Defect energy levels in electron-irradiated and deuterium-implanted 6*H* silicon carbide

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Using deep-level transient spectroscopy, we studied defect energy levels and their annealing behavior in nitrogen-doped 6*H*-SiC epitaxial layers irradiated with 2-MeV electrons and implanted with 300-KeV deuterium or hydrogen at room temperature. Five levels located at E_c-0.34, E_c-0.41, E_c-0.51, E_c-0.62, and E_c-0.64 eV consistently appear in various samples grown by chemical vapor deposition, showing they are characteristic defects in *n*-type 6*H*-SiC epitaxial layers. It is suggested that the E_c-0.51 eV level originates from a carbon vacancy, and that the two levels at E_c-0.34 and E_c-0.41 eV, which likely arise from the occupation of inequivalent lattice sites, and the level at E_c-0.51 eV are different charge states of the carbon vacancy. The annealing kinetics of the E_c-0.51 eV level are first order with an activation energy of 1.45 eV, and a level at E_c-0.87 eV growing upon its decay arises most likely from a vacancy-impurity complex. The results for the E_c-0.62 eV and E_c-0.64 eV levels are consistent with a defect model involving a silicon vacancy on inequivalent sites in the 6*H* lattice. Furthermore, the present results show that at hydrogen doses of 10^{11} cm^{-2} no interaction between hydrogen and the irradiation-induced silicon vacancy takes place even after annealing at temperatures up to 800 °C, in contrast to the results reported for *n*-type silicon.
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I. INTRODUCTION

There has been considerable interest in recent years in silicon carbide (SiC) as a wide-band gap semiconductor material for high-temperature, high-frequency, and high-power applications. Because of recent advances in crystal growth it is now possible to produce both epitaxial and bulk SiC material of high quality. An interesting feature of SiC is its appearance in many different polytypes which differ only in the stacking sequence of the tetrahedrally bonded Si/C bilayers. In polytypes such as 4*H*- and 6*H*-SiC with mixed zinc blende (cubic) and wurtzite (hexagonal) bonding between Si and C atoms in adjacent bilayer planes each type of bond provides a slightly altered atomic environment leading to inequivalent lattice sites. It is therefore possible to obtain generic knowledge about defects in semiconductors by comparing the properties of the same defect both at inequivalent sites in the same polytype and at sites in different polytypes.

Cubic (3*C*)SiC has no inequivalent Si or C lattice sites and therefore, has the advantage of simplicity for defect studies. Defects introduced by mega-electron-volt ion and electron irradiation in bulk 3*C*-SiC crystals and in epitaxial layers grown on Si(100) substrates by chemical vapor deposition (CVD) have been extensively studied using a variety of different experimental techniques, e.g., photoluminescence (PL),[1–3] cathodoluminescence (CL),[4,5] electron spin resonance (ESR),[6–8] and deep-level transient spectroscopy (DLTS).[9–11] An ESR spectrum with D_2 symmetry labeled $T5$ was observed in proton-irradiated *p*-type 3*C*-SiC epitaxial layers and was interpreted as arising from a positively charged carbon vacancy (V_{C}).[8] Itoh *et al.*[1,7] also observed an ESR spectrum with T_d symmetry labeled $T1$ in both *p*- and *n*- type 3*C*-SiC epitaxial layers irradiated with protons or electrons, and a dominant zero-phonon PL line at 1.913 eV labeled *E* in electron-irradiated *n*-type 3*C*-SiC epitaxial layers. Both the $T1$ ESR and the *E* PL centers were identified as a negatively charged silicon vacancy (V_{Si}). PL studies[3,12] also revealed a zero-phonon line at 1.973 eV labeled D_1 in bulk 3*C*- and 6*H*-SiC crystals and in 3*C*-SiC epitaxial layers irradiated with various types of ions or electrons. Choyke *et al.*[3,13] and Itoh *et al.*[1] interpreted the D_1 PL line to be associated with a divacancy.

Recently, Pensl and Choyke[14] reported the presence of two overlapping DLTS peaks located 0.62 and 0.64 eV below the conduction-band edge (E_c) and labeled Z_1 and Z_2 in as-grown *n*-type 6*H*-SiC crystals and in liquid phase epitaxy (LPE)-grown 6*H*-SiC layers irradiated with various types of ions or electrons. These Z_1/Z_2 centers were correlated to the V_{Si}-V_{C} divacancy identified by Vainer and Il'in[15] using the photoinduced ESR technique. In 6*H*-SiC there are three inequivalent sites for Si or C atoms, one hexagonal and two cubic sites, hence three inequivalent Si or C vacancies. It was therefore argued that the peaks Z_1 and Z_2 with slightly differing ionization energies are due to the generated defect occupying inequivalent lattice sites. Several DLTS peaks have also been recently reported in electron-irradiated *n*-type 6*H*-SiC epitaxial layers grown by chemical vapor deposition.[16–18] However, very little has been revealed about the identities and the annealing behavior of the observed defects.

In this paper, we report results from an experimental study of defect energy levels and their annealing behavior in *n*-type CVD-grown 6*H*-SiC epitaxial layers irradiated with 2-MeV electrons and implanted with 300-KeV deuterium or hydrogen at room temperature. These experiments reveal information concerning intrinsic defects in 6*H*-SiC epitaxial

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layers and give additional insight into the interaction of hydrogen with these defects.

II. EXPERIMENTAL PROCEDURE

The *n*-type nitrogen-doped ($\sim 1\times10^{15}-1\times10^{16}\,\mathrm{cm}^{-3}$) 6*H*-SiC epitaxial layers were grown on Si-terminated (0001) surfaces of vicinal (3°–4° off (0001) toward $[11\bar{2}0]$) 6*H*-SiC substrates (*N*-doped to $\sim 2\times10^{18}\,\mathrm{cm}^{-3}$) by chemical vapor deposition to a thickness of 1.5 to 10 μm and were subsequently thermally oxidized to a thickness of 75 nm. Two samples were used in our study, one (labeled *C*) grown by Cree Research and the other (labeled *S*) at the Industrial Microelectronics Center, Stockholm, Sweden by Nordell and co-workers.[19] The samples were irradiated with 2-MeV electrons at nominal room temperature ($\leq 30\,°\mathrm{C}$) to doses in the range of 1×10^{14} to $1\times10^{16}\,\mathrm{cm}^{-2}$. Deuterium implantation was performed at 300 KeV with a dose of $1\times10^{11}\,\mathrm{cm}^{-2}$. The sample surfaces were then chemically cleaned using a 10% hydrofluoric acid solution to remove the oxide layer immediately before Schottky-barrier structures were prepared by deposition of ~100-nm-thick Ni, Cu, or Au films on the samples. The metal films were deposited using electron-beam evaporation in a pressure of $\sim 1\times10^{-7}$ Torr at a rate of 1 nm/s, with the samples kept at room temperature. The deposition was made through a metal mask defining diodes of 1 mm in diameter. Annealing the samples was carried out prior to metal deposition in an atmosphere of pure nitrogen at temperatures between 150 and 1000 °C.

For sample analysis, deep-level transient spectroscopy and capacitance-voltage (C-V) measurements were undertaken at temperatures between 77 and 500 K. In the DLTS measurements six to eight traditional spectra with rate windows in the range of $(100\,\mathrm{ms})^{-1}$ to $(3200\,\mathrm{ms})^{-1}$ were recorded during a single temperature scan. The measurements were performed under reverse-bias conditions, and no forward injection was applied. The experimental setup has been described in detail elsewhere.[20] In the determination of the capture cross sections of the levels, we have assumed a T^2 correction to account for the temperature dependence of the effective density of states in the conduction band and the thermal velocity of the majority carriers. Trap concentration versus depth profiles in selected samples were determined using a single rate window, and the temperature was held at the maximum of the studied peak within ±0.5 K. The steady-state reverse-bias voltage was kept constant, while gradually increasing the amplitude of the majority-carrier pulse, and the depth profiles were extracted from the dependence of the DLTS signal on the pulse amplitude.[21] Depth profiles of impurities such as transition metal atoms in the epitaxial layers were determined by secondary ion mass spectrometry (SIMS) using an O_2^+ primary ion beam. Calibration of the SIMS data was achieved with ion-implanted reference samples.

III. RESULTS

DLTS spectra from *C* and *S* samples of as-grown *n*-type 6*H*-SiC epitaxial layers are shown in Fig. 1. In the *C* samples three levels at E_c-0.53, E_c-0.60, and E_c-0.61 eV are

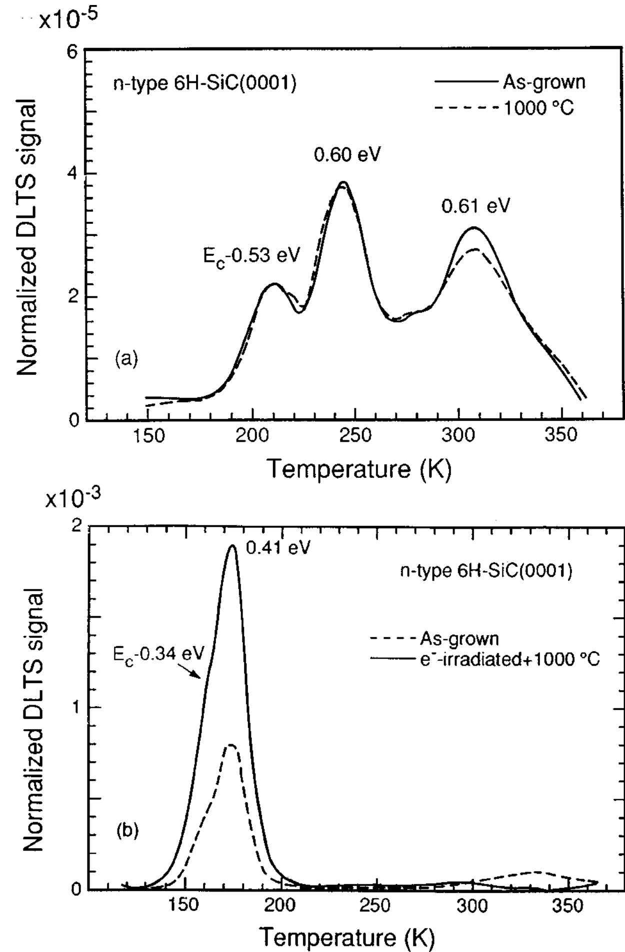

FIG. 1. (a) DLTS spectra from *C* samples of *n*-type 6*H*-SiC epitaxial layers (see text) in the as-grown state and after a 30-min anneal at 1000 °C. (b) DLTS spectra from *S* samples of *n*-type 6*H*-SiC epitaxial layers (see text) in the as-grown state and after irradiation with 2-MeV electrons to a dose of $1\times10^{15}\,\mathrm{cm}^{-2}$ and subsequent annealing for 30 min at 1000 °C. [Rate window $=(3.20\,\mathrm{s})^{-1}$.]

observed with capture cross sections of $\sim 3\times10^{-14}$, $\sim 1\times10^{-14}$, and $\sim 3\times10^{-17}\,\mathrm{cm}^2$, respectively. The three levels are stable at temperatures up to 1000 °C [Fig. 1(a)]. Depth profiles revealed that the three levels are distributed rather uniformly within the epitaxial layer and have essentially the same concentration of $\sim 1\times10^{13}\,\mathrm{cm}^{-3}$. Furthermore, no influence on the emission rate of the three levels by the electric field in the depletion region was found. The absence of a Poole-Frenkel effect[22] suggests that these levels are acceptorlike. In the *S* samples, there is no evidence of the three levels observed in Fig. 1(a) but two new acceptorlike levels appear at E_c-0.34 and E_c-0.41 eV with capture cross sections of $\sim 6\times10^{-15}$ and $\sim 3\times10^{-14}\,\mathrm{cm}^2$, respectively [Fig. 1(b)]. The two levels persist after a 1000 °C anneal and are distributed uniformly within the epitaxial layer as revealed by depth profiling.

In Fig. 2 we show DLTS spectra from *S* samples of *n*-type 6*H*-SiC epitaxial layers irradiated with 2-MeV electrons to doses of 1×10^{15} and $1\times10^{16}\,\mathrm{cm}^{-2}$. Spectra from *C* samples are very similar to those shown in Fig. 2. Three levels at E_c-0.34, E_c-0.41, and E_c-0.51 eV and two overlapping levels at E_c-0.62 and E_c-0.64 eV, with capture cross sections of

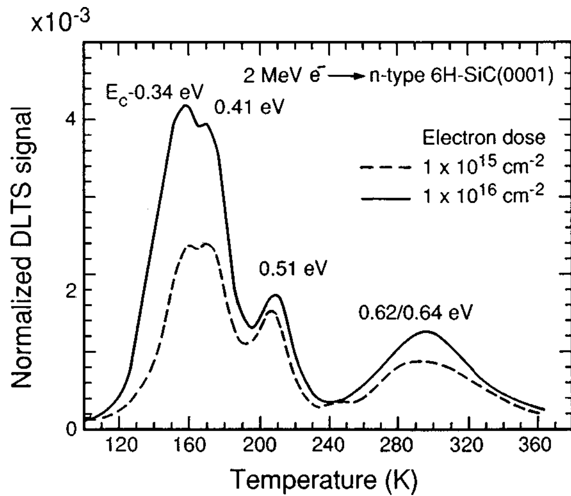

FIG. 2. DLTS spectra from S samples of n-type $6H$-SiC epitaxial layers irradiated with 2-MeV electrons to doses of 1×10^{15} and $1\times10^{16}\,\mathrm{cm}^{-2}$. [Rate window$=(3.20\,\mathrm{s})^{-1}$.]

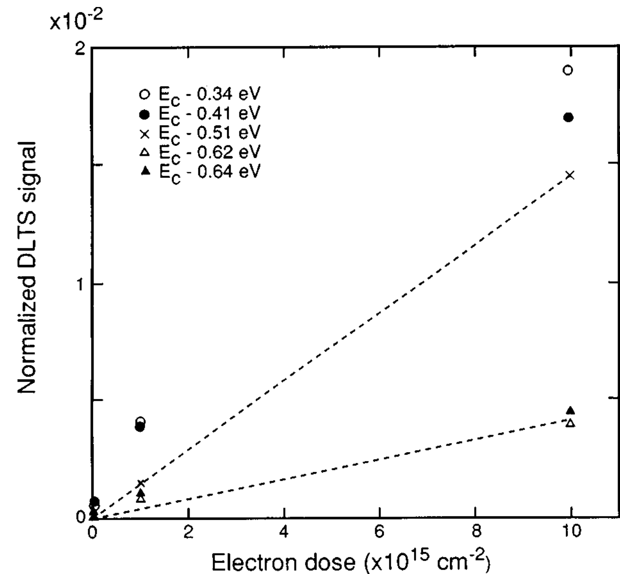

FIG. 3. Production rate data for the dominant energy levels in 2-MeV electron irradiated n-type $6H$-SiC epitaxial layers.

$\sim6\times10^{-15}$, $\sim3\times10^{-14}$, $\sim2\times10^{-14}$, $\sim1\times10^{-16}$, and $\sim1\times10^{-17}\,\mathrm{cm}^2$, respectively, are consistently observed in both samples. The E_c-0.51 eV level is donorlike and the two levels at E_c-0.62 and E_c-0.64 eV are acceptorlike. Also, in the S samples an increase in the intensity of the E_c-0.34 and E_c-0.41 eV levels is observed after electron irradiation [Fig. 1(b)], providing evidence for their intrinsic nature. On the other hand, in the C samples the E_c-0.53, E_c-0.60, and E_c-0.61 eV levels were found not to increase in intensity after electron irradiation, indicating that these levels are most likely impurity related. However, within the sensitivity of the SIMS ($\leq10^{13}$ atoms/cm^3), no transition metal impurities, such as Ti, V, and Cr, are detectable in the epitaxial layers. It should be noted that oxygen and hydrogen may also exist in the epitaxial layers but are not measurable to below 10^{17} atoms/cm^3. In the following, we will concentrate mainly on the levels introduced by electron irradiation and by deuterium implantation (see DLTS spectra in Fig. 7).

Figure 3 shows the results from the dose dependence study of the observed levels. The production data for all levels follow linear increase with the electron dose over the range of doses used in our study. Note that the two levels at E_c-0.62 and E_c-0.64 eV have almost the same production rate as do the levels at E_c-0.34 and E_c-0.41 eV. The production rates of the E_c-0.51 and E_c-0.62 and E_c-0.64 eV levels obtained from the slopes of the respective linear fits are found to be about 0.015 and 0.004 cm^{-1}. The production rate of the E_c-0.34 and E_c-0.41 eV levels is comparable to that of the E_c-0.51 eV level.

Figures 4, 5, and 6 show typical isochronal annealing data obtained from electron-irradiated samples. Several interesting features are shown in Figs. 4, 5, and 6. First, the E_c-0.51 eV level began to anneal at about 180 °C and disappeared at 250 °C [Fig. 4(a)]. Further isothermal annealing experiments have shown that the annealing kinetics of the E_c-0.51 eV level are first order with an activation energy of 1.45 ± 0.01 eV and a frequency factor of $1\times10^{14}\,\mathrm{s}^{-1}$ [Fig. 4(b)]. Upon the decay of the E_c-0.51 eV level, a level located at E_c-0.87 eV, with a capture cross section of $\sim1\times10^{-16}\,\mathrm{cm}^2$, grew. In Fig. 4(c) the growth of the E_c-0.87 eV level is plotted versus the decay of the E_c-0.51 eV level, and within the experimental accuracy a proportionality is obtained. Furthermore, the E_c-0.87 eV level was not observed during isochronal annealing of unirradiated samples. These above results argue that the defect giving rise to the E_c-0.87 eV level evolves from the defect causing the E_c-0.51 eV level. Upon further annealing at higher temperatures, the E_c-0.87 eV level disappeared at about 800 °C. Second, the E_c-0.34 and E_c-0.41 eV levels displayed almost identical annealing behavior and persisted after a 1000 °C anneal. The data in Fig. 5 reveal an increase in the intensity of both levels upon annealing at temperatures in the range of 250 to 300 °C. Because of their small energy difference, and since they have almost the same production rate and identical annealing behavior, we suggest that the E_c-0.34 and E_c-0.41 eV levels are due to a defect occupying inequivalent sites in the $6H$ lattice.

Our isochronal annealing studies have also shown that the E_c-0.62 and E_c-0.64 eV levels displayed two annealing stages. [E_c-0.62 eV] and [E_c-0.64 eV] (brackets denote concentration values) decreased by about 40 and 25 %, respectively, after annealing at 200 °C, and the remaining concentrations of both levels were reduced to the detection limit around 850 °C, as shown in Fig. 6. These data thus indicate that the fraction of the defect annealed at each annealing stage is site dependent.

Figure 7 shows DLTS spectra from S samples of n-type $6H$-SiC epitaxial layers implanted with 300-KeV deuterium to a dose of $1\times10^{11}\,\mathrm{cm}^{-2}$ and subsequently annealed at 800 °C. The disappearance of the E_c-0.34 and E_c-0.41 eV levels in the as-implanted samples suggests that these two levels are affected by the lattice strain[23] associated with the damage induced by deuterium implantation, since the two levels appear after a 30-min anneal at 300 °C and their intensity increases with further annealing to 800 °C. It may also be pointed out that the disappearance of the E_c-0.34 and E_c-0.41 eV levels is not due to a Fermi level effect. The

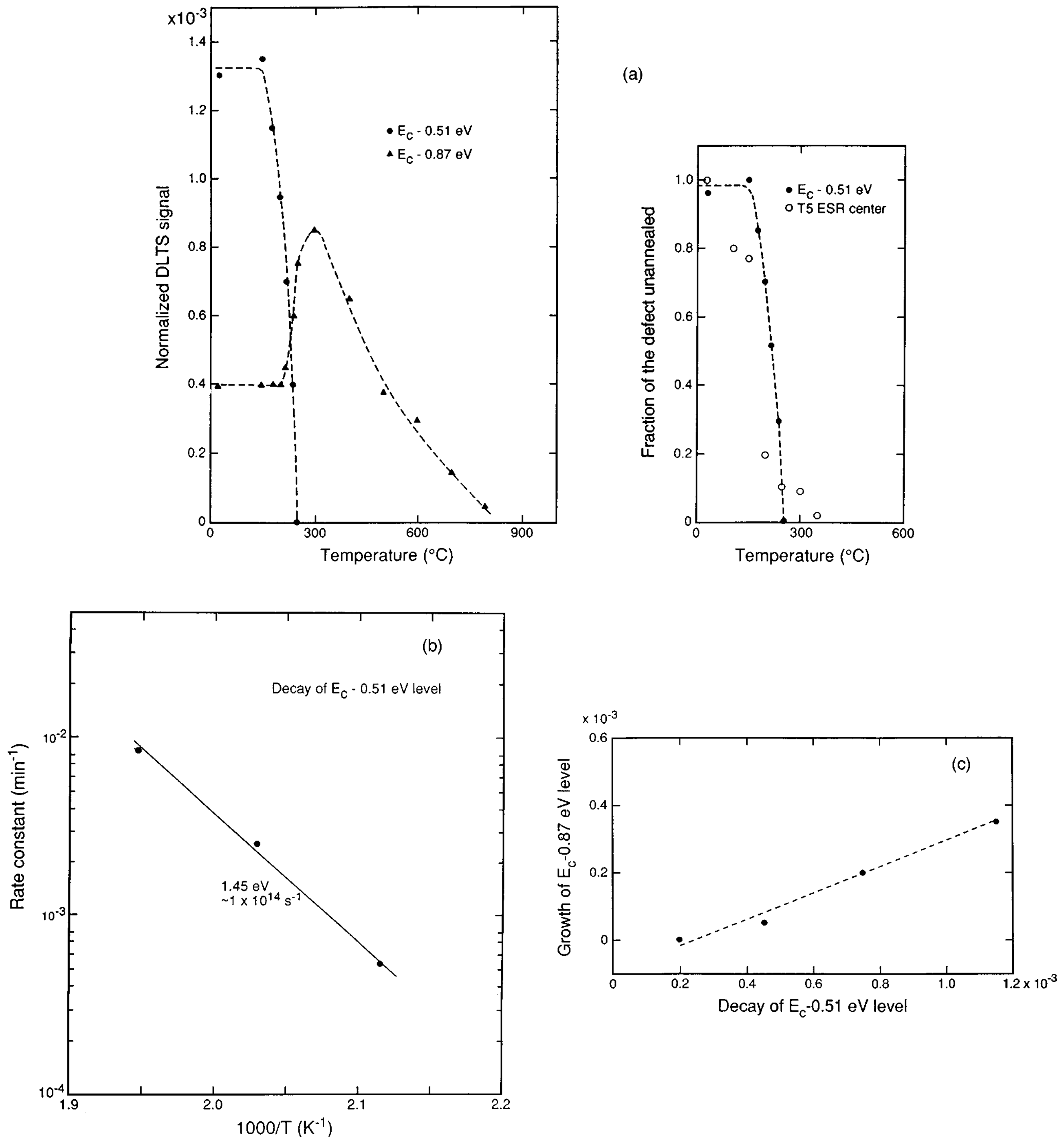

FIG. 4. (a) Isochronal annealing (30 min) data for the levels at E_c-0.51 and E_c-0.87 eV in n-type $6H$-SiC epitaxial layers irradiated with 2-MeV electrons to a dose of $1\times10^{16}\,\mathrm{cm}^{-2}$ and for the $T5$ ESR center observed in ion-irradiated p-type $3C$-SiC epitaxial layers. (b) Arrhenius plot of the rate constant for the decay of the E_c-0.51 eV level. (c) Growth of the E_c-0.87 eV level versus the decay of the E_c-0.51 eV level.

defect concentration was typically at least one order of magnitude smaller than the dopant concentration. Note that the E_c-0.51 eV level is completely eliminated and that [E_c-0.62 eV] and [E_c-0.64 eV] are greatly reduced after the 800 °C anneal. Furthermore, a comparison of DLTS spectra for electron-irradiated and hydrogen-implanted samples (Figs. 2 and 7) shows no hydrogen-related energy levels in the latter.

IV. DISCUSSION

A. E_c-0.51 eV and E_c-0.87 eV levels

The data in Fig. 3 show that the E_c-0.51 eV level grows linearly with the electron dose, suggesting that the defect causing this level is a simple defect. The annealing behavior of the E_c-0.51 eV level, which is donorlike, is almost identical to that of the $T5$ ESR center [Fig. 4(a)], which Itoh

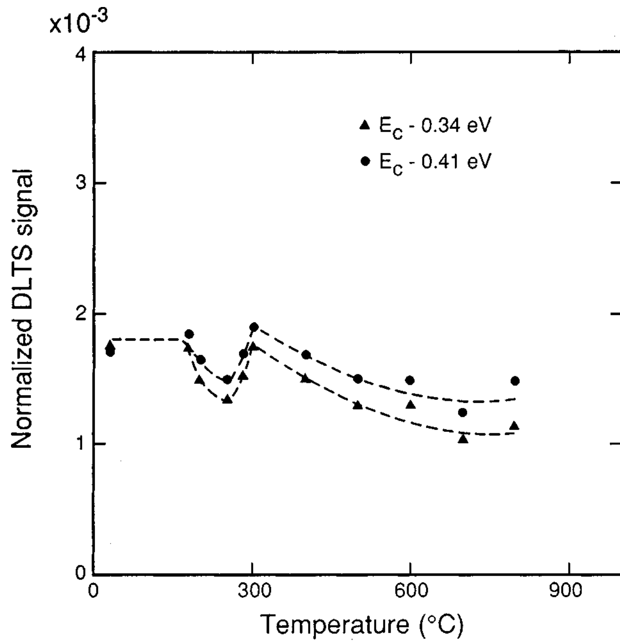

FIG. 5. Isochronal annealing (30 min) data for the levels at E_c-0.34 and E_c-0.41 eV in *n*-type 6*H*-SiC epitaxial layers irradiated with 2-MeV electrons to a dose of $1\times10^{16}\,\mathrm{cm}^{-2}$.

et al.[8] identified as a positively charged carbon vacancy in 3*C*-SiC. We therefore suggest that the E_c-0.51 eV level originates from a carbon vacancy in *n*-type 6*H*-SiC. Theoretical studies[24,25] have shown that the carbon vacancy in 3*C*-SiC acts as a donor and induces a level at E_c-0.80 eV corresponding to a Si dangling-bond state, which is consis-

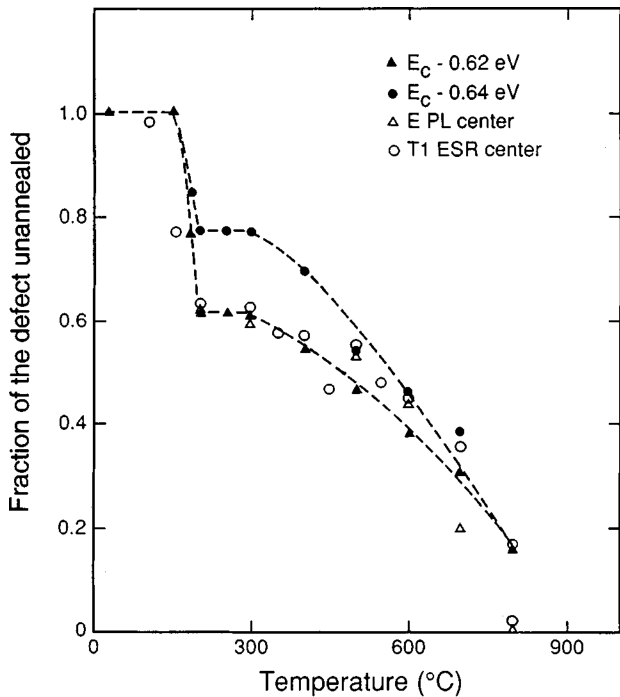

FIG. 6. Isochronal annealing (30 min.) data for the levels at E_c-0.62 and E_c-0.64 eV in *n*-type 6*H*-SiC epitaxial layers irradiated with 2-MeV electrons to a dose of $1\times10^{16}\,\mathrm{cm}^{-2}$ and for the *T*1 ESR and the *E* PL centers observed in ion- and electron-irradiated *n*- and *p*-type 3*C*-SiC epitaxial layers.

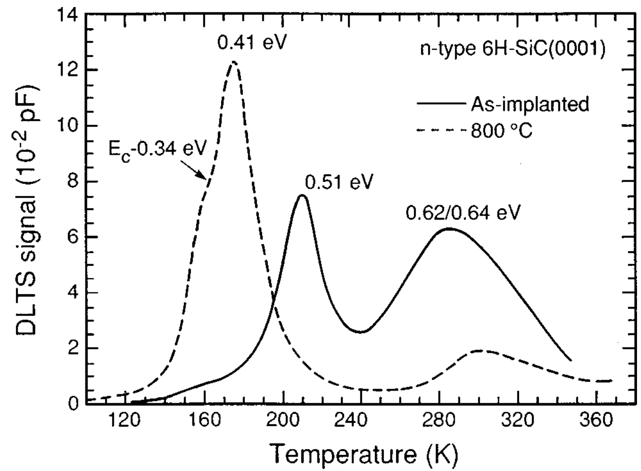

FIG. 7. DLTS spectra from *S* samples of *n*-type 6*H*-SiC epitaxial layers implanted with 300-KeV deuterium to a dose of $1\times10^{11}\,\mathrm{cm}^{-2}$ in the as-implanted state and after a 30-min anneal at 800 °C. [Rate window$=(3.20\,\mathrm{s})^{-1}$.]

tent with the fact that no *T*5 ESR signal has been observed in *n*-type 3*C*-SiC since the defect is not paramagnetic in the neutral charge state.[8] Our results thus indicate that the donor level of the carbon vacancy lies higher in energy in the larger band-gap polytype 6*H*. We note that for silicon, the production rate of the single vacancy-related (vacancy-oxygen) center under 2-MeV electron irradiation is 0.1 cm^{-1} and of the divacancy center is 0.01 cm^{-1}.[26] The lower value for the production rate of the E_c-0.51 eV level (0.015 cm^{-1}) is most likely the result of a higher binding energy for SiC when compared to silicon. It is of interest to mention that the energy position of the *E*-0.51 eV level is identical to that of the E_i level observed by Hemmingsson *et al.*[18] in electron-irradiated *n*-type 6*H*-SiC epitaxial layers. The E_i level anneals out at ~200 °C, which argues for its association with a carbon vacancy.

The decay of the E_c-0.51 eV level is a first-order process with a corresponding growth of the E_c-0.87 eV level. It is known[27,28] from the extensive work on electron-irradiated silicon that vacancies and self-interstitials are mobile at low temperatures, and are readily captured by impurities, resulting in the formation of more stable defects. We expect that the distinction between the annealing temperature of primary and complex defects is also valid for SiC. Hence the E_c-0.87 eV level is probably a complex formed by the trapping of a mobile carbon vacancy by an impurity of relatively high concentration, which is likely to be oxygen. However, as revealed in Fig. 4(c), the decrease in [E_c-0.51 eV] is larger than the corresponding increase of [E_c-0.87 eV]. This indicates that not all of the carbon vacancies giving rise to the E_c-0.51 eV level participate in the above reaction, and in Sec. IV B additional processes involving the carbon vacancy will be discussed.

B. E_c-0.34 eV and E_c-0.41 eV levels

These two levels also grow linearly with the electron dose at almost the same rate, suggesting that they are caused by a simple defect, and moreover, the two levels persist after a 1000 °C anneal. In their PL work, Patrick and Choyke[29]

found that some defects in electron- and ion-irradiated $3C$- and $6H$-SiC crystals persist even after a 1700 °C anneal and that one of these persistent defects gives rise to a low-temperature luminescence spectrum (the D_1 center) that has a characteristic vibronic structure. It was speculated that the D_1 center is a divacancy. However, the production rate of the E_c-0.34 and E_c-0.41 eV levels is comparable to that of the E_c-0.51 eV level (Fig. 3), which argues against the association of these two levels with a divacancy. ESR studies[30] have shown that the carbon vacancy in electron-irradiated $6H$-SiC crystals exists in different charge states and is stable up to temperatures varying markedly with the charge state. Thus, a possible identification of the acceptorlike levels at E_c-0.34 and E_c-0.41 eV is a carbon vacancy presumably residing at inequivalent lattice sites. This identification is consistent with the results of ESR studies showing that the negatively charged carbon vacancy in n-type $6H$-SiC disappears at 1400 °C, whereas in the neutral and positive charge states the defect anneals out at 200–300 °C. These results indicate that the carbon vacancy in $6H$-SiC has both a donor and an acceptor level in the upper half of the band gap. We note that in the case of the E_c-0.51 eV level, there is no indication for a level splitting. This implies that the difference between the inequivalent cubic and hexagonal lattice sites is less important for this deep level probably because of its more localized electron state. Hemmingsson *et al.*[18] have observed two acceptorlike levels of E_c-0.33 and E_c-0.40 eV ($E1$ and $E2$) which we believe are the same as the E_c-0.34 and E_c-0.41 eV levels observed here. However, no annealing studies have been made on the $E1$ and $E2$ levels. Nevertheless, we have found[31] that the E_c-0.34 and E_c-0.41 eV levels almost disappear when both holes and electrons are injected into the space charge region. This behavior may be explained by electron-hole recombination and is consistent with that reported for the $E1$ and $E2$ levels.

The observed increase in the intensity of the E_c-0.34 and E_c-0.41 eV levels, which occurs at temperatures in the range 250–300 °C (Fig. 5), can be interpreted as due to a fraction of the carbon vacancies in the neutral state changing to a negatively charged state by electron capture, and consequently, they become more stable and can no longer react with oxygen impurities. This would then explain the data in Fig. 4(c), and the decay of the E_c-0.51 eV level may be viewed as a mixed process where formation of the vacancy-impurity complexes giving rise to the E_c-0.87 eV level constitutes a significant contribution. Further theoretical studies, however, are needed to establish the electronic states of the carbon vacancy in the $6H$ polytype and provide a more detailed model of the defect.

C. E_c-0.62 eV and E_c-0.64 eV levels

The energy positions of these two levels are identical to those previously observed by Pensl and Choyke[14] in LPE-grown n-type $6H$-SiC layers irradiated with various types of ions or with 2-MeV electrons. As mentioned earlier, these authors correlated the E_c-0.62 and E_c-0.64 eV levels to a divacancy (V_{Si}-V_C) on nearest-neighbor sites with C_{3v} symmetry. They also reported that the two levels are not destroyed by annealing up to 1700 °C. However, the present levels display two annealing stages and almost disappear around 850 °C and are, therefore, not believed to originate from the same center as the levels observed in the LPE-grown samples. The annealing stages of the present levels and their fractions annealed at each annealing stage are strikingly similar to those of the $T1$ ESR and the E PL centers (Fig. 6), which Itoh *et al.*[1,7] identified as a negatively charged silicon vacancy in $3C$-SiC. Thus, we can conclude that the E_c-0.62 and E_c-0.64 eV levels observed here, which are acceptorlike, arise from a silicon vacancy occupying inequivalent lattice sites in n-type $6H$-SiC. This is also consistent with the data in Fig. 3, which show that the production rate of the E_c-0.62 and E_c-0.64 eV levels is significantly lower than that of the E_c-0.51 eV level since, as shown by Nashiyama *et al.*,[32] more carbon interstitials are introduced into SiC by irradiation than silicon interstitials.

Theoretical studies[33] have also shown that C interstitials in $3C$-SiC do not have gap states, while Si interstitials induce gap states. However, as suggested by Itoh *et al.*,[7] Si interstitials probably migrate to combine with some C vacancies at room temperature, resulting in Si_C antisite defects which have no gap states and are energetically much more favorable than the Si interstitials.[34] We also note that [E_c-0.62 eV] and [E_c-0.64 eV] decrease in the same temperature range as where [E_c-0.51 eV] decreases rapidly. This indicates the possibility that some of the C vacancies causing the E_c-0.51 eV level may undergo pairing with Si vacancies resulting in the formation of V_{Si}-V_C divacancies. The V_{Si}-V_C divacancy, however, is expected to give rise to gap states with energy positions close to those of the isolated Si and C vacancies,[35] and no such divacancy-related energy levels were observed. It is possible that the initial decay of the E_c-0.62 and E_c-0.64 eV levels occurs through Si vacancy combining with an interstitial-type defect.[34] Isothermal annealing studies[31] revealed a decay at the later stage of the annealing process with first-order kinetics and an activation energy comparable to that obtained for the annealing of the $T1$ ESR and the E PL centers (~2.2 eV).[1,6] This further supports the identification of the E_c-0.62 and E_c-0.64 eV levels as a Si vacancy. The theoretical calculations by Wenchang *et al.*[24] and Talwar and Feng[25] predict that the Si vacancy in $3C$-SiC induces a level at 0.54 eV above the valence-band edge corresponding to a C dangling-bond state. Our results thus indicate that this level also lies higher in energy in the larger band-gap $6H$ polytype.

As can be seen in Fig. 7, no hydrogen-related energy levels are introduced by hydrogen implantation and subsequent annealing at 800 °C. On the other hand, Patrick and Choyke[36] reported the presence of a H luminescence center in $6H$-SiC crystals implanted with hydrogen to a dose of $3\times10^{14}\,\mathrm{cm}^{-2}$. Based on the observation of a CH bond-stretching mode and an increase in the H luminescence intensity with annealing to 800 °C, they proposed a model for the center where an H atom is bonded to a C atom at a Si vacancy. If such a center, which can be viewed as a Si vacancy with partly hydrogen-saturated C dangling bonds, is formed, it is expected to give rise to gap states originating from a Si vacancy configuration but with a shift in energy positions, and no such energy levels were observed. This indicates that at doses of $10^{11}\,\mathrm{cm}^{-2}$ no interaction between hydrogen and the irradiation-induced Si vacancy takes place even after annealing at temperatures up to 800 °C which al-

lows diffusion of hydrogen. It should be mentioned that no SiH bond-stretching mode was observed by Patrick and Choyke[36] indicating that hydrogen does not bond to Si atoms at C vacancies due presumably to the higher strength of the C-H bond compared to the Si-H bond.[37] The present results are in contrast to those reported for *n*-type Si (Ref. 38) where hydrogen-related energy levels are introduced by low dose ($10^8-10^{10}\,cm^{-2}$) proton implantation and are interpreted to be associated with vacancy-type defects with partly hydrogen-saturated dangling bonds. Further studies to determine the dose dependence of hydrogen-related energy levels in 6*H*-SiC epitaxial layers are currently underway.

V. SUMMARY

The E_c-0.34, E_c-0.41, E_c-0.51, E_c-0.62, and E_c-0.64 eV levels are the dominant levels observed in *n*-type nitrogen-doped 6*H*-SiC epitaxial layers irradiated with 2-MeV electrons or implanted with 300-KeV deuterium or hydrogen at room temperature. It is suggested that the E_c-0.51 eV level originates from a C vacancy, and that the two levels at E_c-0.34 and E_c-0.41 eV, which likely arise from the occupation of inequivalent lattice sites, and the level at E_c-0.51 eV are different charge states of the C vacancy. The annealing kinetics of the E_c-0.51 eV level are first order with an activation energy of 1.45 eV, and a level at E_c-0.87 eV growing upon its decay arises most likely from a vacancy-impurity complex. The E_c-0.62 and E_c-0.64 eV levels are interpreted as arising from a Si vacancy occupying inequivalent sites in the 6*H* lattice. Furthermore, the present results show that at hydrogen doses of $10^{11}\,cm^{-2}$ no interaction between hydrogen and the irradiation-induced Si vacancy takes place even after annealing at temperatures up to 800 °C in contrast to the results reported for *n*-type silicon.

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