# The effects of displacement threshold irradiation energy on deep levels in p-type 6H-SiC

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**Abstract.** We report on the electrical characterization, by means of deep level transient spectroscopy (DLTS), of electron irradiated Al-doped 6H-SiC epilayers. Samples were irradiated with either 116 keV, in order to displace only carbon atoms, or 400 keV and seven deep traps, in the 0.1-1.6 eV range above the valence band, were found. The thermal stability of the detected levels was analyzed by performing an isochronal annealing series in the 100-1800 $^{o}$C temperature range and the atomic structure of most of the detected traps was found to be related to C-displacement.

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## 1. Introduction

Despite its attractive physical and chemical properties [1], several factors still hinder the use of silicon carbide (SiC) as a replacement of Si for a wide range of electronic applications. For instance, cost has prevented SiC from being economically viable but, as it was recently reported [2], 6-inch SiC substrates with micropipe densities lower than 10 $mm^{-2}$ are expected to reduce manufacturing costs thus making SiC-based devices, such as diodes or bipolar transistors, more widely available.

Another issue is the presence of electrically active point defects. These defects, which are present in the as-grown material and can also be generated after particle irradiation, are a well-known cause for the malfunction of SiC electronic devices because they can act as recombination centers and decrease carriers lifetime. The $Z_{1/2}$ in $n-$type material is a notorious example of lifetime-killing defect and its electrical properties and atomic structure have been studied intensively in the past [3, 4, 5, 6, 7].

On the contrary, due to the difficulty of finding suitable ohmic contacts and because of lower doping activation percentage, not much effort was devoted to the study of electrically active point defects in $p-$type material. In the last few years, deep level transient spectroscopy (DLTS) studies performed on Al-doped 4H-SiC have appeared in the literature [8, 9, 10] and, recently, on 6H-SiC polytype, as well [11, 12, 13].

DLTS on as-grown [11] and high-energy electron irradiated [12] Al-doped 6H-SiC, have revealed the presence of several traps, but apart from the identification of the D-center and the B-acceptor, the microscopic nature of the other defects is still an unanswered question. In order to investgate the atomic structure of these defects, we carried out an electrical characterization study of p-type 6H-SiC epilayers irradiated with 116 keV (to displace only C atoms) or 400 keV electrons (to displace both C and Si atoms), because this method has proven helpful to unveil the nature of the detected defects [14, 15].

## 2. Experimental details

We employed 10 $\mu m$ thick Al-doped 6H-SiC epilayers ($N_a \sim 10^{16} cm^{-3}$) irradiated with an electron-beam of 116 or 400 keV at room temperature (dose $1 \times 10^{15} cm^{-2}$, irradiation time 8 min) by NHV Corp. (Kyoto, Japan). Prior to irradiation, a tri-layer of Ti/Al/Ni was deposited by thermal evaporation on the backside of the samples and then sintered for 10 min at $1000^o C$.

After irradiation, the samples underwent an isochronal annealing series(time step 15 min) from 100 to $1800^o C$ using either a rapid thermal annealing (RTA) furnace or a chemical vapor deposition (CVD) chamber, both in Ar flow, for heat treatments in the 100-1000 and 1100-$1800^o C$ range, respectively. For annealing at temperatures above $1100^o C$, a carbon cap was employed so to prevent surface decomposition. Each annealing step was followed by the deposition of Ti (diameter 1 $mm$) on the samples surface so to make electrical characterization by Fourier-Transform DLTS possible [16] (reverse bias 6 V, pulse voltage 0 V and filling pulse width 1 ms). Electrical characterization

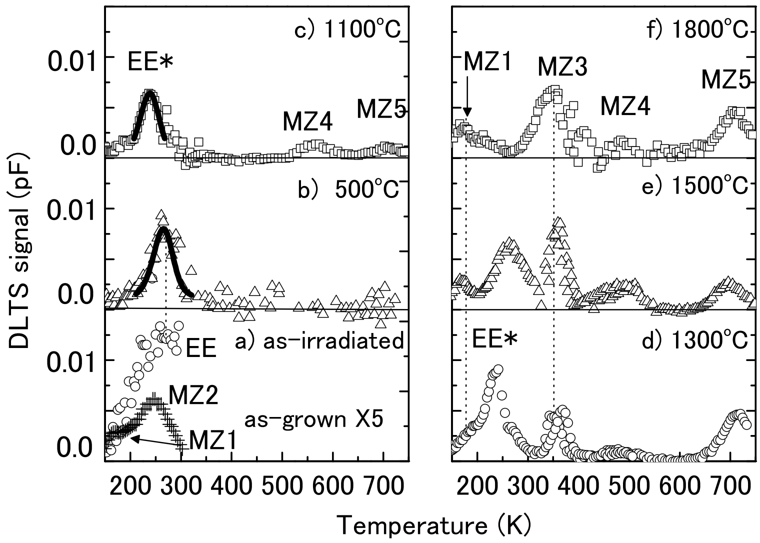


**Figure 1.** DLTS spectra of the (a) as-irradiated, (b) 500, (c) 1100, (d) 1300, (e) 1500 and (f) 1800 $^{o}$C annealed 116 keV electron irradiated samples (period width 0.2 s). In (a) the DLTS spectrum of the as-grown sample (magnified ×5) is added for comparison.

was performed in the 150-700 K range and for annealing temperatures up to $400^{o}C$ the highest temperature limit of the DLTS measurement was set so to coincide with the annealing temperature.

## 3. Results and discussion

Figure 1 shows the results of the DLTS measurements on the a) as-irradiated (and as-grown sample, for comparison), b) 500, c) 1100, d) 1300, e) 1500 and f) 1800 $^{o}C$ annealed samples after 116 keV $e^{-}$-irradiation, respectively.

In the as-grown sample, two levels are present, MZ1 and MZ2 [11] and after irradiation with 116 keV, only one level labelled EE could be detected at around $\sim$ 280 K. This level is thermally stable after heat treatment at $500^{o}C$ but is annihilated when the sample undergoes heat treatment at $1100^{o}C$. In fact, a new level arises at lower temperatures ($\sim$ $250K$), labelled EE* and the presence of a small shoulder-shaped peak at lower temperatures ($\sim$ 180 K) is revealed. In addition, two more DLTS peaks were found at around $\sim$ 500 and $\sim$ 700 K, which we identify as the MZ4 and MZ5, respectively [11]. Subsequent heat treatments (figure 1d) result in the formation of the MZ3 level, previously identified as the D-center [11]. The earlier mentioned shoulder peak, labelled as MZ1 [11] and identified as the B-acceptor, is now more clearly visible next to the EE* level. Annealing at $1600^{o}C$ results in the annihilation of the EE* level

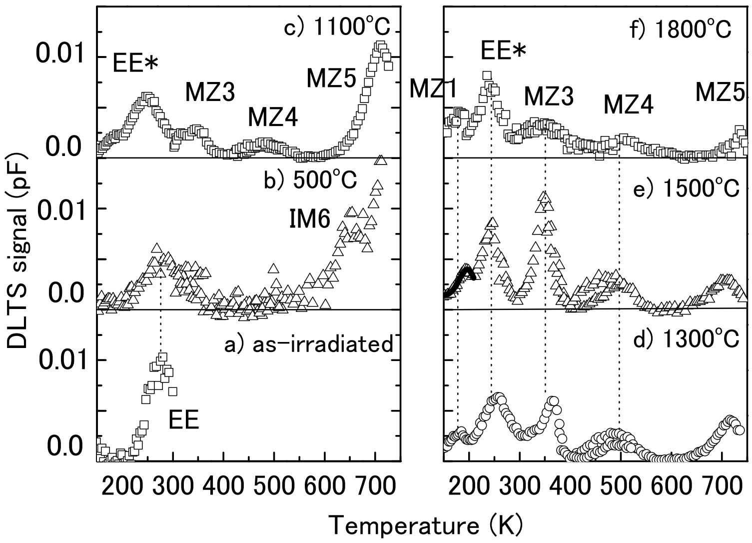


**Figure 2.** DLTS spectra of the (a) as-irradiated, (b) 500, (c) 1100, (d) 1300, (e) 1500 and (f) 1800 $^oC$ annealed 400 keV electron irradiated samples (period width 0.2 s).

while MZ1, MZ3, MZ4 and MZ5 are still present even after $1800^oC$.

The DLTS spectra of the 400 keV $e^-$-irradiated samples, are presented in figure 2. In figure 2a, the EE level could be detected in the as-irradiated sample and heat treatments at $500^oC$ (Fig.2b) result in the formation of a defect, in the shape of a shoulder of a bigger DLTS peak that was not detectable due to the temperature limit set in our DLTS measurement. This shoulder has the same thermal stability and energy position of a level detected in 1 MeV $e^-$-irradiated 6H-SiC and thus identified as the IM6 center [12]. Similarly to the 116 keV irradiated sample, also for the 400 keV irradiates sample, annealing at 1100 $^oC$ gives rise to the EE*, MZ4 and MZ5 levels but, in the present case, the MZ1 and MZ3 are more clearly distinguishable. Defects detected after subsequent heat treatments at higher temperatures (figure 2d) show high thermal stability up to 1800 $^oC$.

The energy position in the band gap above the valence band ($E_V$) and capture-cross sections of the detected levels are reported in Table 1 and due to a rather poor DLTS signal-to-noise ratio we employed a fitting procedure for the FT-DLTS peaks [16] in order to obtain more reliable values of the energy position in the bandgap and capture cross section for the EE, EE* and MZ1 levels (solid lines in figures 1b, 1c and figure 2e).

In figure 3, the isochronal annealing behavior of the EE and EE* traps is shown. It can be seen that both EE and EE* display similar concentration values after irradiation with either 116 or 400 keV electrons, with the exception of EE* which, in the case of the 116 keV irradiation, anneals out at 1600 $^o$ C. This annealing behavior was modelled according to a first-order annealing process (see Ref. [10] for details) with an activation

**Table 1.** Labeling, energy position above $E_V$ and capture cross section ($\sigma$) for the seven detected levels.

| Label | Energy (eV) | $\sigma$ ($cm^2$) | Comments |
|---|---|---|---|
| EE | 0.31±0.03 | $\sim 2 \times 10^{-17}$ | Anneals out below 1100 $^o$C |
| EE* | 0.28±0.08 | $\sim 2 \times 10^{-16}$ | Stable up to 1800 $^o$C after 400 keV irradiation |
| MZ1 | 0.21±0.09 | $\sim 3 \times 10^{-16}$ | Stable up to 1800 $^o$C |
| MZ3 | 0.57±0.09 | $\sim 10^{-16}$ | Stable up to 1800 $^o$C |
| MZ4 | 0.66±0.05 | $\sim 10^{-10}$ | Stable up to 700 $^o$C |
| MZ5 | 1.60±0.12 | $\sim 10^{-12}$ | Stable up to 1800 $^o$C |
| IM6 | 1.20±0.45 | $\sim 3 \times 10^{-13}$ | Anneals out below 1000 $^o$C |

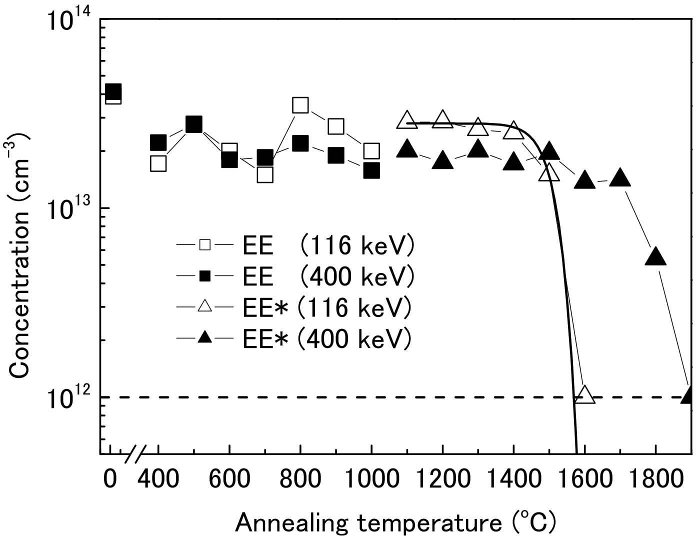


**Figure 3.** Isochronal annealing behavior of the EE and EE* traps for the 116 and 400 keV electron irradiated samples. The time step was of 15 min. The solid line represents a first order annealing process with an activation energy of 4.8 eV and a pre-exponential factor of $10^{13}s^{-1}$. Dashed line represents the detection limit.

energy of 4.8 eV.

We now proceed to discuss the nature of the detected defects so to possibly find the presence of C-related defects in $p-$type 6H-SiC. To do this, we compare the results of the present study with those of previous experimental and theoretical studies found in the literature, as DLTS does not provide any direct information on the microscopic structure of the detected levels.

It can be noted that all the reported levels, with the exception of EE and EE*, have already been detected in either as-grown or 1 MeV $e^-$-irradiated material and their nature discussed in detail. However, we can benefit from the results of the present study to either support or amend the previous conclusions and we start our discussion from

EE and EE*, because the existence of shallow levels in p-type SiC is still an unsolved riddle for theoreticians. Experimental results claimed the such shallow levels could be associated to complexes involving vacancies and doping atoms [17]. However, according to theory, complexes such as $Al_{Si}V_C$ or either $B_{Si}C_i$ are located well above $E_V + 0.5$ eV, thus excluding the possible participation of dopants in the microscopic structure of such levels [17]. This also applies to the levels reported in the present study, EE ($E_V + 0.31$ eV) and EE* ($E_V + 0.28$ eV).

EE ($E_V + 0.31$ eV) has a very similar energy position of two levels reported in 4H-SiC ($E_V + 0.37$) by Matsuura et al. [18] who did not comment on its microscopic structure. A carbon cluster, $(C_i)_2$ can be a possible candidate for the EE center: In fact, Bockstedte et al. [19] predicted $(C_i)_2$ to be located at cubic sites (6H-SiC has a cubic to hexagonal site ratio of 2:1) and located at $E_V + 0.38$ eV which is very similar to that of EE and Gali et al. predicted that such cluster should anneal at around 900 $^oC$ [20], which is still the case.

EE* ($E_V + 0.28$ eV) arises after annealing at temperatures above $900^oC$ and as it can be seen from figure 2, EE* anneals out after heat treatments at $1600^oC$ in the 116 keV while it is still present after annealing at 1800 $^oC$, in the 400 keV irradiated sample. This different annealing behavior can be explained if the EE* level is associated with the $V_CSi_C$ center because this complex is predicted to anneal out at $1600^oC$ with an activation energy of 4.4 eV [21], which is close to that estimated in figure 3. On the contrary, for the 400 keV irradiated sample, while the $V_CSi_C$ complex may also break up, the surplus of Si interstitials created by irradiation is such that Si atoms migrate and occupy empty C-sites (which have a very high thermal stabiliy) and consequently build up new $V_CSi_C$ centers.

Regarding the nature of those levels common to either as-grown or 1 MeV $e^-$-irradiated material, the MZ4 level may be too shallow to be related to Al and since it is present after 116 keV $e^-$-irradiation, has high thermal stability and a very close energy position to the Hp1 level found by Storasta et al. [22], after 200 keV $e^-$-irradiation in 4H-SiC, we believe that C may be involved in its microscopic structure. The involvement of Al in the microscopic structure of the detected defects, may be invoked for the case of the deepest level, the MZ5 level ($E_V + 1.6eV$) for which $Al_{Si}V_C$ can be a suitable candidate, as theory predicts that this level has very high thermal stability (at least $1700^oC$) and a level in the gap at $E_V + 1.5$ eV [17]. The nature of the IM6 level was tentatively associated to the $V_CC_{Si}$ center [12], yet, as Umeda et al. [23] have reported, when the annealing of such center occurs also the $V_C$ should anneal out, while in the present case, only the IM6 anneals out and no other DLTS peak.

It should not be surprising that most of the levels in the present study may be C-related: In fact, in $p-$type material the presence of C-related point defects (e.g, vacancies) is more energetically favorable than that of Si [24]. Moreover, the annealing mechanisms of point defects in $p-$type are different from those that occur in $n-$type. In fact, in p-type SiC, C Frenkel-pairs are positively charged and cannot recombine so, by migrating, they can be trapped by doping or build up clusters [19]. The same applies to Si Frenkel pairs for which, the migration/recombination energy is higher than that for transformation and, as a result, $V_{Si}$ transforms into a $V_C C_{Si}$ complex [19]. This leads us to the question of reproducibility: How different should experimental conditions be, so that similar studies yield different results?

In the study by Luo et al. [13], like in the present one, Cree epilayers with the same doping concentration were irradiated with 400 keV electron energy. However, differently from what expected, striking differences in the DLTS results could be noted, as Luo et al. [13], with the exception of the MZ4 level, reported fewer levels and with lower thermal stability than those found in the present study. Indeed, the different irradiation doses and sample preparation (different annealing time steps) may play a role because these can influence the average distribution and concentration of defects, affecting the vacancy-interstitial recombination/diffusion.

For example, under particular conditions (irradiation dose and/or annealing time) $V_{Si}$ may arise which, due to its instability, transforms into a low thermally stable $V_C C_{Si}$ complex. When this complex anneals out, so does also $V_C$ [23]thus explaining why no defect survives 1600$^o$C annealing. Furthermore, the use of Au Schottky diodes by Luo et al. [13], in contrast to Ti used in the present study, may also contribute to explain the differences, as in $p-$type 6H-SiC Au has a smaller Schottky barrier than Ti [25] which should yield a higher leakage current and worsening of the signal-to-noise ratio, making the detection of minor DLTS peak difficult.

## 4. Conclusions

In conclusion, we identified seven levels in the 0.21-1.6 eV range above $E_V$, in $p-$type 6H-SiC epilayers, after irradiation with 116 or 400 keV. The microscopic structure of all of the detected levels, with the exception of MZ1 and IM6, was related to carbon displacement and the discrepancies with a similar study were explained by invoking the presence of the $V_{Si}$ whose annealing mechanism in $p-$type material follows a different path than that of $n-$type.

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