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Electric field assisted annealing and formation of prominent deep-level defect in ion-implanted *n*-type 4*H*-SiC

J. Wong-Leung[1,a)] and B. G. Svensson[2]
[1]*Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Australian National University, Canberra, Australian Capital Territory 0200, Australia*
[2]*Physics Department, Centre for Materials Science and Nanotechnology, University of Oslo, P.B. 1048 Blindern, Oslo N-0316, Norway*

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High-purity and low-doped *n*-type epitaxial layers of 4*H*-SiC have been implanted with N and C ions by using energies in the MeV range and doses from 2×10^8 to 1×10^9 cm^{-2}. Postimplant annealing was performed at 1100 °C prior to sample analysis by deep-level transient spectroscopy (DLTS). A drastic and irreversible instability of the prominent EH7 deep-level defect occurs during the first DLTS temperature scan because of the electric field applied during the measurements. Depending on the implanted species, EH7 can decrease (N implants) as well as increase (C implants) in strength and the effect is attributed to charge-state controlled annealing and formation processes of EH7. The origin of EH7 is discussed and the experimental data support a model invoking interstitial C atoms. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2907693]

SiC is a promising semiconductor for high power and high temperature electronics. These potentials are nevertheless compromised by the presence of persistent deep-level defects. Two main defects are widely reported in *n*-type 4*H*-SiC, namely, the $Z1/Z2$ defect at ≈0.7 eV below the conduction band edge E_C and the EH6/EH7 defect located at around $E_C-1.5$ eV. The nature of the $Z1/Z2$ defect still remains unresolved but very recent studies provide evidence for the involvement of C interstitials.[1,2]

EH6/EH7 was first reported in 4*H*-SiC by Hemmingsson *et al.*[3] and deep-level transient spectroscopy (DLTS) filling pulse width variation studies revealed a center with a large electron capture cross section ($\geqslant 5\times10^{-15}$cm^2). The EH6/EH7 peak has been found to be a combination of two contributions, EH6 and EH7,[4] and Storasta *et al.*[5] demonstrated that irradiation by low energy electrons, causing atomic displacement on the C sublattice only, enhances the relative intensity of EH7. Hence, the generation of EH7 invokes fundamental C-related point defects while EH6 is believed to be a higher order cluster.[6] For as-grown samples, Kimoto *et al.*[7] reported suppression of EH6/EH7 concentrations by using C-rich conditions during chemical vapor deposition growth and this was also observed by Zhang *et al.*[8] In contrast, Pintilie *et al.*[9] reported EH6/EH7 equal in concentration during the first DLTS temperature upscan for samples with different C/Si growth ratios followed by enhanced annihilation during the subsequent downscan for samples with low C/Si ratio. The latter observations are more consistent with the involvement of C interstitials C_I rather than C vacancies V_C, as proposed in Refs. 5, 7, and 8.

The apparent discrepancy between these different studies suggests that the C/Si growth ratio is not the only decisive factor but other parameters, e.g., the growth and cooling rates, play a crucial role.[9] In addition, the complex behavior of the EH6/EH7 peak is confused by the fact that there are several defect configurations with closely positioned energy states present. In this study, we show that the EH6/EH7 peak contains at least two distinctly different contributions using ion-implanted and annealed high-purity epitaxial layers. In particular, one single level, positioned ≈1.44 eV below E_C and ascribed to EH7, displays instability when subjected to an electric field at moderate temperatures (≈700 K) and it can both increase and decrease in intensity depending on the implanted species. The identity of this $E_C-1.44$ eV level is discussed in some detail and on the basis of the experimental results, it is argued to involve C interstitials.

6 MeV N^{3+} and 5 MeV C^{3+} ions were implanted into *n*-type 4*H*-SiC epilayers, which are 10 μm thick with carrier concentration around 1×10^{15} cm^{-3}, grown on highly *n*-type doped (0001) substrate, and with an 8° miscut off axis, supplied by CREE. The projected ranges R_p for the N and C implantations are 3.29 and 3.24 μm, respectively, according to SRIM simulations.[10] The implanted doses ranged from 2×10^8 to 1×10^9 cm^{-2} and the implants were performed in a direction close to the wafer normal to minimize channeling.[11] After implantation, the samples were annealed at 1100 °C for 1 h under flowing Ar in a conventional quartz tube. Schottky diodes were then fabricated by evaporating Ni using an e-beam evaporator at a pressure of $\leqslant 1\times10^{-5}$ Torr. The samples were analyzed by employing a refined version of the DLTS setup described in Ref. 12 using a high temperature cryostat in the temperature range of 100–750 K. The reverse biases V_b applied ranged from −12 to −14 V, and are adequate for probing the implant range region. Six DLTS spectra with rate windows between 20 and 640 ms^{-1} were simultaneously acquired in one temperature upscan or downscan with a typical ramp rate of 2 K min^{-1}.

The inset in Fig. 1 shows the DLTS spectrum of the as-grown control sample after annealing at 1100 °C for 1 h. Two distinct defect levels are observed in the sample; around 287 K, the $Z1/Z2$ defect level occurs with a position of $E_C-0.68$ eV and at 621 K, a single defect peak is identified with $E_C-1.44$ eV. Simulations of the two DLTS peaks display close agreement with the experimental data, as illustrated for the 640 ms^{-1} rate window (see inset in Fig. 1).

Figure 1 compares the first upscan DLTS spectrum of the sample implanted with 5×10^8 cm^{-2} N to that of the as-grown sample both after a 1100 °C anneal (1 h). First, we note that the $Z1/Z2$ level is enhanced by the N implantation

a)Electronic mail: jwl109@rsphysse.anu.edu.au.

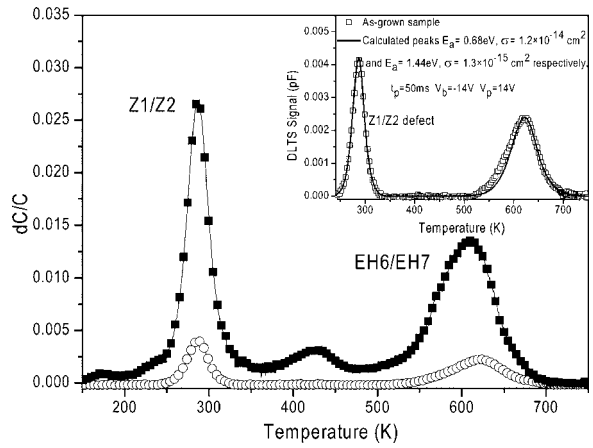

FIG. 1. DLTS spectra of (a) (○) as-grown SiC sample (V_b=−14 V, V_p=14 V) and (b) (■) 5×10^8 cm^{-2} N implanted sample after 1 h anneal at 1100 °C (V_b=−12 V, V_p=12 V), both with a pulse width of 50 ms. Inset shows a DLTS spectrum of as-grown 4*H*-SiC sample after 1 h anneal at 1100 °C during temperature upscan.

and the peak can be simulated with the same parameters used for the control sample. Second, the higher temperature peak is also enhanced but appears to be skewed toward lower temperatures compared to the $E_C-1.44$ eV level. In fact, this peak cannot be properly fitted by assuming a single defect level, i.e., it is composed of the $E_C-1.44$ eV level and at least one additional contribution. In the following, the high temperature peak will be labeled EH6/EH7, in accordance with the notation used by other authors.[3]

In all the implanted samples, a difference is observed between the first DLTS upscan and the subsequent downscan or upscan spectra. This effect is especially pronounced in the case of the N implanted samples. Figure 2(a) shows a typical example of this effect by comparing the first DLTS upscan spectrum to the first downscan spectrum of the same sample. First, we note that the $Z1/Z2$ peak remains identical in the two spectra, clearly indicating that the ramp rate was sufficiently slow, causing no shift in peak position. Second, the amplitude of the EH6/EH7 peak decreased by about half in the downscan spectra and it also exhibits a shift toward lower temperatures, indicating that there is more than one contributing level. A second upscan displayed little difference relative to the first downscan, suggesting that defect annihilation occurred during the first upscan. We note that the same reverse bias was used for the upscan and downscan and depth profiling of this peak (not shown) confirms that the depletion region probed is just beyond the implant peak. A similar behavior was also observed for the other two N doses studied and the results are summarized in Table I.

For the C implanted samples, the opposite trend is observed, i.e., an increase in the amplitude of the EH6/EH7 peak occurs after the first upscan, as illustrated by the second upscan spectrum in Fig. 2(b) for the 5×10^8 cm^{-2} C implanted sample. Moreover, especially for the 2×10^8 and 5×10^8 cm^{-2} C doses, the increase in the EH6/EH7 peak concentration is accompanied by a decrease in the $Z1/Z2$ peak. In addition, the subtraction of the first upscan spectrum by the second upscan for the 5×10^8 cm^{-2} C implanted sample gives a defect peak which can be ascribed to a single level at $E_C-1.43$ eV. Within the experimental accuracy, the energy position (and apparent capture cross section) of this level is identical with that of the $E_C-1.44$ eV level observed in the control sample. Further, the EH6/EH7 peak (in the

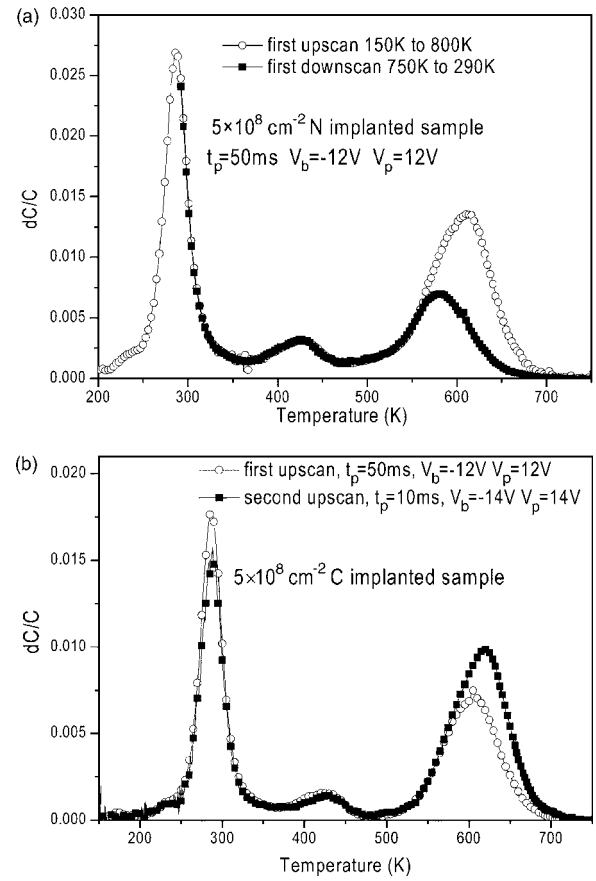

FIG. 2. DLTS spectra of SiC samples implanted with (a) N to dose of 5×10^8 cm^{-2} (upscan and downscan) and (b) C to dose of 5×10^8 cm^{-2} (first upscan and second upscan), both after annealing at 1100 °C for 1 h.

second upscan) can be adequately simulated for all the C implanted samples with the $E_C-1.44$ eV level and an additional smaller contribution from a single level at $E_C-1.40$ eV with an apparent capture cross section of $\approx4\times10^{-15}$ cm^2. The experimental results are summarized in Table I.

The shift in the EH6/EH7 peak toward lower temperatures in the N implanted samples and toward higher temperatures in the C implanted samples (see Table I) strongly suggests that one specific defect, presumably of the same origin, is suppressed or enhanced after the first upscan. Figure 3 compares the DLTS spectra of the two first successive temperature upscans for the 5×10^8 cm^{-2} N implanted sample and the difference spectrum is also included; the residual peak can be adequately simulated using the parameter values determined for the $E_C-1.44$ eV level in the control sample. Here, it should be emphasized that the control sample did not show any difference between the first upscan and the first downscan, clearly demonstrating that the high temperature instability is due to the implantation process. These samples have been annealed at 1100 °C (1 h) prior to the DLTS measurements and the instability must be caused by the electric field applied during the DLTS analysis in combination with a sufficiently high temperature. Further, we did not succeed in restoring the initial strength of the EH6/EH7 peak by varying the sample bias conditions at different temperatures, suggesting that the instability observed is irreversible.

The $E_C-1.44$ eV level occurs on the high temperature side of the EH6/EH7 peak and is identified as EH7, following the labeling introduced by Hemmingsson *et al.*[3] The for-

TABLE I. Summary of changes in defect concentrations observed between the first and second temperature upscans after 1100 °C anneal.

	N implanted samples			C implanted samples		
		EH6/EH7			EH6/EH7	
Dose (cm^{-2})	$Z1/Z2$	Amplitude	Shift	$Z1/Z2$	Amplitude	Shift
2×10^8	6% increase	31% decrease	Low temperatures	13% decrease	24% increase	No shift
5×10^8	No change	50% decrease	Low temperatures	19% decrease	26% increase	High temperatures
1×10^9	13% decrease	38% decrease	Low temperatures	No change	12% increase	High temperatures

mation of EH7 involves fundamental C-related defects (V_C or C_I)[5] and it may be anticipated to exhibit a complex evolution during ion implantation and subsequent annealing.

For the implantation conditions used in this work, the defect generations (elastic energy deposition) by the N and C ions are almost identical with a relative deviation of less than 15% according to SRIM simulations.[10] Hence, the drastic difference in evolution of the EH6/EH7 peak in the two sets of samples is associated with the implanted species. In fact, the EH6/EH7 peak concentration, as deduced from depth profiling measurements, is of the same order of magnitude as that of the implanted ions.[10] Notably, for the samples and postannealing used (1100 °C, 1 h), extrinsic conditions prevail. The Fermi level is positioned around $E_C-1.4$ eV at 1100 °C, which implies that the EH6/EH7 states remain occupied by electrons and are not emptied prior to the first DLTS scan. It is, therefore, tempting to suggest that the instability observed is related to a change in the charge state of EH6/EH7 and/or of other defects with levels close to the midgap. The atomic structures of both C_I and interstitial Si (Si_I) are unveiled by first principles density functional calculations[13] to be charge-state dependent and for split-interstitial configurations at a C site, they possess levels near the midgap. In Ref. 13, it is also shown that charge-state changes of C_I and Si_I can drastically enhance defect reactions such as the formation of antisite defects. Hence, a scenario is considered whereby EH7 involves C_I and becomes unstable when charge-state changes take place during the first DLTS scan. When excess C atoms are present, a competing generation of EH7 occurs and it can become the dominant process, as evidenced by results for the C implanted samples [Fig. 2(b) and Table I] and also supported by observations in samples grown with different C/Si ratios.[9] We also note that the strength of the residual EH7 peak after the first DLTS upscan in the N implanted samples [Fig. 2(a)] is comparable to that in the control sample.

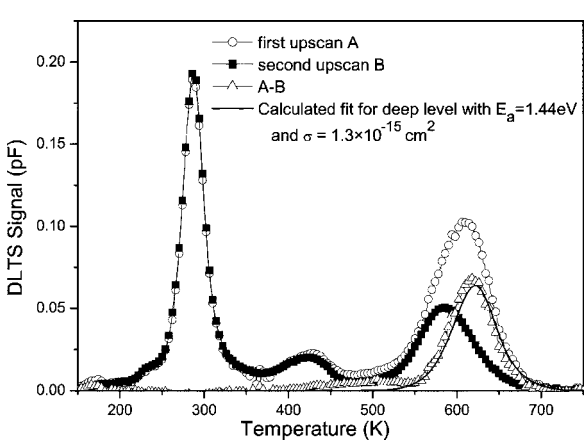

FIG. 3. DLTS spectra of SiC sample implanted with N to dose of 5×10^8 cm^{-2} and annealed at 1100 °C for 1 h.

Contrary to EH7, the peak amplitudes of $Z1/Z2$ and EH6 essentially remain constant in the N implanted samples during the different DLTS scans while an interplay is revealed between the peaks in the C implanted samples. Generally, the growth of the EH6/EH7 peak, which is mainly due to the generation of EH7 with some small contribution from EH6, is accompanied by loss in $Z1/Z2$. This may indicate that the gain in EH7 is due to the interaction of implanted C atoms with the $Z1/Z2$ centers. Further work is underway to provide quantitative evidence for this suggestion.[14]

In summary, by using low dose ion-implanted and annealed n-type 4H-SiC epitaxial layers, the EH6/EH7 peak has been studied in detail. The peak exhibits a substantial instability when the samples are subjected to an electric field at moderate temperatures (≈700 K). This holds especially for EH7 which is identified as a single level at $\approx E_C-1.44$ eV. During the first DLTS scan, EH7 drastically decreases in N implanted samples and slightly increases in C implanted samples. This irreversible instability is attributed to charge-state controlled annihilation and generation processes of EH7. The experimental data are consistent with an interpretation where EH7 is assigned to a defect structure involving interstitial C, possibly arising from an interaction between $Z1/Z2$ centers and excess C atoms.

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