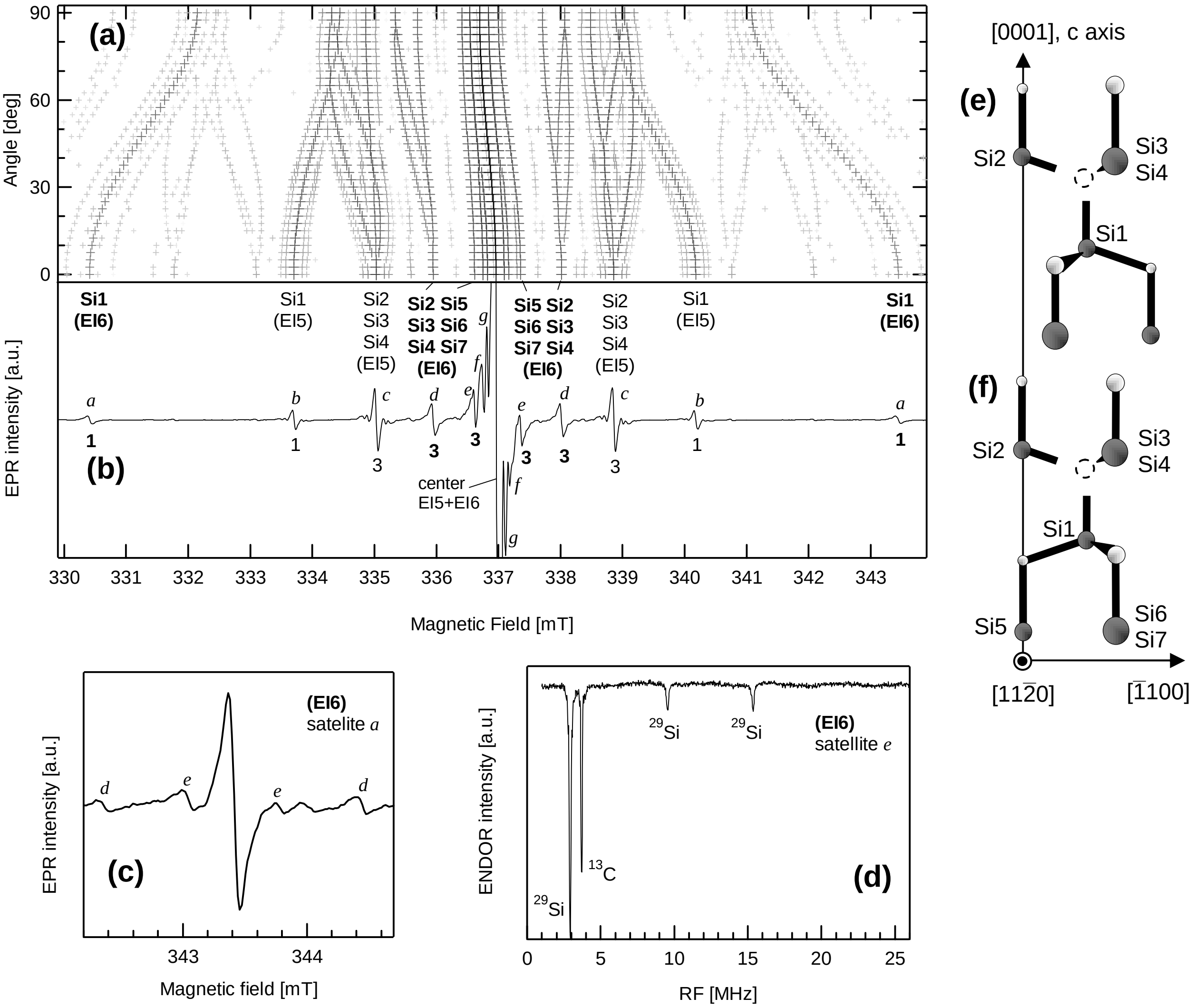

Fig. 1. EPR measuremts of electron-irradiated *p*-type 4*H*-SiC at 150 K. (a) Angular dependence for **B** rotation in the ($\bar{1}$100) plane. (b) EPR spectrum for **B** || c. For HF satellites, their relative intensities and origins are given. (c) High-field-side HF satellite *a* (EI6) shows weak HF satellites *d* and *e*. (d) Pulsed-ENDOR spectrum for satellite *e* (EI6) measured at 10 K, **B** || c. This spectrum ensures that satellite *e* originates from a ^{29}Si HF interaction. (e) Atomic models for EI5 (cubic carbon vacancy) and (f) for EI6 (hexagonal carbon vacancy).

According to the literatures, satellite *a* is a doublet ^{29}Si HF structure of EI6 [1], and satellites *b* and *c* are ^{29}Si HF structures of EI5 [2]. Also Son et al. [2] have shown that satellite *b* arises from a Si1 site of V_C [see Fig. 1(e)] and satellite *c* originates from Si2, Si3, and Si4 sites. Our angular-dependence data for EI5 were consistent with those of Son et al. Therefore, the identification of EI5 is unchanged, and in this paper, our analyses will be focused on the EI6 center.

For other HF satellites (*d* to *g*), their angular dependence has not been reported yet. Since the central lines of EI5 and EI6 completely overlapped each other, a simple judgment on the center position of HF satellites was meaningless. Thus, to classify HF satellites *d* to *g* into either EI5 or EI6, we measured weak HF structures of satellite *a* (EI6), as shown in Fig. 1(c). Satellite *a* clearly showed two HF satellites, and their splitting widths coincided exactly with those of *d* and *e*. We therefore concluded that satellites *d* and *e* originate from EI6. Also a similar analysis has been performed for satellite *c* (EI5). Then, it was found that satellites *f* and *g* belong to EI5.

Relative intensities of HF satellites are estimated in Fig. 1(b); for EI5, $b : c = 1 : 3$; for EI6, $a : d : e = 1 : 3 : 3$. These values were consistent with those revealed by the recent 240-GHz EPR study of Konovalov et al. [3]. These intensities give us an information about the number of ^{29}Si (natural abundance = 4.7 %) or ^{13}C (1.1%) atoms in a defect center. We already know that satellite *a* corresponds to a single ^{29}Si atom (namely, the fractional intensity of this satellite is close to 4.7 % of a total intensity of EI6) [1,3]. Therefore, satellites *d* and *e* should originate from three ^{29}Si atoms in the EI6 center. Furthermore, we carried out pulsed-EDNOR measurements on satellite *e*, and confirmed that this satellite is a ^{29}Si HF structure [Fig. 1(d)]. Consequently, all of satellites *a*, *d*, and *e* are assigned to ^{29}Si HF satellites.

In the next place, angular-dependence patterns are discussed. The angular pattern of satellite *d* (EI6) is very similar to that of *c* (EI5). This means that satellite *d* originates from Si2, Si3, and Si4 sites [Fig. 1(f)], as similarly to the case of EI5. We also found a close similarity of the patterns between satellites *a*, *e* (EI6) and *b* (EI5). These satellites commonly showed an axially-symmetric ^{29}Si HF interaction around the c axis. In the original model of a simple Si_C^+, the origins of satellites *a* and *e* were ascribed as a Si_C site and a Si1 site, respectively [1]. However, this assignment is incompatible with our and Konovalov's data that satellite *e* is related to three Si sites. To explain our results reasonably, a hexagonal V_C^+ model, proposed by a theoretical calculation [4], is quite appropriate. Namely, we consider that satellite *a* arises from a Si1 site and satellite *e* does from Si5, Si6, and Si7 sites. The theoretical calculation predicted that ^{29}Si HF interactions of Si_C^+ are much smaller than the observed HF interactions, but those of hexagonal V_C^+ are relatively closer to the observed values of EI6 [4]. Moreover, the fact that EI5 and EI6 have a similar thermal stability supports the present identification.

Accordingly, we conclude that both EI5 and EI6 are V_C^+ defects and their locations are cubic and hexagonal site, respectively.

HEI1 in *n*-type 4*H*-SiC. In *n*-type radiation-damaged samples, EPR spectrum [Fig. 2(b)] was more complicated, as compared to *p*-type samples. However, we can clearly detect a new signal (HEI1, $S = 1/2$), in addition to the EI5 signal. Also very weak EI6 signal was present [see Fig. 2(a)]. The HEI1 signal was detected in the temperature range between 100 and 150 K. At lower temperatures, the EI6 signal became strong, instead of HEI1. The g values of HEI1 were $g_{\parallel} = 2.00399$ and $g_{\perp} = 2.00380$ at 150 K. The trend of g anisotropy ($g_{\parallel} > g_{\perp}$) was opposite of those for EI5 and EI6 ($g_{\parallel} < g_{\perp}$), which suggests that the HEI1 center corresponds to a negatively-charged state. The HEI1 signal has a HF satellite, labeled *a* [Fig. 2(b)]. This HF satellite showed axially symmetry around the c axis and its intensity was approximately 4.7 % of a total HEI1 signal. Thus, this was quite similar to the Si1 HF satellites of EI5 and EI6. Based on these experimental data as well as an analogy with EI5 and EI6, we tentatively speculated that the HEI1 center is a sort of negatively-charged carbon vacancies. Satellite *a* might be due to a Si1 site of negative carbon vacancy. The HEI1 signal also showed other HF satellites *b* to *e*, which is evident in Fig. 2(c). The HF splitting widths of *b* to *e* were much smaller than those of Si2 to Si6 of EI5 and EI6. This suggests that the wave function of HEI1 is more delocalized than that of EI5 and EI6, probably because an unpaired electron would occupy the anti-bonding state of V_C. The angular dependence of satellites *b* to *e* has not been resolved yet, because of their too small splitting widths. The conclusive identification of HEI1 will be achieved after the examination of their full angular dependences.

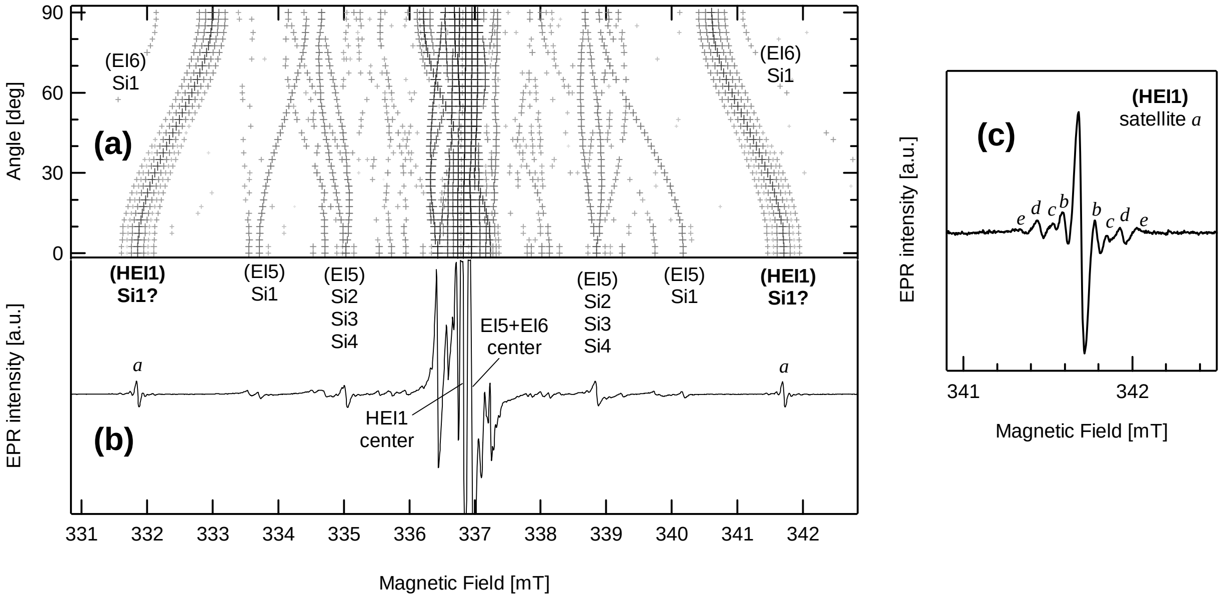

Fig. 2. EPR measurement of electron-irradiated *n*-type 4*H*-SiC at 150 K. (a) Angular dependence for **B** rotation in the (11$\bar{2}$0) plane. (b) EPR spectrum for **B** || c. (c) High-field-side HF satellite *a* of HEI1.

Summary

We have studied thermally-stable intrinsic defects in SiC by means of EPR/ENDOR and high-temperature (850 °C) electron-radiation experiments. Typical residual defects were EI5, EI6, and HEI1 (new defect). Although the EI5 and EI6 centers were originally identified as V_C^+ and Si_C^+, respectively, our complete EPR data demonstrated that both EI5 and EI6 are V_C^+ defects but EI5 is located at cubic sites and EI6 at hexagonal sites. It was also notable that these carbon vacancies were thermally stable over 1000 °C, which is much higher than the anneal-out temperatures known so far (≤ 600 °C). We also showed EPR data of HEI1 and discussed its origin tentatively.

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