

The effects of illumination on deep levels observed in as-grown and low-energy electron irradiated high-purity semi-insulating 4H-SiC

G. Alfieri, L. Knoll, L. Kranz, and V. Sundaramoorthy

ABB Corporate Research, Segelhofstrasse 1K, 5405 Baden-Dättwil, Switzerland

(Received 23 January 2018; accepted 19 April 2018; published online 4 May 2018)

High-purity semi-insulating 4H-SiC can find a variety of applications, ranging from power electronics to quantum computing applications. However, data on the electronic properties of deep levels in this material are scarce. For this reason, we present a deep level transient spectroscopy study on HPSI 4H-SiC substrates, both as-grown and irradiated with low-energy electrons (to displace only C-atoms). Our investigation reveals the presence of four deep levels with activation energies in the 0.4–0.9 eV range. The concentrations of three of these levels increase by at least one order of magnitude after irradiation. Furthermore, we analyzed the behavior of these traps under sub- and above-band gap illumination. The nature of the traps is discussed in the light of the present data and results reported in the literature. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5023337>

I. INTRODUCTION

Silicon carbide (SiC) is a very promising candidate for the replacement of Si for power electronic applications. High-purity semi-insulating (HPSI) 4H-SiC is typically employed in order to reduce the parasitic capacitance which is detrimental for the correct functionality of electronic devices. The semi-insulating properties are achieved by vanadium doping, either by introducing V during growth or by implantation. Vanadium is an amphoteric impurity which gives rise to a donor and an acceptor in the lower and upper parts of the band gap, respectively. However, since V has a low solubility, HPSI SiC can also be obtained by point defect engineering. Kaneko *et al.*¹ have shown that, by irradiating n-type 4H-SiC with 400 keV electrons ($\sim 2 \times 10^{18} \text{ cm}^{-2}$), a resistivity higher than $10^{10} \Omega \text{ cm}$ could be obtained. This was attributed to the increased presence of carbon vacancies (V_C), namely, the $Z_{1/2}$ level, located at 0.68 eV below the conduction band edge (E_C), which is the lifetime killer in n-type 4H-SiC. Also, Son *et al.*² have shown, by electron paramagnetic resonance (EPR), that V_{Si} and the carbon vacancy-carbon antisite ($V_C C_{Si}$) complex are also suitable candidates for achieving semi-insulating properties. Based on this finding, it was suggested that appropriate growth conditions can give rise to those defects necessary for obtaining semi-insulating 4H-SiC.

HPSI SiC has been employed for radiation detectors^{3,4} but also for photoconductive semiconductor switches (PCSS).^{5,6} For the latter case, carriers are generated by a light trigger and a photocurrent is then detectable. By employing light in the 532 and 1064 nm range, charge carriers have been generated⁵ and the higher the photon energy, the higher the photocurrent. This was attributed to the presence of traps, like the V acceptor levels, that do not ionize for wavelengths longer than 532 nm.⁵

More recently, HPSI SiC has attracted the interest of researchers for solid-state qubit applications^{7,8} as it was found that, by high-energy irradiation, it was possible to engineer an ultra-bright single photon emitter at room temperature.⁹

These studies have shown that HPSI SiC is responsive to optical excitation, possibly due to the presence of defects that become ionized under illumination. However, unlike semi-conducting 4H-SiC for which electrically active levels have been thoroughly studied,^{11–13} not much is known on this topic in HPSI 4H-SiC and whether or not these levels are affected by optical excitation.

Deep level transient spectroscopy investigation (DLTS), in the current mode, performed on 360 μm thick HPSI 4H-SiC substrates, revealed the presence of two electrically active levels with activation energies of 0.33 and 1.29 eV, respectively, thermally stable up to 1700 °C.¹⁰ It was also shown that, under constant illumination, two more levels could be found.¹⁰ An admittance spectroscopy study¹⁴ showed the presence of five traps in the 0.27–1.06 eV energy range above the valence band edge (E_V). Based on the annealing behavior and previous reports on semiconducting 4H-SiC, Iwamoto *et al.*¹⁴ attributed the nature of the detected levels to V_C -related defects.

In the present investigation, we report on the electrical characterization of HPSI 4H-SiC by means of current-mode DLTS. These measurements were carried out in the dark and under illumination (sub- and above-band gap light) in order to find out whether or not point defects are affected by optical excitation. Furthermore, we electrically characterized a low-energy electron irradiated material, so to displace only C atoms and verify the presence of C-related defects in HPSI 4H-SiC.

II. EXPERIMENTAL DETAILS

500 μm thick 4-in. on-axis HPSI 4H-SiC (0001) substrates (resistivity $10^7 \Omega \text{ cm}$), purchased from NORSTEL, have been electrically characterized by Fourier-transform current-mode deep level transient spectroscopy (I-DLTS).¹⁵ Similar to what has been reported in the literature,^{10,14} I-V measurements, performed in the dark and at room temperature [Fig. 1(a)], reveal that our substrates possess p-type conductivity. Diodes had a leakage current of $\sim 300 \text{ pA}$ for a reverse bias (V_r) of 2 V, at room temperature. Two sets of $1 \times 1 \text{ cm}^2$

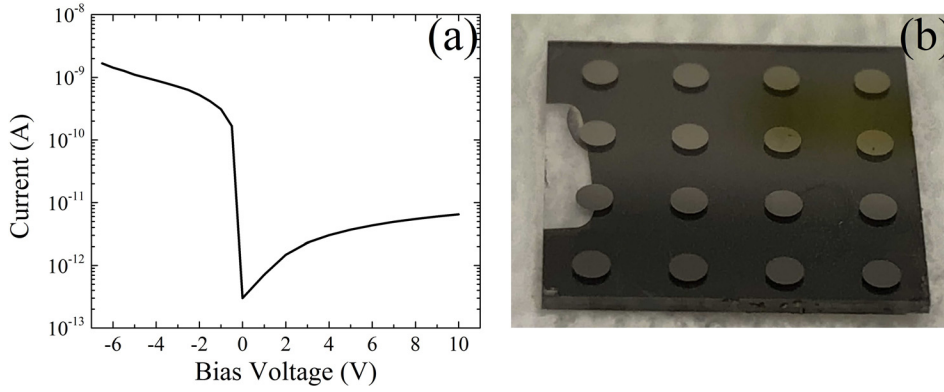


FIG. 1. (a) Photograph of the HPSI 4H-SiC $1 \times 1 \text{ cm}^2$ samples employed in this study. The 1 mm diameter Ti Schottky contacts are visible in the front, while the black area is due to the Ti/Al bilayer on the backside. (b) I-V characteristic of the Ti Schottky diodes, measured in the dark at RT.

samples [Fig. 1(b)] were prepared, as-grown and electron irradiated. Electron irradiation was carried out at the Risø High Dose Reference Laboratory of the Technical University of Denmark, using an energy of 116 keV (dose 10^{15} cm^{-2}) on the Si-face, in order to displace only C-atoms. Both sets have been annealed in the 1000–1800 °C temperature range for 30 min. For heat treatments above 1100 °C, a graphitic cap was employed to avoid surface roughness by Si desorption. The graphitic cap was then removed by O_2 plasma ashing. Samples underwent again a cleaning procedure and a Ti/Al ohmic contact (annealed at 1000 °C) was deposited on C-face and 1 mm Ti Schottky contact was deposited on the Si-face [Fig. 1(b)]. For the irradiated samples, the Ti/Al contact was formed prior to electron irradiation. Electron irradiation was carried out on the bare side. I-DLTS was performed in the 150–520 K temperature range in order to keep the leakage current below 1 mA, which would otherwise affect the measurement. Samples were kept under reverse bias ($V_r = 2 \text{ V}$), and for the measurements in the dark, a filling pulse to 0 V for 1 ms was employed, whereas for measurement under illumination, an optical pulse of 100 ms was used. Two different wavelengths were employed: above band gap UV light (355 nm, 30 mW) and below band gap (405 nm, 650 nm, 30 mW). I-DLTS, performed using UV light, does not allow the distinction between majority and minority carrier traps¹⁶ so, unless stated otherwise, we will report the trap activation energy without any reference to either valence or conduction band.

III. RESULTS AND DISCUSSION

In Fig. 2, the I-DLTS spectra as-grown HPSI 4H-SiC are shown, in the dark and under illumination. In dark conditions, the electrical characterization reveals the presence of one level, labeled SA1 with an energy position in the band gap of $E_V + 0.9 \text{ eV}$, capture cross section of $3.5 \times 10^{-16} \text{ cm}^2$ and concentration of $1.7 \times 10^{15} \text{ cm}^{-3}$. When the measurement is performed by using sub-band gap illumination, three new traps are found, SA2, SA3, and SA4 at $\sim 220 \text{ K}$, $\sim 240 \text{ K}$, and $\sim 340 \text{ K}$, respectively. We point out that SA4 is in the form of a shoulder peak, meaning that the estimation of the energy position in the band gap will be affected by a large error. These traps possess an activation energy of 0.46 eV (capture cross section of $\sim 10^{-14} \text{ cm}^2$), 0.48 eV ($\sim 10^{-14} \text{ cm}^2$), and 0.59 eV ($\sim 10^{-15} \text{ cm}^2$), respectively. The same traps are found also after above-band gap (355 nm) illumination, with a higher I-DLTS signal. As a matter of fact, compared to 405 nm

(650 nm) illumination, the concentration increases almost one order of magnitude, from $6 \times 10^{12} \text{ cm}^{-3}$ ($3 \times 10^{11} \text{ cm}^{-3}$) to $2 \times 10^{13} \text{ cm}^{-3}$ for SA2, from $7.5 \times 10^{12} \text{ cm}^{-3}$ ($5 \times 10^{11} \text{ cm}^{-3}$) to $2.1 \times 10^{13} \text{ cm}^{-3}$ for SA3, and from $1 \times 10^{13} \text{ cm}^{-3}$ ($5 \times 10^{12} \text{ cm}^{-3}$) to $9 \times 10^{13} \text{ cm}^{-3}$ for SA4. After annealing at 1800 °C, it can be seen that SA1, SA2, and SA3 are still detected without any significant change in concentration, whereas SA4 anneals out at $> 1500 \text{ °C}$.

After low energy electron irradiation, the I-DLTS spectrum of HPSI 4H-SiC, under dark conditions, shows the presence of the SA1 level (Fig. 3). This level displays a similar concentration to the as-grown sample ($\sim 1.3 \times 10^{15} \text{ cm}^{-3}$). Electrical characterization with sub- and above-band gap illumination shows an increased concentration for both the SA2 and SA3 levels. For 405 nm (650 nm) illumination, SA2 becomes $3 \times 10^{14} \text{ cm}^{-3}$ ($1 \times 10^{13} \text{ cm}^{-3}$) and SA3 $5 \times 10^{14} \text{ cm}^{-3}$ ($5 \times 10^{13} \text{ cm}^{-3}$). For above band gap illumination, SA2 is $8 \times 10^{14} \text{ cm}^{-3}$ and SA3 is $1 \times 10^{15} \text{ cm}^{-3}$. Also SA4 shows the same pattern.

As our results show, the spectra detected under UV illumination do not differ from those obtained by sub-band gap illumination. This means that the reported activation energies can be referred to E_V (see Table I).

In order to explain the reason for the lack of difference between the spectra detected with UV or sub-band gap light, we carried out a 1-D simulation.¹⁷ In Fig. 4, the band

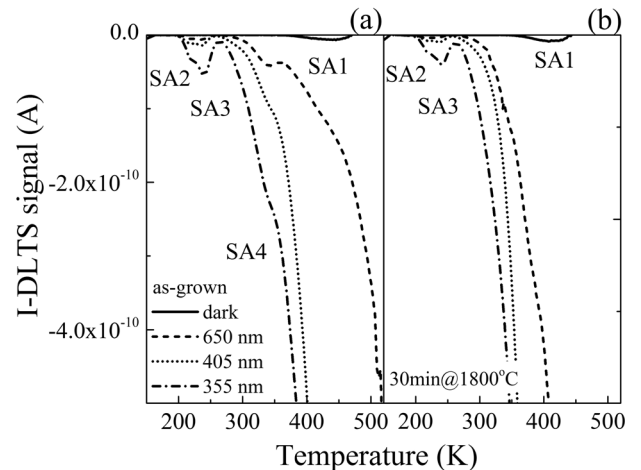


FIG. 2. I-DLTS spectrum of the (a) non-annealed and (b) 1800 °C annealed as-grown HPSI 4H-SiC, using an electrical pulse (1 ms) or an optical pulse (100 ms) with 650, 405, or 355 nm light. The period width is 0.2 s.

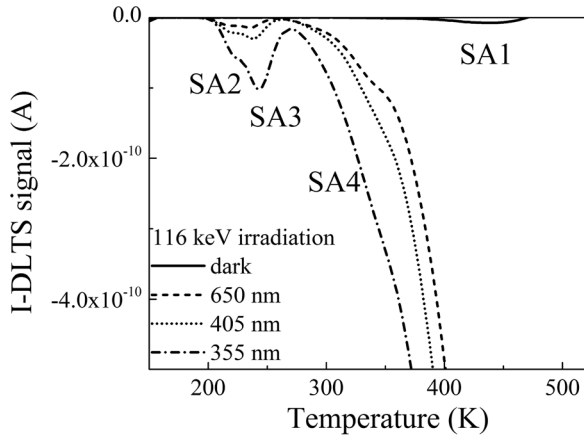


FIG. 3. I-DLTS spectrum of the 116 keV electron irradiated HPSI 4H-SiC, using an electrical (1 ms) or an optical (100 ms) pulse. Light of 650, 405, and 355 nm wavelength was employed. The period width is 0.2 s.

diagram for a 2 V reverse biased Schottky diode, in dark and under UV illumination. We employed a resistivity of $10^7 \Omega \text{ cm}$, a penetration depth of $100 \mu\text{m}$ for the 355 nm wavelength,¹⁸ and a trap (E_T) located at 0.46 eV above the valence band edge (E_V). In the dark, E_T lies below the quasi Fermi levels of holes, F_p [Fig. 4(a)]. For this reason, E_T is mainly filled with electrons. Under UV illumination [Fig. 4(b)], the photon energy is enough to produce electron-hole pairs, so there is an increased concentration of holes in the valence band and electrons in the conduction band. This is evident from the modified position of F_n and F_p . The UV illumination is also able to ionize E_T , that is, priming E_T of the electrons. Such electrons can be emitted to the conduction band. When the UV illumination is turned off [Fig. 4(a)] and since E_T is below F_p , the primed E_T will need to be filled with electrons. This will be done by trapping (emitting) electrons (holes) from (to) the valence band. A similar explanation can be carried out in order to account for the I-DLTS spectrum detected under illumination with sub-band gap light. As the photon energy is not enough to generate electron-hole pairs, no difference in the band diagrams between dark and illumination with sub-band gap light is seen. Thus, Fig. 4(a) represents the reverse biased Schottky diode with and without sub-band gap illumination. When no light pulse is employed, E_T is mainly filled with electrons, as it lies below F_p . When sub-band gap light is used, the photon energy is enough to prime E_T of electrons. In particular, for 650 nm illumination, these electrons will possibly be trapped by another center, e.g., the positive charge state

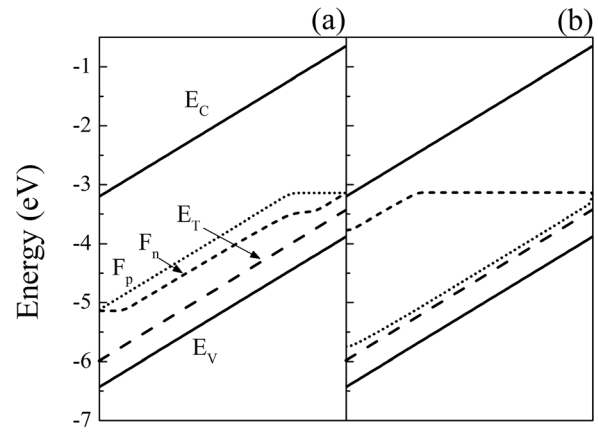


FIG. 4. Band diagram of a Schottky diode on HPSI 4H-SiC under reverse bias (2 V) for (a) dark or 405 nm illumination and (b) 355 nm illumination. The Ti Schottky barrier height is 1.9 eV . E_T is the trap, and F_n and F_p are the quasi-Fermi levels for electrons and holes, respectively. The horizontal axis represents the width of the space charge region.

of V_C located at mid-gap ($E_C - 1.6 \text{ eV}$), as the photon energy is not enough to excite these electrons to the conduction band. When the sub-band gap light is turned off, E_T will trap (emit) electrons (holes) from (to) the valence band.

Regarding the nature of the detected traps, little can be said about it due to the scarce information available in the literature on the characterization of HPSI 4H-SiC. In the as-grown material, Son *et al.*² have reported the presence of a deep level with an activation energy of $\sim 0.9 \text{ eV}$. However, the authors reported an n -type conductivity for their HPSI 4H-SiC, meaning that the measured activation energies refer to E_C . In the present case, our HPSI SiC has p -type conductivity, so the SA1 level is referred to E_V . For this reason, the SA1 level has an energy position in the band gap which is close to that of HK2, detected by Danno¹¹ in p -type 4H-SiC. The identification of SA1 as the HK2 is also supported by the fact that both levels are thermally stable up to at least 1500°C , that they are found in the as-grown as well as in the low energy electron irradiated material, and that no clear increase in the concentration of HK2 is seen after electron irradiation. Thus, it is reasonable to associate the microscopic structure of SA1 to a Si-related defect. As a matter of fact, the SA1 shares a similar energy position in the band gap to that of the doubly negative charge state of the silicon vacancy (V_{Si}), as reported by Torpo *et al.*,¹⁹ it is thermally stable²⁰ and its concentration is not affected by low-energy electron irradiation. As for the SA2 and SA3, these two levels have very similar activation energies which, based on the results of our simulations above, can be referred to E_V . Since no similar traps have been detected in p -type 4H-SiC,¹¹ it is difficult to draw any conclusion on their nature. However, Bockstedte *et al.*²¹ have reported that positive charged carbon di-interstitials [$(Csp)_2$] are located in the $0.4\text{--}0.5 \text{ eV}$ range, above E_V . This energy range is very close to that of the SA2 and SA3 levels. Di-interstitials possess also a high dissociation energy ($4\text{--}5 \text{ eV}$),²¹ which can explain the high thermal stability of both SA2 and SA3. For the SA4 level, we put forward the hypothesis of the identification with the divacancy ($V_{Si}V_C$).²² Torpo *et al.*²² have predicted the

TABLE I. Label, activation energy (referred to E_V), capture cross section and conditions for detection for the levels detected in this study.

Label	Activation energy (eV)	Capture cross section (cm^2)	Condition
SA1	0.90 ± 0.05	$(3.5 \pm 0.02) \times 10^{-16}$	As-grown, dark
SA2	0.46 ± 0.04	$(1.4 \pm 0.08) \times 10^{-14}$	As-grown/irradiation, illumination
SA3	0.48 ± 0.04	$(2 \pm 0.1) \times 10^{-14}$	As-grown/irradiation, illumination
SA4	0.59 ± 0.09	$(9.8 \pm 0.3) \times 10^{-16}$	As-grown/irradiation, illumination

presence of negatively charged $V_{Si}V_C$ between 0.52 and 0.69 eV above E_V , for $V_{Si}V_C$ at hexagonal or cubic (or mixed hexagonal/cubic) sites. This agrees well with the measured energy position in the band gap of SA4 ($E_V + 0.59$ eV). In addition, Son *et al.*²³ have shown that the dissociation of the $V_{Si}V_C$ starts at $\sim 1600^\circ\text{C}$. Indeed, we have found that the SA4 levels anneal out after heat treatments above 1500°C . We also note that recently, photoluminescence measurements of HPSI SiC, purchased from NORSTEL (like in our study), have shown that divacancies are affected by optical excitation.⁸

IV. CONCLUSIONS

Four electrically active levels have been detected in HPSI 4H-SiC, with activation energies in the 0.4–1 eV range, by using electrical or optical pulses (above or below the band gap). The analysis of the band diagram suggests that the levels with activation energies of 0.46, 0.48, and 0.59 eV are majority carrier traps; thus, their activation energy can be referred to the top of the valence band. Low energy electron irradiation, so to displace only C-atoms, shows an increase in concentration for three of the detected traps and their nature is associated with either carbon interstitials or carbon vacancies. As we have shown that illumination can affect traps in HPSI 4H-SiC, it is then suggested that care should be taken when optical UV characterization techniques are employed, e.g., microwave photoconductance decay for lifetime (τ) measurements. According to our results, electrically active levels, arising under UV illumination, might undermine the correct estimation of τ . This would make electrical measurements, such as open circuit voltage decay, more accurate in this case.

- ¹H. Kaneko and T. Kimoto, *Appl. Phys. Lett.* **98**, 262106 (2011).
- ²N. T. Son, P. Carlsson, J. ul Hassan, B. Magnusson, and E. Janzen, *Phys. Rev. B* **75**, 155204 (2007).
- ³K. C. Mandal, R. M. Krishna, P. G. Muzykov, S. Das, and T. S. Sudarshan, *IEEE Trans. Nucl. Sci.* **58**, 1992 (2011).
- ⁴K. C. Mandal, P. G. Muzykov, R. M. Krishna, and J. R. Terry, *IEEE Trans. Nucl. Sci.* **59**, 1591 (2012).
- ⁵J. S. Sullivan and J. R. Stanley, *IEEE Trans. Dielectr. Electr. Insul.* **14**, 980 (2007).
- ⁶S. Jiang, C. Song, L. Zhang, Y. Zhang, W. Huang, and H. Guo, *IEEE Trans. Electron Devices* **63**, 1582 (2016).
- ⁷W. F. Koehl, B. B. Buckley, F. J. Heremans, G. Calusine, and D. D. Awschalom, *Nature* **479**, 84 (2011).
- ⁸D. A. Golter and C. W. Lai, *Sci. Rep.* **7**, 13406 (2017).
- ⁹S. Castelletto, B. C. Johnson, V. Ivady, N. Stavrias, T. Umeda, A. Gali, and T. Oshima, *Nat. Mater.* **13**, 151 (2014).
- ¹⁰G. Alfieri, T. Kimoto, and G. Pensl, *Mater. Sci. Forum* **645–648**, 455 (2010).
- ¹¹K. Danno and T. Kimoto, *J. Appl. Phys.* **101**, 103704 (2007).
- ¹²M. A. Mannan, S. K. Chaudhuri, K. V. Nguyen, and K. C. Mandal, *J. Appl. Phys.* **115**, 224504 (2014).
- ¹³M. A. Mannan, K. V. Nguyen, R. O. Pak, C. Oner, and K. C. Mandal, *IEEE Trans. Nucl. Sci.* **63**, 1083 (2016).
- ¹⁴N. Iwamoto, A. Azarov, T. Ohshima, A. M. M. Moe, and B. G. Svensson, *J. Appl. Phys.* **118**, 045705 (2015).
- ¹⁵S. Weiss and R. Kassing, *Solid State Electron.* **31**, 1733 (1988).
- ¹⁶Z. Li, *Nucl. Instrum. Methods Phys. Res. A* **403**, 399 (1998).
- ¹⁷SimWindows, see www.simwindows.com for information and download of the software.
- ¹⁸T. Kimoto and J. A. Cooper, *Fundamentals of Silicon Carbide Technology* (Wiley, 2014).
- ¹⁹L. Torpo, M. Marlo, T. E. M. Staab, and R. M. Nieminen, *J. Phys.: Condens. Matter* **13**, 6203 (2001).
- ²⁰U. Gerstmann, E. Rauls, T. Frauenheim, and H. Overhof, *Phys. Rev. B* **67**, 205202 (2003).
- ²¹M. Bockstedte, A. Mattheusch, and O. Pankratov, *Phys. Rev. B* **69**, 235202 (2004).
- ²²L. Torpo, T. E. M. Staab, and R. M. Nieminen, *Phys. Rev. B* **65**, 085202 (2002).
- ²³N. T. Son, P. Carlsson, J. Ul Hassan, E. Janzen, T. Umeda, J. Isoya, A. Gali, M. Bockstedte, N. Morishita, T. Ohshima, and H. Itoh, *Phys. Rev. Lett.* **96**, 055501 (2006).