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Kyoto University
High-temperature annealing behavior of deep levels in 1 MeV electron irradiated p-type 6H-SiC

Giovanni Alfieri1,a and Tsunenobu Kimoto1,2

1Department of Electronic Science and Engineering, Kyoto University, Kyotodaigakaku-katsura, Nishikyo, Kyoto 615-8510, Japan
2Photonics and Electronics Science and Engineering Center, Kyoto University, Kyotodaigakaku-katsura, Nishikyo, Kyoto 615-8510, Japan

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We report on the thermal stability of deep levels detected after 1 MeV electron irradiated p-type 6H-SiC. The investigation was performed by deep level transient spectroscopy, and an isochronal annealing series was carried out in the 373–2073 K temperature range. We found seven traps located between 0.23 and 1.3 eV above the valence band edge ($E_V$). Two traps anneal out at temperatures below 1273 K, while the others display a high thermal stability up to 2073 K. The nature of the detected traps is discussed on the basis of their annealing behavior and previous data found in the literature. © 2008 American Institute of Physics. [DOI: 10.1063/1.2964184]

In the past few years, a number of investigations aimed to understand the nature of electrically active defects in n-type 4H-SiC have been performed,1,5 and only recently, a few reports on p-type 4H-SiC have appeared in the literature.6–8 Analogously, only scarce information can be found in the literature on p-type 6H-SiC.9–11 and despite a few studies on defects detected after particle irradiation/implantation of p-type 6H-SiC,12,13 no investigations on defects generated after high energy electron irradiation, for temperatures higher than 873 K, are reported in the literature.

For these reasons, we present the results of our study on the isochronal annealing behavior in the 373–2073 K range of electrically active defects generated in 1 MeV electron irradiated p-type 6H-SiC. We have detected seven deep levels, five of which show a high thermal stability up to at least 2073 K and their nature is discussed in the light of the previous theoretical and/or experimental reports found in the literature. However, the previous studies on particle irradiated/implanted p-type 6H-SiC date back to 1999, and due to the recent progress of SiC epitaxial growth techniques and improvement of epitaxial layer quality,14 we found several discrepancies between our data and those of the aforementioned reports. Therefore, by assuming the energy alignment of the valence bands ($E_V$) among the different SiC polytypes,15,16 we could compare our results with more recent studies performed on electron irradiated p-type 4H-SiC.

The starting material was Al-doped p-type 6H-SiC epitaxial layers, grown on p-type substrates purchased from Cree. The net acceptor concentration and thickness were about 10¹⁶ cm⁻³ and 10 µm, respectively. A Ti/Al/Ni layer sintered at 1273 K was employed as backside Ohmic contacts, and the epilayer surface was irradiated with 1 MeV electrons (irradiation time: 8 min, dose: $1 \times 10^{15}$ cm⁻²) by NHV Corp. (Kyoto, Japan). Epilayers were annealed in the 373–2073 K temperature range for 15 min, using a chemical vapor deposition reactor with an Ar flow and after every heat treatment, and Schottky diodes were prepared by thermal evaporation of Ti on the epilayers. Samples were characterized by Fourier transform deep level transient spectroscopy (DLTS) in the 200–750 K range, by setting the reverse bias voltage to 10 V with a pulse voltage and width of 0 V and 1 ms, respectively, and a period width of 0.2 s. For heat treatments up to 673 K, the higher temperature limit of the DLTS measurement was set to the annealing temperature in order to avoid any unintentional annealing of minor species during the scan.

In Fig. 1, the results of the DLTS measurements on the electron irradiated 6H-SiC samples after different heat treatments are shown. A total of seven levels could be detected, and their labeling and energy position in the band gap are reported in Table I. The energy positions were determined by assuming a temperature-independent capture cross section. In Fig. 1(a), for the as-irradiated sample, hints of an unresolved DLTS peak can be seen at temperatures lower than 200 K and only after further heat treatment at 373 K could we reveal the presence of a level located at ~260 K, labeled E1 ($E_V$+0.48 eV), which is thermally stable up to 573 K. After heat treatment at 673 K, two new levels arise at ~310 and ~600 K, labeled E2 ($E_V$+0.52 eV) and IM6 ($E_V$+0.68 eV). Two traps anneal out at 1273, 1373, 1773, and 2073 K, respectively, and only after further heat treatment at 373 K could we reveal the presence of a level located at ~260 K, labeled E1 ($E_V$+0.48 eV), which is thermally stable up to 573 K. After heat treatment at 673 K, two new levels arise at ~310 and ~600 K, labeled E2 ($E_V$+0.52 eV) and IM6 ($E_V$+0.68 eV).

![DLTS spectra of 1 MeV electron irradiated 6H-SiC](image)

**Fig. 1.** DLTS spectra of 1 MeV electron irradiated 6H-SiC for (a) as-irradiated, 573 K, 673 K, and 1173 K, and (b) 1273, 1373, 1773, and 2073 K annealed samples. Solid lines represent a single DLTS peak simulation.

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*a*Electronic mail: giovanni@semicon.kuee.kyoto-u.ac.jp.
at a higher temperature of 1773 K. This shoulder was identified as MZ5 after high temperature heat treatments but it can be reproduced by a DLTS simulation using its experimental parameters. The simulation of the EI2 peak detected after annealing at 1273 K clearly shows the presence of a shoulder at ~360 K, which can be better resolved after annealing at a higher temperature of 1773 K. This shoulder was identified as the MZ3 center ($E_V + 0.55$ eV). The detection of RE2, MZ3, and MZ4 after high temperature heat treatments can be explained in terms of diffusion of carbon vacancies and/or interstitial, which can either aggregate, giving rise to clusters, or be trapped by dopants, giving rise to complexes.

The next step for the complete characterization of the detected traps is the identification of their microscopic nature. Due to the scarcity of studies on irradiated/implanted $p$-type 6H-SiC, and more generally on $p$-type materials, this turns out to be a rather challenging task. However, an isochronal annealing study can give useful information on the nature of the hitherto mentioned centers.

In Fig. 2 we show the isochronal annealing behavior for the most thermally stable traps found in our study, namely, EI2, RE2, MZ3, MZ4, and MZ5. On the contrary, the EI1 level may be related to a different defect. Indeed, the multiple-step isochronal annealing behavior of EI2 is an indication of the complex nature of this center. The MZ3 center, similar to what has been observed in the as-grown material, could be detected after annealing at temperatures above 1273 K. This level was identified as the D center, and its nature is still a matter of discussion even though it is thought to be a complex involving boron, either B$_{Si}$C or BC-.

The MZ4 displays a gradually decreasing concentration with increasing annealing temperatures, and its energy level is close to that of the Hp1 level reported in 4H-SiC. However, Rybicki$^{10}$ also reported the presence of a level at $E_V + 0.69$ eV in both as-grown and ion irradiated $p$-type 6H-SiC. The MZ4 could also be detected in the as-grown material, and for this reason, we believe that the MZ4 level is the same level detected by Rybicki, who suggested an Al-related complex to explain the nature of this center. The deepest level, the MZ5 level, is close in energy position to the as-grown material.

### Table I. Labeling, energy position above $E_c$, and condition for detection for the seven detected levels.

<table>
<thead>
<tr>
<th>Label</th>
<th>Energy$^a$ (eV)</th>
<th>Comments</th>
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<tr>
<td>EI1</td>
<td>0.48 ± 0.03</td>
<td>Annals out below 673 K</td>
</tr>
<tr>
<td>EI2</td>
<td>0.52 ± 0.08</td>
<td>Stable up to 2073 K</td>
</tr>
<tr>
<td>IM6</td>
<td>1.2 ± 0.07</td>
<td>Annals out below 1273 K</td>
</tr>
<tr>
<td>RE2</td>
<td>0.23 ± 0.04</td>
<td>Stable up to 2073 K</td>
</tr>
<tr>
<td>MZ3</td>
<td>0.55 ± 0.07</td>
<td>D center</td>
</tr>
<tr>
<td>MZ4</td>
<td>0.64 ± 0.07</td>
<td>Present in the as-grown material</td>
</tr>
<tr>
<td>MZ5</td>
<td>1.3 ± 0.1</td>
<td>Present in the as-grown material</td>
</tr>
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$^a$Above $E_c$. 

+1.2 eV), respectively. Higher heat treatments up to 1173 K show that while the EI2 is still persistent, no hints of the IM6 level can be seen. A DLTS peak with a maximum at ~720 K was detected and identified as MZ5 ($E_V + 1.3$ eV). This peak could not be completely resolved due to the temperature limitation of our DLTS system, but the complete shape could be obtained by simulating the DLTS signal.

In Fig. 1b, after annealing at 1273 K, two new levels can be detected and identified as RE2 ($E_V + 0.23$ eV) (Ref. 12) and MZ4 ($E_V + 0.64$ eV). The MZ4 peak is rather weak, but it can be reproduced by a DLTS simulation using its experimental parameters (period width, energy position, and concentration). The simulation of the EI2 peak detected after annealing at 1273 K clearly shows the presence of a shoulder at ~360 K, which can be better resolved after annealing at a higher temperature of 1773 K. This shoulder was identified as the MZ3 center ($E_V + 0.55$ eV). The detection of RE2, MZ3, and MZ4 after high temperature heat treatments can be explained in terms of diffusion of carbon vacancies and/or interstitial, which can either aggregate, giving rise to clusters$^{18}$, or be trapped by dopants, giving rise to complexes$^{19}$.

The next step for the complete characterization of the detected traps is the identification of their microscopic nature. Due to the scarcity of studies on irradiated/implanted $p$-type 6H-SiC, and more generally on $p$-type materials, this turns out to be a rather challenging task. However, an isochronal annealing study can give useful information on the nature of the hitherto mentioned centers.

In Fig. 2 we show the isochronal annealing behavior for the most thermally stable traps found in our study, namely, EI2, RE2, MZ3, MZ4, and MZ5. On the contrary, the EI1 level is close in energy position to the as-grown material (concentration of $1.5 \times 10^{13}$ cm$^{-3}$ after annealing at 373 K) and IM6 ($9 \times 10^{13}$ cm$^{-3}$ at 673 K) anneal out at 673 and 1273 K, respectively. No presence of the EI1 center could be found in previous reports although Ghaffour et al.$^{11}$ found a level, labeled Di1, at $E_V + 0.49$ eV in an implanted $n^p$-junction diode. However, we can exclude the possible identification of the EI1 center with the Di1 level because of the different temperature positions of the EI1 DLTS peak maximum. The relatively low thermal stability of the EI1 center may be explained by invoking the participation of a silicon vacancy ($V_{Si}$) in the nature of this defect. In fact, theoretical studies suggested that in electron irradiated $p$-type 4H-SiC, the annealing of $V_{Si}$ occurs at 623 K.$^{18}$ In our case, the annealing of the EI1 level occurs in the 573–673 K temperature range, suggesting that $V_{Si}$ may play a role in the atomic structure of EI1.

The IM6 levels were previously detected in hydrogen implanted 4H-SiC,$^5$ but no hypothesis was put forward to explain its nature. The DLTS peak temperature position of IM6 is close to that of the HK4 center observed in electron irradiated $p$-type 4H-SiC,$^7$ but a possible identification with this center can be ruled out since the HK4 and IM6 have different thermal stabilities, indicating that they may be two defects of different nature. On the contrary, the annealing temperature of IM6 agrees with that of a $V_{C-Si}$ related complex which has been detected in $p$-type 4H-SiC.$^{20}$

The RE2 level, which is stable up to 2073 K, was found by Reshanov et al.$^{12}$ in He implanted $p$-type 6H-SiC, and due to its vicinity to the Al acceptor, it was believed that its nature was related to a complex involving an Al atom. Its annealing behavior follows a multiple-step annealing pattern, with a plateau in the 1473–1873 K range, which has been observed also for the case of the $Z_{1/2}$ center after high-energy electron irradiation$^2$ and associated with complexes. Also, the RE2 center appears after relatively high temperature annealing and this behavior may support the idea that the nature of the RE2 center is likely to be related to a complex. The EI2 level displays a similar behavior: its concentration increases at 1073 K and after reaching a constant value in the 1073–1573 K range decreases again. We could not find any evidence of this center in the literature, therefore we cannot draw any conclusion on its microscopic identification. Its energy position is quite close to that of the UK2 center ($E_V + 0.58$ eV) observed in electron irradiated $p$-type 4H-SiC,$^7$ but the UK2 center anneals out below 1673 K; thus, the EI2 level may be related to a different defect. Indeed, the multiple-step isochronal annealing behavior of EI2 is an indication of the complex nature of this center. The MZ3 center, similar to what has been observed in the as-grown material, could be detected after annealing at temperatures above 1273 K. This level was identified as the D center,$^7$ and its nature is still a matter of discussion even though it is thought to be a complex involving boron, either B$_{Si}$C or BC-$V_c$.

The MZ4 displays a gradually decreasing concentration with increasing annealing temperatures, and its energy level is close to that of the Hp1 level reported in 4H-SiC by Storasta et al.$^6$ However, Rybicki$^{10}$ also reported the presence of a level at $E_V + 0.69$ eV in both as-grown and ion irradiated $p$-type 6H-SiC. The MZ4 could also be detected in the as-grown material, and for this reason, we believe that the MZ4 level is the same level detected by Rybicki, who suggested an Al-related complex to explain the nature of this center.

The deepest level, the MZ5 level, is close in energy position to the as-grown material.
to the HK3 level in 4H-SiC and shares a close annealing trend to that of MZ4, in the 1373–2073 K temperature range, suggesting that these two centers may have a similar atomic structure.

In conclusion, we have detected seven electrically active levels in the 0.23–1.3 eV range above \( E_V \) in 1 MeV electron irradiated \( p \)-type 6H-SiC, and we studied their thermal stability by carrying out an isochronal annealing series up to 2073 K. Their energy positions and annealing behavior were compared to those of centers already reported in the literature, including the 4H-SiC polytype, and we reported on the high thermal stability of several deep levels as well as the presence of the D center.

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