

Article

Properties of Z_1 and Z_2 Deep-Level Defects in n -Type Epitaxial and High-Purity Semi-Insulating 4H-SiC

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Abstract: For the first time, the Z_1 and Z_2 defects with closely spaced energy levels having negative- U properties are revealed in high-purity semi-insulating (HPSI) 4H-SiC using Laplace-transform photoinduced transient spectroscopy (LPITS). In this material, after switching off the optical trap-filling pulse, either the one-electron or the two-electron thermally stimulated emission from these defects is observed at temperatures 300–400 K. It is found that the former corresponds to the $Z_1^{0/+}$ and $Z_2^{0/+}$ transitions with the activation energies of 514 and 432 meV, respectively, and the latter is associated with the $Z_1^{-/+}$ and $Z_2^{-/+}$ transitions with the activation energies of 592 meV and 650 meV, respectively. The Z_1 and Z_2 defect concentrations are found to increase from 2.1×10^{13} to $2.2 \times 10^{14} \text{ cm}^{-3}$ and from 1.2×10^{13} to $2.7 \times 10^{14} \text{ cm}^{-3}$, respectively, after the heat treatment of HPSI 4H-SiC samples at 1400 °C for 3 h in Ar ambience. Using the electrical trap-filling pulse, only the thermal two-electron emission from each defect was observed in the epitaxial 4H-SiC through Laplace-transform deep level transient spectroscopy (LDLTS). The activation energies for this process from the Z_1 and Z_2 defects are 587 and 645 meV, respectively, and the defect concentrations are found to be 6.03×10^{11} and $2.64 \times 10^{12} \text{ cm}^{-3}$, respectively. It is postulated that the Z_1 and Z_2 defects are the nearest-neighbor divacancies involving the carbon and silicon vacancies located at mixed, hexagonal (h), and quasi-cubic (k) lattice sites.

Keywords: 4H-SiC; Z_1 and Z_2 defects; negative- U properties; LDLTS; LPITS



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1. Introduction

The Z_1 and Z_2 defect centers were detected for the first time by Hemmingsson et al. in n -type 4H-SiC epitaxial layers, grown through chemical vapor deposition (CVD), with the net donor concentration in the range of 2×10^{14} – $5 \times 10^{15} \text{ cm}^{-3}$ [1]. It is worth stressing that due to the small difference between the thermal electron emission rates, the time constants separation of the two exponential components associated with the electron emission from the Z_1 and Z_2 defects occurring in the capacitance relaxation waveforms measured in the range of 260–340 K was not possible through the correlation procedure applied in conventional deep level transient spectroscopy (DLTS). As a result of the strong overlapping of two DLTS signals, only one peak in the spectrum was observed, and to mark that the two kinds of defects contribute to the thermal electron emission, this peak was named $Z_{1/2}$. However, it was possible to resolve the two exponential components induced by the thermal emission of electrons from the Z_1 and Z_2 centers by direct fitting the capacitance relaxation waveforms with the sum of exponential functions [1]. In this way, the thermal activation energies for electron emission from the Z_1 and Z_2 centers were found to be 0.72 and 0.76 eV, respectively [1].

Additional measurements performed by Hemmingsson et al. indicated that when the sample was illuminated with 2.64 eV photons before each short (50 ns) voltage pulse filling

the defect centers in the space charge region, the two new peaks, associated with the two shallower donor levels $Z_1^{0/+}$ and $Z_2^{0/+}$, appeared in the DLTS spectrum, while merely the trace signal corresponding to the $Z_{1/2}$ peak was recorded [1]. The activation energies for the thermal electron emission leading to the $Z_1^{0/+}$ and $Z_2^{0/+}$ charge state changes were found to be 0.52 and 0.45 eV, respectively [1]. On the grounds of the DLTS results, a model attributing negative- U properties to the Z_1 and Z_2 defects was proposed [1]. It is worth adding that a defect has the negative- U properties if it can capture two electrons from the conduction band and the second is more strongly bound than the first [1–3]. A possible explanation for this phenomenon is that the energy gained through electron pairing combined with a lattice relaxation and/or a change in the atomic configuration in the defect's vicinity might overcome the Coulombic repulsion at the site. In this way, the effective net attraction needed to give a defect negative- U properties would arise [1–3]. According to the model, each of the Z_1 and Z_2 defects can capture two electrons, and the thermal emission of these electrons to the conduction band is reflected in the DLTS spectrum through the $Z_{1/2}^{-/+}$ peak [1,2]. This model also assumes that outside the area of the space charge layer, the Z_1 and Z_2 defects are singly positively ionized donors, and after capturing one electron, they become neutral [1]. As a result of capturing two electrons, they behave as negatively ionized acceptors. The illumination with 2.64 eV photons results in removing one electron, enabling, in this way, in the DLTS experiment, the transitions $Z_1^{0/+}$ and $Z_2^{0/+}$ to be observed [1,2]. It has been suggested that the Z_1 and Z_2 centers originate from the same point defect located at the hexagonal (h) and quasi-cubic (k) lattice sites, without specifying the defect type and its charge state [1].

On the grounds of the other model, based on the Laplace-transform DLTS (LDLTS) results combined with the calculations made using the density functional theory (DFT), the Z_1 and Z_2 centers are believed to be acceptors attributed to the carbon vacancy (V_C) located at the h and k sites of the 4H-SiC lattice, respectively [4]. Before filling with electrons in the LDLTS experiment, the $V_C(h)$ and $V_C(k)$ acceptors are neutral, and by capturing one or two electrons, they become singly negatively ionized, $V_C(h)^-$ and $V_C(k)^-$, or doubly negatively ionized, $V_C(h)^{2-}$ and $V_C(k)^{2-}$, respectively. The energy levels of the $Z_1^{-/0}$ and $Z_2^{-/0}$ transitions involving the one-electron thermal emission, identified with the $V_C(h)^{-/0}$ and $V_C(k)^{-/0}$ charge state changes, are located at 0.48 and 0.41 eV below the conduction band minimum (CBM), respectively [4]. The deeper energy levels of the $Z_1^{2-/0}$ and $Z_2^{2-/0}$ transitions, involving the two-electron thermal emission and identified with the $V_C(h)^{2-/0}$ and $V_C(k)^{2-/0}$ charge state changes, are located at 0.59 and 0.67 eV, respectively [4].

For over 25 years, the Z_1 and Z_2 defects have been observed in n -type epitaxial 4H-SiC through conventional DLTS as a single electron trap, labeled $Z_{1/2}$, with the activation energies 0.63–0.68 eV and concentrations in the range of 10^{12} – 10^{13} cm $^{-3}$ [5–9]. As a result of extensive investigations, several experimental facts have been established. Firstly, by using low-energy electron (100–200 keV) irradiation, it has been found that the $Z_{1/2}$ trap can be created through primary displacements of carbon atoms [8,9]. Secondly, it has been shown that in the 4H-SiC epilayers grown under C-rich conditions, the $Z_{1/2}$ trap concentration is clearly lower [5]. Thirdly, the $Z_{1/2}$ center has been found to be a thermally stable defect, as no changes in its concentration during annealing up to 1600 °C have been observed [7]. Furthermore, during the CVD growth at temperatures ranging from 1550 to 1750 °C and the C/Si ratio of 1.5, the $Z_{1/2}$ center concentration has been found to increase from $\sim 5 \times 10^{11}$ to $\sim 1 \times 10^{13}$ cm $^{-3}$, respectively, indicating that the interstitials' involvement in its formation is unlikely [7,9]. Fourthly, the possibility of removing the $Z_{1/2}$ center by implanting C $^+$ ions followed by annealing has been found [6]. It should be stressed that the most important results aiming at finding the atomic configuration of the $Z_{1/2}$ center were obtained by Son et al. [10], who used electron paramagnetic resonance (EPR) to determine the energy levels of V_C and revealed the defect's negative- U properties. By performing combined studies using EPR and DLTS, it was found that the most common defects occurring in epitaxial 4H-SiC, namely, the $Z_{1/2}$ and EH_7 centers, are related to the double acceptor level of V_C , corresponding to the (2–/0) charge state change, and to the single donor level of V_C ,

corresponding to the $(0/+)$ transition, respectively [10]. However, all of these experimental results do not allow for attributing unambiguously the $Z_{1/2}$ center to V_C or presenting an alternative atomic configuration for the center [5–10].

To obtain deeper insight into the Z_1 and Z_2 defects properties, we investigated the thermal electron emission from these defects in high-purity semi-insulating (HPSI) 4H-SiC wafers after filling them with the excess charge carriers generated by 3.31 eV photons. These unique studies were conducted using the Laplace-transform photoinduced transient spectroscopy (LPITS), which enabled the four deep levels for both defects to be resolved. In view of the LDLS results, the Z_1 and Z_2 electron traps represent the defects located at the h - and k -lattice sites, which means the activation energies for electron emission are slightly different and can be distinguished only through high-resolution spectroscopic techniques [4]. Apart from the activation energies and capture cross-sections, the concentrations of the Z_1 and Z_2 defects contributing to the one-electron thermal emission as well as the two-electron thermal emission are determined. The defects' properties and concentrations are compared for the pristine and annealed HPSI 4H-SiC samples. For comparison, the electronic properties and concentrations of the Z_1 and Z_2 defects are also studied in a nitrogen-doped epitaxial layer of 4H-SiC with a net donor concentration of $\sim 1.2 \times 10^{15} \text{ cm}^{-3}$. The results indicating the possible identification of the Z_1 and Z_2 defects with divacancies $V_C V_{Si}$ involving the neighboring carbon and silicon vacancies located at h - and k -sites of the 4H-SiC lattice are discussed.

2. Materials and Methods

The Z_1 and Z_2 defects were characterized in both conducting 4H-SiC epitaxial layers and semi-insulating wafers originating from a bulk crystal of HPSI 4H-SiC. The epitaxial layers were grown in an Epigress VP508 horizontal hot-wall chemical vapor deposition (CVD) reactor (Epigress, Lund, Sweden) using silane and propane as precursors. The layers with a thickness of $\sim 10 \text{ }\mu\text{m}$ were deposited in a flow of hydrogen, used as a carrier gas, at a temperature of $1600 \text{ }^\circ\text{C}$. The epitaxial growth was performed on standard epi-ready n -type 4H-SiC wafers with a net donor concentration of $\sim 2 \times 10^{18} \text{ cm}^{-3}$, oriented 4° off of the (0001) plane toward the [11–20] direction. The substrates of $15 \times 15 \text{ mm}^2$ in size were cut out from the wafers with a 4-inch diameter. The samples for the LDLS measurements were in the form of Schottky diodes with a 1 mm diameter, made by evaporating a 20 nm layer of Ti and a 150 nm layer of Ni on the epitaxial layers' surface for the Schottky contacts and by evaporating 4 nm of Ti and a 150 nm layer of Ni on the substrate back side for the Ohmic contacts. After the electrodes deposition, the samples were annealed at $500 \text{ }^\circ\text{C}$. To determine the net donor concentration ($n = N_D - N_A$) at room temperature (RT), the samples were initially characterized through capacitance–voltage (C - U) measurements.

For investigations of the Z_1 and Z_2 defects' properties and concentrations, the capacitance relaxation waveforms induced by the thermal electron emission were measured by means of the state-of-the-art experimental system built using a Boonton 7200 capacitance meter, a home-made compensator of the steady-state capacitance, a Janis nitrogen cryostat, and a LakeShore 340 temperature controller. The measurements were performed at a temperature range of 270–370 K with a temperature increment of 3 K. They were carried out at a constant reverse bias of -5 V and a filling pulse amplitude of 4 V. The filling pulse width was 100 μs , and the filling pulse repetition period was 100 ms. To extract the Z_1 and Z_2 defects' electronic properties from the temperature-induced changes in the capacitance relaxation waveforms, the two-dimensional (2D) analysis were used to transform the waveforms into the 2D spectra by means of both the correlation procedure and the numerical calculations based on the inverse Laplace transformation algorithm (ILT) implemented in the CONTIN code [11]. In this way, the temperature dependences of the emission rate (e_T) for the detected defects were found and visualized in the 3D space as the ridgelines of the folds in the surfaces created above the plane defined by the absolute temperature (T) and emission rate (e_T) axes. The temperature and emission rate values were taken from the ridgelines to draw the Arrhenius plots illustrating the dependences

of $\ln(T^2/e_T)$ versus $1/k_B T$, where k_B denotes the Boltzmann constant. The plots were in the form of straight lines, and the values of the electron emission activation energy E_a and pre-exponential factor A in the Arrhenius equation were calculated from the slope and intercept of each line, respectively, by means of linear regression. The electron capture cross-sections for the Z_1 and Z_2 defects were determined as $\sigma_n = A/\gamma_n$, where γ_n is the electron effective mass-dependent material constant, which, for 4H-SiC, was calculated to be equal to $2.51 \times 10^{21} \text{ cm}^{-2} \text{ s}^{-1} \text{ K}^{-2}$. For the convenience of the results presentation, the folds associated with the thermal electron emission were projected onto the plane defined by the (T, e_T) axes, and the ridgelines illustrating the temperature dependences of the emission rate for the Z_1 and Z_2 defects were depicted. The defects' concentrations were derived from the amplitudes of the two exponential components of the capacitance relaxation waveforms using the method typical of the DLTS technique [4,5]. However, assuming that the two-electron emission occurs from the Z_1 and Z_2 defects [1,4], the concentration values obtained in this way were divided in half.

The LPITS studies of the Z_1 and Z_2 defects' properties and concentrations were carried out using chips of $1 \times 1 \text{ cm}^2$ in size cut out from a HPSI 4H-SiC wafer with a thickness of 500 μm and a diameter of 100 mm supplied by Wolfspeed. The wafer was of “epi-ready” type with both sides perpendicular to the c -axis ($\langle 0001 \rangle$ direction). The surfaces of both sides were polished; however, the front surface of the wafer lying in the (0001) plane (Si-face) was especially prepared through mechano-chemical polishing (MCP) so that it could be directly used for epitaxy. The LPITS studies were performed using the pristine chips as well as the chips subjected to annealing at 1400 $^\circ\text{C}$ for 3 h in argon ambience at a pressure of 100 mbar. The samples were cooled from 1400 to 700 $^\circ\text{C}$ for 0.5 h and for 1 h from 700 $^\circ\text{C}$ to room temperature. It is worth adding that during the annealing, the morphology evolution of the (0001) plane surface took place. According to the results of atomic force microscopy (AFM) observation, the regularly stepped terraces were formed. The width, length, and height of adjacent terraces were (1–3) μm , (8–10) μm , and $\sim 1.3 \text{ nm}$, respectively. The surface roughness values (Ra), determined for the regions of $20 \times 20 \mu\text{m}^2$ on the pristine and annealed samples surfaces, were $2.09 \pm 0.2 \text{ nm}$ and $2.3 \pm 0.3 \text{ nm}$, respectively.

For the LPITS measurements, the arrays of co-planar contact pairs with an inter-distance of 0.7 mm were evaporated by using an electron-beam. The contacts, in the shape of the squares of $2.5 \times 2.5 \text{ mm}^2$ in size, were made using a 20 nm layer of Cr and a 200 nm layer of Au. After the deposition of contacts, the chips were diced into samples with dimensions of $4 \times 7 \text{ mm}^2$, which were used for the photocurrent transient measurements as well as for the measurements of the dark current and mobility–lifetime product temperature dependences. The photocurrent transients were measured in the range of 300–400 K with a temperature increment of 3 K. The pulses of 3.31 eV photons generating the excess electron–hole pairs were emitted using a semiconductor laser produced by Power Technology. The transients were amplified using a Keithley 428 fast current amplifier, operating as a conductance–voltage converter, and then digitized with a 12-bit amplitude resolution and a 1 μs time resolution. In order to improve the signal to noise ratio, the digitally recorded photocurrent transient resulted from averaging of 500 waveforms. The photon flux, the duration of the excitation pulses, and their repetition period were $\sim 1.9 \times 10^{18} \text{ cm}^{-2} \text{ s}^{-1}$, 50 ms, and 500 ms, respectively. The voltage applied between the two co-planar contacts separated by 0.7 mm was 20 V.

The properties of Z_1 and Z_2 defects were extracted from the temperature-induced changes in the photocurrent relaxation waveforms observed after switching off the UV pulse. The relaxation waveforms were analyzed under the assumption that the decay time of each waveform is much longer than the charge carrier's lifetime [12,13]. According to the assumed model, each relaxation waveform is described by the sum of the exponential components, whose the temperature-dependent time constants are equal to the reciprocals of the thermal emission rate of charge carriers for the defects contributing to the thermal emission process [12,13]. Therefore, the temperature dependences of the electron emission rate for the Z_1 and Z_2 defects, and, derived from these dependences, the defects' electronic

properties, were experimentally found by means of the 2D analysis of the photocurrent relaxation waveforms, performed in a similar way as in the case of the capacitance relaxation waveforms. The concentrations of the Z_1 and Z_2 defects were determined from the amplitudes of the exponential components of the photocurrent relaxation waveforms, assuming that the amplitudes are proportional to the concentrations' electrons trapped by the defects when the optical excitation pulse was switched off. The detailed description of the method used for deriving the concentrations of defect centers from LPITS measurements was published earlier [12].

The measurements of dark current as a function of temperature were carried out to compare the activation energy of dark conductivity (E_{ADC}) values for the pristine and annealed HPSI 4H-SiC samples. Because the resistivity of the samples at room temperature was of the order of $10^{11} \Omega\text{cm}$, the measurements were carried out in the broad temperature range of 300–700 K at an applied voltage of 20 V. The E_{ADC} values were determined from the slope of linear parts of the dark current characteristics plotted in coordinates of $\log(T^{3/2}/I)$ against $1000/T$, where T and I denote the absolute temperature and electrical current, respectively. The temperature dependences of the $\mu\tau$ product for both kinds of samples were also determined in the range of 300–700 K using the transient photocurrent method (TPM), based on the assumption that the $\mu\tau$ value at a given temperature is proportional to the amplitude of the photocurrent pulse when the optical pulse generating the excess charge carriers is terminated [14]. The $\mu\tau$ measurements were carried out at a voltage of 20 V and a possibly low flux of 3.31 eV photons, being $\sim 9.7 \times 10^{14} \text{ s}^{-1}\text{cm}^{-2}$, to minimize the effect of lifetime shortening by a higher concentration of the optically generated charge carriers [12].

3. Results

3.1. Properties and Concentrations of Z_1 and Z_2 Deep-Level Defects in Epitaxial 4H-SiC

The aim of the studies was to verify the earlier results obtained through LDITS that demonstrated the presence in lightly nitrogen-doped epitaxial 4H-SiC of two separate defects, Z_1 and Z_2 , with slightly different electronic properties instead of one deep-level defect, labeled $Z_{1/2}$ [4]. The resolution of the LDITS technique is much better than that of the conventional DLTS based on the correlation procedure in which the capacitance relaxation waveforms are analyzed in various emission rate windows [4,5]. Apart from the differences in the resolution of results obtained by means of the procedures based on the correlation and Laplace-transform algorithms, we demonstrate the advantage of the two-dimensional approach to the analysis of the temperature-induced changes in the capacitance relaxation waveforms. By using this approach, the waveforms can be transformed either into the correlation spectral surfaces or into the Laplace spectral surfaces, with the folds corresponding to the thermal emission of charge carriers from defect centers. The ridgelines of the folds occurring on the surfaces depict the temperature dependences of the thermal emission rate.

Figure 1a illustrates the broad correlation fold corresponding to the thermal electron emission from the $Z_{1/2}$ defect center. The center is observed as the electron trap T0, whose activation energy (E_a) and electron capture cross-section (σ_n), determined by means of fitting the ridgeline data with the Arrhenius equation, are 655 meV and $4.0 \times 10^{-15} \text{ cm}^2$, respectively. It is worth adding that the thermal electron emission from the $Z_{1/2}$ center was usually observed at 300–350 K, and the reported values of E_a and σ_n were in the ranges of 0.58–0.68 eV and 3.0×10^{-15} – $2.0 \times 10^{-14} \text{ cm}^2$, respectively [6–8]. Figure 1b shows the projection of the fold associated with the $Z_{1/2}$ center onto the plane defined by the temperature and emission rate. In this figure, the projection of the ridgeline more clearly visualizes the dependence of the thermal emission rate as a function of temperature for the $Z_{1/2}$ center. At temperatures of 310 and 360 K, the thermal electron emission rate values are around 32 and 1000 s^{-1} , respectively.

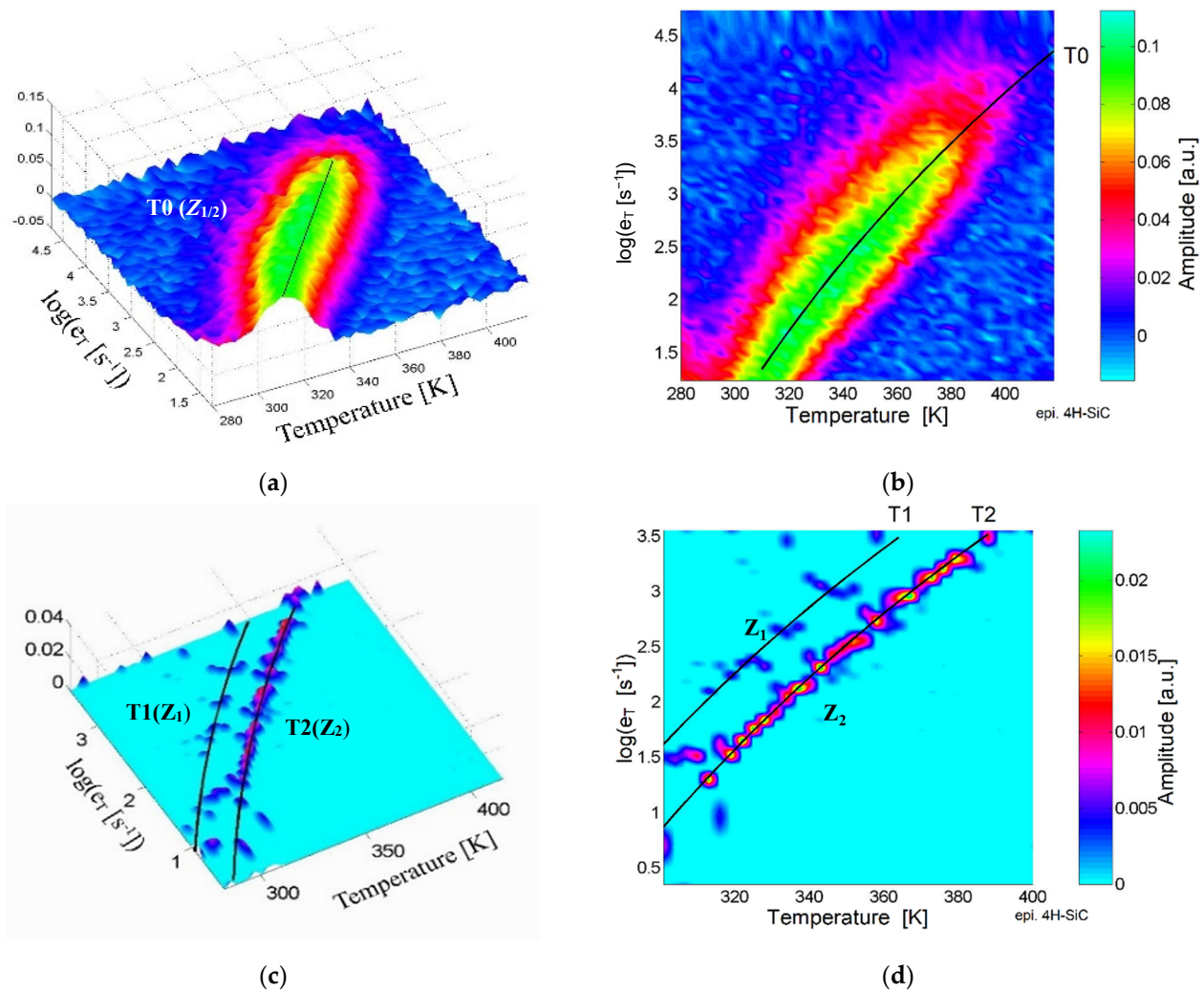


Figure 1. Correlation and Laplace spectra derived from the capacitance relaxation waveforms induced by thermal electron emission from Z_1 and Z_2 defects. (a) Correlation spectral surface visualized in the 3D space above the plane defined by the temperature (T) and emission rate (e_T) axes. (b) Projection of the correlation spectral surface on the (T, e_T) plane. (c) Sharp Laplace spectral surfaces for separated Z_1 and Z_2 defects visualized in the 3D space. (d) Projection of the Laplace spectral surfaces on the (T, e_T) plane. The black solid lines depict the ridgelines on the spectral surfaces and visualize the temperature dependences of the electron emission rate for the $Z_{1/2}$ and separated Z_1 (trap $T1$) and Z_2 (trap $T2$) defects, respectively.

It should be noted that the $Z_{1/2}$ electron trap is related to an apparent defect representing the resultant properties of the Z_1 and Z_2 defects, which have not been resolved for a long time. Therefore, the spread in the values of the $Z_{1/2}$ trap parameters reported in various studies may be due to different ratios of the Z_1 and Z_2 defects' concentrations in the 4H-SiC epitaxial layers in which the $Z_{1/2}$ trap properties were investigated. It is worth adding that the $Z_{1/2}$ trap was observed in the epilayers grown at various temperatures, C/Si ratios, and doping levels, as well as in the epilayers subjected to electron irradiation and ion implantation [5–9].

In all of these studies, the capacitance relaxation waveforms used for deriving the $Z_{1/2}$ trap parameters were non-exponential because they were the sums of two exponential components induced by the thermal electron emission from the Z_1 and Z_2 defects. Nonetheless, a number of valuable experimental results were obtained. In particular, on the grounds of the DLTS and electron paramagnetic resonance (EPR) results, performed using the samples of the same epilayers irradiated by low-energy electrons, it has been shown that the $Z_{1/2}$

trap and V_C are the dominant defects responsible for the charge compensation [8–10]. This fact allows us to postulate that the thermal emission of two electrons from the $Z_{1/2}$ center to the conduction band may be identified with the $V_C^{2-/0}$ transition. The energy level corresponding to the $V_C^{2-/0}$ charge state change, determined through photo-EPR, was found to be located with respect to the CBM at around only 0.2 eV deeper than that corresponding to the charge state change of the $Z_{1/2}$ center [8,10].

The Laplace spectral fringes for the Z_1 and Z_2 defects are visualized in the 3D space (Figure 1c) and on the plane defined by the temperature and emission rate (Figure 1d). It seems that there is an important difference between the correlation spectral surface for the $Z_{1/2}$ center and the separated Laplace spectral surfaces for the Z_1 and Z_2 defects. The latter are not continuous, and they consist of the spikes occurring at specific temperatures. Therefore, the ridgelines depicting the temperature dependences of the emission rate are determined by the positions of the spikes' tops. The solid lines drawn in Figure 1c,d illustrate the dependences of the Z_1 and Z_2 defects' emission rate as a function of temperature resulting from fitting the data with the Arrhenius equation

$$e_T(T) = AT^2 \exp(-E_a/k_B T). \quad (1)$$

For example, at 310 K, the thermal electron emission rate values for these defects are around 80 and 20 s^{−1}, respectively, and at 360 K, the e_T values increase up to 2512 and 400 s^{−1}, respectively. It is worth noting that the emission rate values at these temperatures for the $Z_{1/2}$ center lie in between those for the Z_1 and Z_2 defects. This fact is confirmed by the Arrhenius plots (Figure 2) received from the 2D Laplace spectra for the resolved Z_1 and Z_2 defects as well as from the 2D correlation spectrum for the $Z_{1/2}$ center.

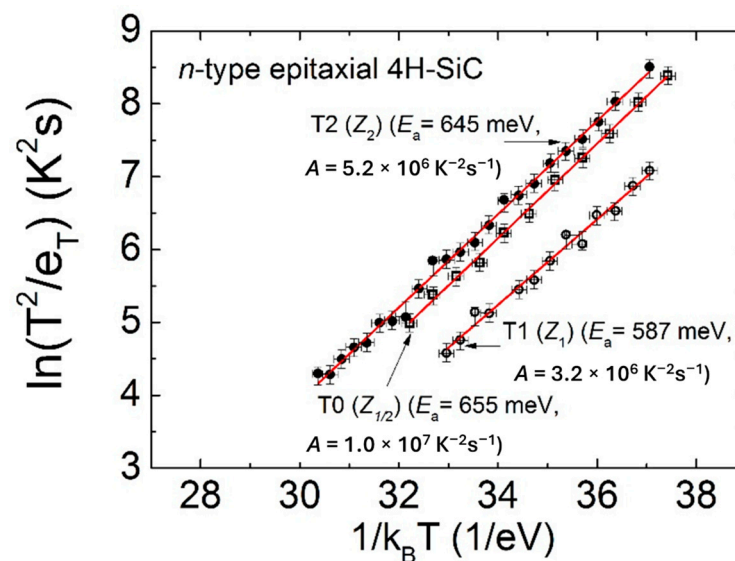


Figure 2. Arrhenius plots for thermal electron emission plotted for the $Z_{1/2}$ and separated Z_1 and Z_2 defects detected in *n*-type epitaxial 4H-SiC. The straight lines are fitted through linear regression to the experimental data taken from the ridgelines of spectral surfaces.

The Arrhenius plots for the Z_1 and Z_2 defects are distinctly separated in Figure 2, and the activation energy values, determined from the lines' slope, as well as the values of the pre-exponential factor in the Arrhenius equation, obtained from the lines' intercepts with the ordinate axis, are shown. For comparison, the Arrhenius plot for the $Z_{1/2}$ center is attached, and the center's parameters are given. It is seen that this plot lies only slightly below the plot for the Z_2 defect and clearly above the Arrhenius plot for the Z_1 center. Consequently, the values of the $Z_{1/2}$ center parameters are very close to those of the Z_2 defect, which means that the $Z_{1/2}$ center properties practically reflect the Z_2 center properties. This is because the Z_2 defect concentration in the material is several times

higher than that of the Z_1 center, and the contribution of the former to the electron thermal emission observed through the capacitance relaxation waveforms is predominant. It is worth noting that the much higher concentration of the Z_2 defect compared to that of the Z_1 center is well-visible in the Laplace spectral fringes shown in Figure 1c,d through the large difference between the fringes' amplitudes.

The properties and concentrations of Z_1 and Z_2 defects, derived from LDLS measurements utilizing the two-dimensional analysis of the capacitance relaxation waveforms, are summarized in Table 1. The presented values of the activation energy for thermal electron emission are in good agreement with those published by Capan et al. [4], also received through LDLS; however, these were obtained by using the one-dimensional computational procedure in the analysis of the capacitance relaxation waveforms. The latter values for the Z_1 and Z_2 defects are 590 and 670 meV, respectively [4]. It is worth stressing that there is excellent agreement between the ratio of the Z_2 and Z_1 defects' concentrations ($[Z_2]/[Z_1]$) given in Table 1 and that reported by Capan et al. [4]. The $[Z_2]/[Z_1]$ values are 4.38 and 4.4, respectively. The substantial difference between the concentrations of defects strongly suggests that they originate from different kinds of defects and they are not related to the same defect occurring in different charge states. In other words, they are a pair of various point defects with closely spaced energy levels in the 4H-SiC bandgap.

Table 1. Activation energies (E_a), pre-exponential factors in the Arrhenius equation (A), and apparent capture cross-sections (σ_n) for Z_1 and Z_2 defects in n -type epitaxial 4H-SiC as well as the defects' concentrations (N_T) revealed by means of LDLS.

Trap	E_a (meV)	A ($K^{-2}s^{-1}$)	σ_n (cm^2)	N_T (cm^{-3})	Defect
T1	587 ± 10	$(3.2 \pm 1) \times 10^6$	1.24×10^{-15}	6.03×10^{11}	Z_1
T2	645 ± 10	$(5.2 \pm 1) \times 10^6$	2.05×10^{-15}	2.64×10^{12}	Z_2

On the grounds of earlier DLTS results, the Z_1 and Z_2 defects were proposed to possess the negative- U properties [1], which means that each of these defects before capturing electrons acts as a singly positively ionized donor and during the experiment it captures one or two electrons, becoming the neutral donor or singly ionized acceptor, respectively. According to the model presented by Hemmingsson et al. [1], the defects' properties given in Table 1 may be associated with the thermal emission of two electrons, resulting in the $Z_1^{-/+}$ and $Z_2^{-/+}$ charge state changes. It was suggested that the two-electron emission processes occur in two stages. First, there is a single thermal electron emission leading to the $(- / 0)$ charge state change, and next the $(0 / +)$ transition occurs [1]. The activation energies for the two-electron emission leading to the $Z_1^{-/+}$ and $Z_2^{-/+}$ transition were found to be 0.72 and 0.76 eV, respectively [1]. These values are likely to be overestimated because they were derived from direct fitting the capacitance relaxation waveforms with two exponential signals at the fixed relation between these signals' amplitudes [1]. According to the model put forward by Capan et al. [4], the two-electron thermal emission from the Z_1 and Z_2 defects is related to the $Z_1^{2- / 0}$ and $Z_2^{2- / 0}$ charge state changes. This means that before capturing two electrons in the LDLS experiment, the defects are neutral acceptors and, as a result of filling with electrons during the measurements, they become double negatively ionized. Taking into account the theoretical considerations indicating that the $Z_1^{2- / 0}$ and $Z_2^{2- / 0}$ charge state transitions follow those predicted for the negative- U ordered acceptor levels of V_C , as well as a number of experimental results obtained for the $Z_{1/2}$ center properties, the Z_1 and Z_2 defects were proposed to be identified with the carbon vacancies, being the nearest neighbors occupying the hexagonal (h) and quasi-cubic (k) lattice sites ($V_C(h)$ and $V_C(k)$), respectively [4,9,10].

3.2. Properties and Concentrations of Z_1 and Z_2 Deep-Level Defects in HPSI 4H-SiC

Figure 3a shows the Laplace spectral fringes obtained through the two-dimensional analysis of the photocurrent relaxation waveforms for a sample of HPSI 4H-SiC, which

was not subjected to the heat treatment. As it can be seen, in the semi-insulating bulk material apart from the two traps T1 and T2, which were found in the epitaxial 4H-SiC and identified with the two-electron emission from the Z_1 and Z_2 defects, an additional two traps, labeled T1A and T2A, are detected. It is worth noting that the fringes for the latter traps are located above those for the T1 and T2 traps, which means that the thermal emission rate values for the T1A and T2A traps are higher. In other words, the activation energies for thermal emission of charge carriers from these traps are lower than that from T1 and T2 traps. The proximity of the fringes for these traps to those for the T1 and T2 traps indicates that although the thermal emission from the shallower T1A and T2A traps comes to be observable at the lower temperatures, in the range of 320–360 K, the fringes for all of the traps are well-resolved, and the differences in the thermal emission rate values are clearly seen. This fact means that within these temperatures, the photocurrent relaxation waveforms are composed of the four exponential signals, and the temperature changes in the time constants of these signals are well-resolved.

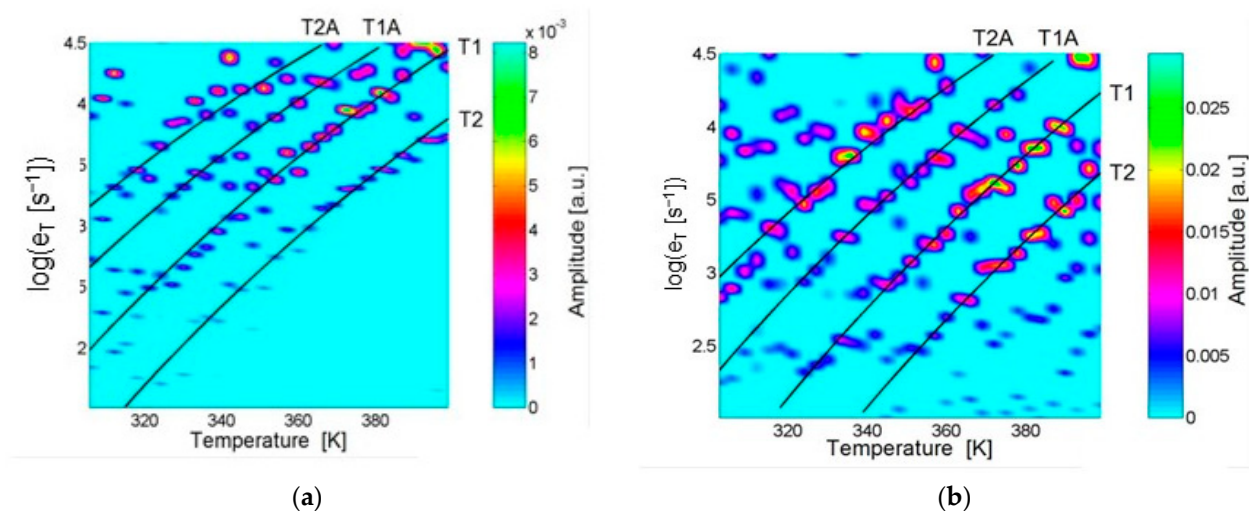


Figure 3. Laplace spectral fringes for the thermal emission of charge carriers from the T1, T2, T1A, and T2A traps related to the various charge state changes of Z_1 and Z_2 defects in HPSI 4H-SiC. **(a)** The fringes for the defects detected in the pristine material. **(b)** The fringes for the defects in the material subjected to the heat treatment at 1400 °C for 3 h in Ar atmosphere. The solid lines illustrating the temperature dependences of the emission rate are described using the Arrhenius equation and result from fitting the fringes' data by means of least squares.

Figure 3b shows the Laplace spectral fringes used to determine the temperature dependences of the charge carriers' emission rate for the T1, T2, T1A, and T2A traps detected in a sample of HPSI 4H-SiC after annealing at 1400 °C for 3 h in Ar ambience. The emission rate temperature changes shown in Figure 3a,b can be well-exemplified by the values in the range of 340–360 K. With increasing temperature from 340 to 360 K, the e_T values for the T1 and T2 traps rise from 700 ± 82 to 2800 ± 325 and from 180 ± 21 to 570 ± 65 s^{−1}, respectively. For the T1A and T2A traps, the e_T values go up from 3600 ± 409 to 9000 ± 1028 and from 9000 ± 1050 to $23,000 \pm 1584$ s^{−1}, respectively. These data indicate that within the error margin not exceeding $\pm 12\%$ the same emission rate values are determined for the T1, T2, T1A, and T2A traps detected in the pristine HPSI 4H-SiC as well as in the annealed material. On the other hand, the significantly higher amplitudes of the fringes for these traps in the latter material, clearly visible in Figure 3, allow us to assume that the traps' concentrations are much higher in the material subjected to the heat treatment.

The Arrhenius plots of the four traps detected in the HPSI 4H-SiC, received from the $e_T = f(T)$ dependences shown in Figure 3, are presented in Figure 4. The straight lines shown in this figure for the T1 and T2 traps excellently match the lines drawn in Figure 2 using the

results of LDLS measurements performed for the *n*-type epitaxial 4H-SiC samples. It is well-visible that the former represent the extensions of the former for the higher emission rate values determined at higher temperatures. Arrhenius plots are defects' signatures, and this fact proves that the T1 and T2 traps are related to the same kinds of defects present in both crystals obtained using different methods. In other words, these traps are observed either through the photocurrent relaxation or capacitance relaxation due to the two-electron thermal emission from the Z_1 and Z_2 defects. This result is of great importance, for it indicates that the two-electron thermal emission from these defects is not affected by the electric field strength. It should be noted that in the LDLS experiment, before the emission the defects are filled with the electrons being the equilibrium majority charge carriers in the material, while during the LPITS measurements they capture the electrons which are optically generated excess charge carriers. It is worth adding that in the LDLS experiment, the thermal electron emission took place in the space charge layer at the electric field of $\sim 5 \times 10^4$ V/cm, while the LPITS measurements were carried out in the bulk material at the electric field of $\sim 3 \times 10^2$ V/cm.

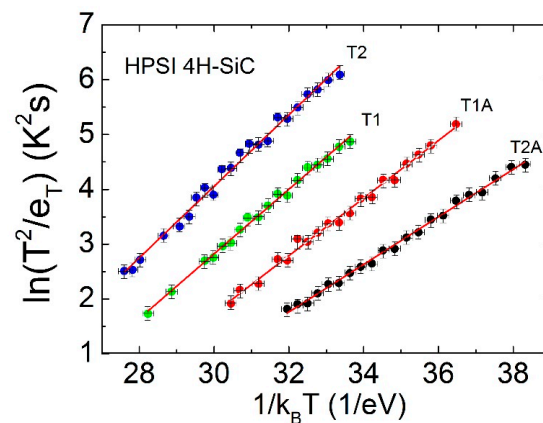


Figure 4. Arrhenius plots for thermal electron emission associated with various charge state changes of the Z_1 and Z_2 defects detected in pristine and annealed HPSI 4H-SiC. The plots for T1 and T2 traps reflect the emission rate temperature dependences for the two-electron thermal emission from the Z_1 and Z_2 defects, while those for the T1A and T2A traps depict the dependences for the one-electron thermal emission from these defects. The straight lines are fitted through linear regression to the experimental data taken from the Laplace spectral fringes shown in Figure 3.

The slopes of the lines corresponding to the T1, T2, T1A, and T2A visible in Figure 4 perfectly confirm the fact that the Z_1 and Z_2 defects are negative- U centers in 4H-SiC. In other words, they show that the activation energies for electron thermal emission from the defects that captured two electrons are higher than those that captured only one electron. The accurate values of the thermal electron emission activation energy (E_a), pre-exponential factor (A) in the Arrhenius equation, and apparent electron capture cross-section, as well as the Z_1 and Z_2 defects' concentrations, participating in the two- and one-electron emission in the pristine and annealed HPSI 4H-SiC samples, are listed in Table 2. The results in Table 2 are interpreted following the model presented in Ref. [1], according to which, before trapping electrons, the Z_1 and Z_2 defects are positively charged donors and, after the capture of two electrons, the defects become singly ionized acceptors (traps T1 and T2). As a result of trapping one electron, they become electrically neutral (traps T1A and T2A). According to the results shown in Figures 3 and 4, the thermally induced charge state transitions occur in the comparatively narrow temperature range, from 300 to 400 K. Furthermore, at each temperature within this range, the one-electron emission is much faster compared to that when two electrons are emitted, which is reflected in the lower activation energies of the T1A and T2A traps.

Table 2. Electronic properties and concentrations determined for Z_1 and Z_2 defects detected in either pristine or annealed at 1400 °C for 3 h in Ar atmosphere HPSI 4H-SiC.

Trap	$E_a(\text{meV})$	$A (\text{K}^{-2}\text{s}^{-1})$	$\sigma_n (\text{cm}^2)$	$N_T (\text{cm}^{-3})$		Defect Transition
				Pristine	Annealed	
T1	592 ± 10	$(4.3 \pm 1.0) \times 10^6$	$(1.7 \pm 0.4) \times 10^{-15}$	2.1×10^{13}	2.2×10^{14}	$Z_1^{-/+}$
T2	650 ± 10	$(7.3 \pm 1.5) \times 10^6$	$(2.9 \pm 0.6) \times 10^{-15}$	1.2×10^{13}	2.7×10^{14}	$Z_2^{-/+}$
T1A	514 ± 10	$(1.1 \pm 0.4) \times 10^6$	$(4.4 \pm 1.4) \times 10^{-16}$	1.9×10^{13}	1.7×10^{14}	$Z_1^{0/+}$
T2A	432 ± 10	$(1.9 \pm 0.4) \times 10^5$	$(7.6 \pm 1.4) \times 10^{-17}$	9.6×10^{12}	1.0×10^{14}	$Z_2^{0/+}$

It is easy to notice that in the pristine and annealed materials, there are small differences between the concentrations of the Z_1 defect in the (−) and neutral charge states. In both materials, the Z_1^- concentrations are slightly higher than those of the Z_1^0 , and the former are assumed to be representative. Similarly, the concentrations of Z_2^- are higher than those of Z_2^0 and represent this defect's concentrations in both materials. Because the electron capture process's efficiency is strongly dependent on the charge state and temperature, trapping two electrons through the positively charged Z_1 and Z_2 defects occurring at higher temperatures is likely to be more efficient than trapping one electron [1,2]. The comparison of the Z_1 and Z_2 defects' concentrations in the pristine and annealed HPSI 4H-SiC indicates that the heat treatment resulted in the increase of the defects' concentrations by more than the order of magnitude. The interesting result is that in the pristine material, the T1 trap related to the Z_1 defect is predominant, with the concentration being nearly by a factor of two higher than that of the T2 trap, attributed to the Z_2 . On the other hand, in the annealed crystal, the relationship between the defects' concentrations is the opposite; however, the T2 trap's concentration is only ~23% higher. This fact becomes understandable if we assume that the Z_1 and Z_2 defects are identified with isolated point defects, such as carbon vacancies, $V_C(h)$ and $V_C(k)$, located at the h and k sites in the 4H-SiC lattice, or they are attributed to complexes, e.g., $V_C(h)V_{Si}(k)$ and $V_C(k)V_{Si}(h)$, which are composed of different isolated defects occupying the mixed lattice sites [15]. Under the influence of the heat treatment, the point defects migrate, and the HPSI 4H-SiC crystal becomes more homogeneous, which is reflected by equalizing the concentrations of the same type of defects occupying different lattice sites [16,17].

The equilibrium concentration of charge carriers in the samples of HPSI 4H-SiC was negligibly small at temperatures 300–400 K, which was similar to in the depletion region of the n -type epitaxial 4H-SiC samples. The electrical characteristics of the former, giving a deeper insight in the properties of the semi-insulating materials in which the Z_1 and Z_2 defects were investigated, are shown in Figure 5. According to the results presented in Figure 5a, the sufficiently high dark current, indicating the rise in the materials' conductivity, appears above 600 K. The activation energies for dark conductivity (E_{ADC}) for the pristine and annealed materials are 1534 and 1330 meV, respectively, and these values represent the extrapolated-to-absolute zero Fermi level positions [18]. It can be assumed that these Fermi levels are pinned to the levels of the predominant point defects compensating the shallow donors, related to residual nitrogen atoms, or the shallow acceptors, related to residual boron atoms [19]. The E_{ADC} values indicate that the energy levels of defects predominantly contributing to the charge compensation in the pristine and annealed HPSI 4H-SiC samples are located near the middle of the 4H-SiC bandgap. It is also seen that the defects with different properties become predominant after annealing. This fact indicates that as a result of point defects' migration and interaction during annealing, the defects are transformed, which leads to the new kinds of defects with different properties [16,19].

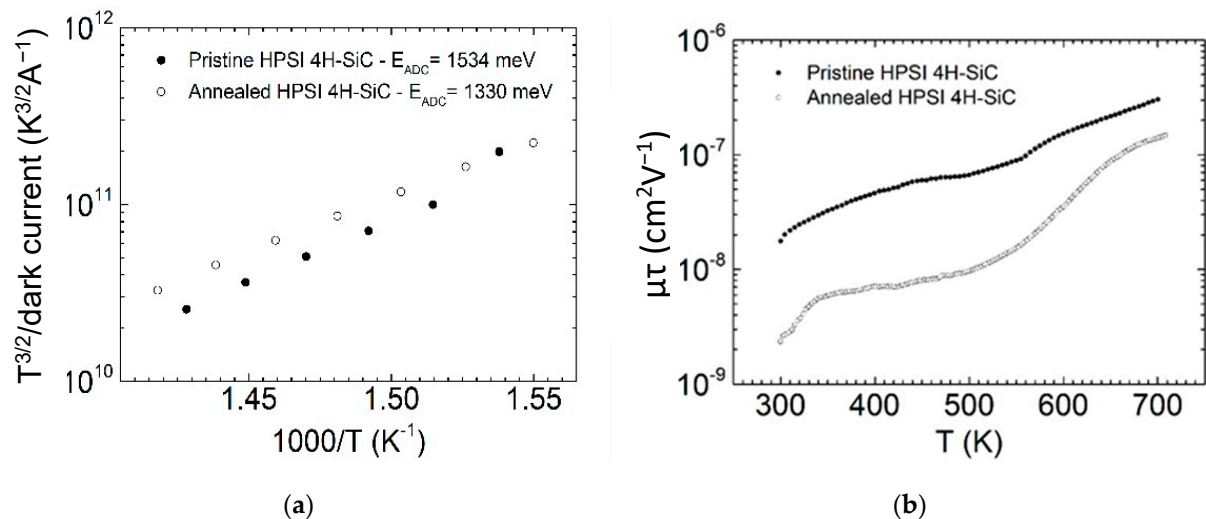


Figure 5. Comparison of the temperature dependences of the dark current reciprocals (a) and the mobility–lifetime products (b) for samples of pristine and annealed HPSI 4H-SiC.

The temperature dependences of the $\mu\tau$ product in Figure 5b confirm the fact that annealing can induce a substantial change in the HPSI 4H-SiC defect structure. This change is reflected by a large decrease in the charge carriers' lifetime, which is most likely due to an increase in other point defects' concentrations, similarly to the case of the Z_1 and Z_2 defects. The relations illustrated in Figure 5b indicate that with rising temperature from 300 to 700 K, the charge carriers' lifetime for the pristine and annealed materials continuously increases by more than the order of magnitude. In particular, a significant increase in the lifetime is observed within the range of 300–400 K, in which the thermal emission from the Z_1 and Z_2 defects occurs. It is worth noting that either at 300 K or at 400 K, the lifetime in the annealed material, with the higher Z_1 and Z_2 defects' concentrations, is by an order of magnitude shorter than that in the pristine one. This result is consistent with the earlier reported findings indicating that the $Z_{1/2}$ defect is an efficient recombination center in epitaxial 4H-SiC [6]. The efficient excess charge carriers' recombination with the involvement of the Z_1 and Z_2 defects can be understood, taking into account that they are deep acceptors with the large cross-section for electron capture [20]. According to the Shockley, Read, Hall (SRH) mechanism, the recombination rate involving these defects depends on the rate of electron capture, the rate of electron emission, and the rate of hole capture [20]. At temperatures around 300 K, the recombination rate is very high because the Z_1 and Z_2 defects are almost permanently filled with the electrons captured from the conduction band, and they immediately capture excess holes from the valence band. At temperatures in the vicinity of 400 K, the rate of thermal electron emission from the defects becomes sufficiently high, and only a small percentage of their concentration remains occupied by electrons, which results in the slowdown of the hole capture process. As indicated by the E_{ADC} values (Figure 5a), in the pristine and annealed HPSI 4H-SiC are also other point defects with energy levels located closer to the middle of the bandgap. These deeper defects act as recombination centers as well, and the $\mu\tau$ values at temperatures above 400 K are determined by their properties and concentrations. Similarly to the case of the Z_1 and Z_2 defects, the rate of thermal emission of charge carriers from these deeper centers exponentially rises with temperature, which leads to emptying the centers and increasing the lifetime.

4. Discussion

The positions of the Z_1 and Z_2 defects' energy levels found in this work in comparison with those determined by Hemmingsson et al. [1] and Capan et al. [4] are illustrated in Figure 6. It is worth stressing that the LPITS results for the T1, T2, T1A, and T2A traps represent the first demonstration of the Z_1 and Z_2 defects' charge state transitions in HPSI

4H-SiC. This new finding is of great importance in terms of understanding their atomic configurations and formation mechanisms. The data shown in Figure 6 significantly enlarge the current status of the knowledge on the defects' properties and encourage theoreticians to further calculate the defects' transition levels using the currently available powerful computational tools [21–23]. The results clearly reveal not only that the energy levels of the Z_1 and Z_2 defects lie in negative- U ordering, but also the fact that the levels are closely spaced. The small differences between the ionization energies of the same kind of point defects, below 100 meV, are typical of 4H-SiC crystals due to the complex lattice structure in which each substitutional defect (vacancy, antisite, impurity atom) can take up two inequivalent sites, namely hexagonal and quasi-cubic, being in an environment with the slightly different electric field distribution [21–23]. For example, the ionization energy for nitrogen atoms, commonly dopants used in 4H-SiC as shallow donors, are 60 and 110 meV when they are located in the h and k sites, respectively [22].

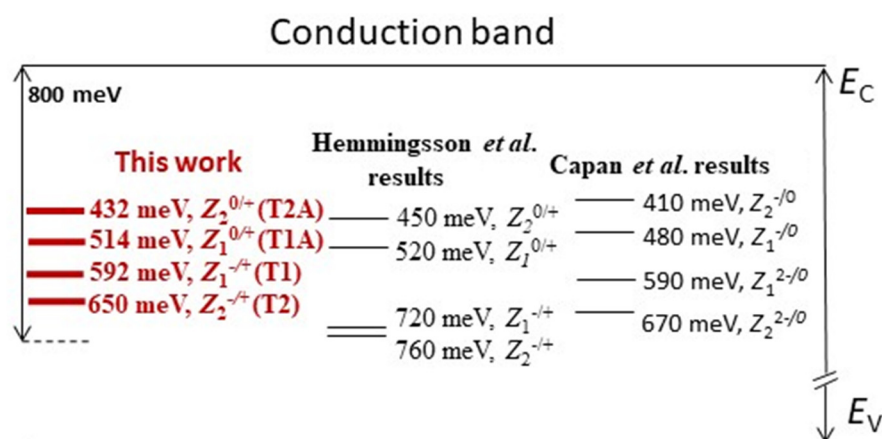


Figure 6. Comparison of deep levels' positions in 4H-SiC bandgap for the charge state changes of Z_1 and Z_2 defects in epitaxial 4H-SiC and HPSI 4H-SiC found in this work with those determined by Hemmingsson et al. [1] and Capan et al. [4] in epitaxial 4H-SiC.

According to the model presented by Capan et al. [4], the Z_1 and Z_2 defects in 4H-SiC can adopt three charge states, $2-$, $1-$, and 0 , similarly to the carbon vacancies. This means that before trapping electrons, the defects are neutral. Such a model was earlier investigated for the oxygen negative- U center in GaAs [3], and it was found that the defect's atomic configurations for the two negatively charged states are very similar; however, those of the neutral charge state clearly differ from the former. From the recent calculations, which employed hybrid density functionals, it has been found that the configuration coordinate diagrams for the negative and doubly negative charge states of V_C , occupying the h - and k -sites in the 4H-SiC lattice are also very similar but substantially differ from that for the neutral V_C . In other words, the capture of one or two electrons vitally changes the arrangement of the four Si atoms in the defect's vicinity. The interpretation of the charge state changes of Z_1 and Z_2 defects given by Hemmingsson et al. [1] is unlike that proposed in Ref. [4]. Although it has also been assumed that each of the defects can be in the three charge states, these states are $1-$, 0 , and $1+$. This means that before the electron capture, the defects are positively charged and behave like typical donors, becoming neutral after the capture of one electron. On the other hand, after capturing two electrons, they behave like acceptors, being negatively charged. Such a model allows us to understand why in the normal DLTS experiment only the two-electron thermal emission is observed, and special modifications in the traps' filling procedure are needed to avoid the accumulation of the centers in the negative charge state. In other words, generating the capacitance relaxation waveforms corresponding to the $Z_1^{0/+}$ and $Z_2^{0/+}$ transitions is difficult, even in the LDLTS experiment. This is because the Coulombic interaction between the positively charged defects and free electrons enhances the capture of two electrons from the conduction band.

In the experiment described in Ref. [1], to reveal the one-electron emission, the sample was illuminated with 2.64 eV photons before each filling pulse of a 50 ns width. In this way, the first electron was optically released from the negatively charged Z_1 and Z_2 defects, and the second was thermally emitted from the neutral defects. In the experiment described in Ref. [4], when using LDITS, the one-electron emission signals were detected by applying filling pulses of a 100 ns width after quickly cooling the sample from room temperature down to 220 K at a reverse bias of -5 V.

The negative- U properties, similar to those proposed for the Z_1 and Z_2 defects in Ref. [1], were established experimentally for interstitial boron in silicon [2]. According to the EPR results and the model proposed by Watkins and Troxell, interstitial boron in this material exists in three charge states, $1-$, 0 , and $1+$, giving rise to two energy levels lying in the upper half of the silicon bandgap [2]. These are the donor level at $E_C - 0.13$ eV and the acceptor level at $E_C - 0.37$ eV. It should be added that the former was detected only through the modified DLTS experiment in which an optical trap-filling pulse was used to prevent the B_i atom from getting into the negative charge state [2]. In our LDITS experiment aimed at the studies of the Z_1 and Z_2 defects' properties and concentrations in epitaxial 4H-SiC, only the electrical trap-filling pulse was used, and the defects were predominantly transferred to the negative charge state during each pulse. Therefore, the measured capacitance relaxation waveforms were induced by the thermal emission of two electrons from the defects' acceptor levels. In the LPITS experiment, the $Z_1^{0/+}$ and $Z_2^{0/+}$ transitions, involving the thermal one-electron emission from the donor levels, and the $Z_1^{-/+}$ and $Z_2^{-/+}$ transitions, involving the thermal two-electron emission from the acceptor levels, are perfectly separated. It is worth noting that all of the transitions with the various emission rates were detected in the same temperature range, 300–400. According to the Laplace spectral fringes shown in Figure 4, the photocurrent relaxation waveform induced by the thermal electron emission at 340 K was composed of the four exponential components related to the $Z_2^{0/+}$, $Z_1^{0/+}$, $Z_1^{-/+}$ and $Z_2^{-/+}$ transitions with the time constants of around 0.11, 0.28, 1.4, and 5.6 ms, respectively. The time constants of the exponential components induced by these transitions and resolved in the waveform recorded at 360 K were 0.044, 0.11, 0.35, and 1.8 ms. The fact that the charge state transitions of the particular defects could be well-determined indicates that the defects' donor and acceptor levels had been almost fully filled electrons before the thermal emission began. It should be added that the excess electrons trapped by the defects were excited from the valence band by illuminating the samples with 3.31 eV photons when the optical excitation pulse was turned on. During the illumination, two processes took place. Firstly, two electrons were captured by the positively charged Z_1 and Z_2 defects, placing the defects in the negative charge states, and then the second electron was by the optical emission transferred back to the conduction band, leaving the defects in the neutral charge states [1,2]. When the optical trap-filling pulse was turned off, the thermal emission of single electrons began, and the electrons released from these states were recaptured by the positively charged defects, which again appeared. This process is possible because the electron capture rate is much higher than the rate of either one-electron or two-electron thermal emission, which is strongly temperature-dependent [1,2].

The question of whether the thermal one-electron emission follows the electron capture by the donor or acceptor levels of the Z_1 and Z_2 defects is still unsolved [1,4,10]. However, the results of this work shown in Figure 6 are more in line with the model of Hemmingsson et al. [1] than with that of Capan et al. [4]. The values of the T2A and T1A traps' activation energy are very close to that of the former and clearly higher than that of the latter. The diminished values of the activation energy reported in Ref. [4] may result from the effect of the electric field on the emission rate, known as the Poole–Frenkel effect [2,24]. During the measurements described in Ref. [4], the thermal emission took place in the depletion region of the Schottky diodes, where the electric field was around 5×10^4 V/cm. On the one hand, the photocurrent transients generated in the HPSI 4H-SiC samples were measured at the electric field of $\sim 3 \times 10^2$ V/cm. According to the Poole–Frenkel effect, the electric

field enhances the emission rate in the case of charge carrier emission from a Coulombic attractive center due to lowering the potential barrier by an amount proportional to the square root of the electric field. It should be noted that the Arrhenius plots shown in Ref. [4] for the one-electron emission from the Z_1 and Z_2 defects are shifted towards lower temperatures by ~ 50 K with respect to those plotted in Figure 5, and their slopes are accordingly smaller. These facts unambiguously indicate that the lower activation energy values obtained by Capan et al. [4] compared to those obtained in this work for the T1A and T2A traps are due to the Poole–Frenkel effect [2,24]. Thus, the assumption made in Ref. [4] that the one-electron emission occurs from the acceptors levels of Z_1 and Z_2 defects is in contradiction with the LPITS results and requires further experimental verification. It is worth stressing that the activation energy values for the T1 and T2 traps related to the two-electron emission from the defects' acceptor levels are in good agreement with those determined in Ref. [4]. This result confirms the theoretical predictions that in the case of thermal electron emission from acceptor levels, the Poole–Frenkel effect is inactive [2].

The experimental findings of this work show that the $[Z_2]/[Z_1]$ values determined for the epitaxial 4H-SiC as well as for the pristine and annealed semi-insulating materials are 4.38, 0.57, and 1.23, respectively. Simultaneously, the $[Z_1^-]/[Z_1^0]$ values after filling the defects with electrons for the pristine and annealed HPSI 4H-SiC are 1.11 and 1.29, respectively, and the $[Z_2^-]/[Z_2^0]$ values are, accordingly, 1.25 and 2.7. The view that Z_1 and Z_2 defects are associated with specific point defects residing at the h and k sites has been, so far, widely assumed [1,4,10]. However, the question arises as to whether these defects can be identified with an individual point defect, like a carbon vacancy being in a certain charge state, e.g., $(V_C^-(h), V_C^-(k))$, occupying the different lattice sites [4,9,10], or a complex defect, such as the divacancy, which may be neutral, negatively charged, or positively charged and consists of the nearest-neighbor carbon and silicon vacancies located at the mixed lattice sites, e.g., $(V_C(h)V_{Si}(k))^-$ [15,25,26]. It should be added that in the 4H-SiC lattice, the $V_C V_{Si}$ complex can take on four possible configurations, namely hh , kk , hk , and kh , and in each of them it can be in various charge states [23]. Moreover, the $V_C V_{Si}$ axis can be parallel or inclined at the angle of $\sim 109.5^\circ$ to the c -axis and, as a result, the defect can exhibit either the high, axial (C_{3v}) or the low, orthorhombic (C_{1h}), symmetry [23]. The defects with the former and latter symmetries are referred to as the axial and basal plane divacancies, respectively [23]. The primitive cell of 4H-SiC with the divacancies formed by the V_C and V_{Si} occupying the same and mixed lattice sites is schematically illustrated in Figure 7.

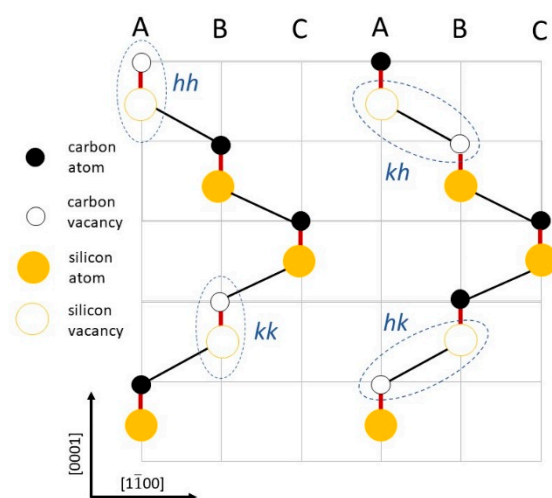


Figure 7. Schematic illustration of stacking sequences and the four possible divacancy configurations in the 4H-SiC lattice, hk , kh , hh , and kk , where h and k denote the inequivalent hexagonal and quasi-cubic lattice sites, respectively. The various configurations of the V_C and V_{Si} pairs are encircled by dashed lines.

The discrepancy between the $[Z_2]/[Z_1]$ values determined for the three kinds of 4H-SiC crystals subjected to various technological treatments can be discussed by taking into account how far from the thermodynamical equilibrium these materials were during these processes [17]. Under the equilibrium conditions, the h and k sites are likely to be equally occupied by the isolated V_C and V_{Si} . This postulate is theoretically supported by the close values of the formation energy (E_f) for neutral $V_C(h)$ and $V_C(k)$. For stoichiometric 4H-SiC, these values are 4.21 and 4.07 eV, respectively, which means that the concentration ratio of $[V_C(k)]/[V_C(h)]$ is 1.15 [15]. The E_f values for the neutral $V_{Si}(h)$ and $V_{Si}(k)$ in stoichiometric 4H-SiC are 8.26 and 8.37 eV, respectively, which gives the $[V_{Si}(k)]/[V_{Si}(h)]$ ratio of 0.9 [15]. Furthermore, the calculated energy barriers for V_C migration in 4H-SiC along axial (h - h , k - k) and basal (h - k - h - k) paths are approximately the same [16,27]. It has been stated that even ion implantation, which is an extremely non-equilibrium process, generates approximately equal concentrations of $V_C(h)$ and $V_C(k)$, irrespective of the defect distribution between the sites prior to implantation [16]. Thus, the $V_C(k)/V_C(h)$ ratio considerably higher than 1 for the epitaxial material seems to be unlikely [16,23,27]. In other words, assuming that the Z_1 and Z_2 defects originate from the two point defects involving different atomic configurations is fully justified.

It is worth noting that in the pristine and annealed semi-insulating materials, the concentrations of the Z_1 defect in the two charge states (0) and ($-$), arising after the capture of one or two electrons, respectively, are approximately equal, which indicates that all of the Z_1 defects present in these materials are taking part in the charge state transitions. However, in the case of the Z_2 defect, the $[Z_2^-]/[Z_2^0]$ ratio is close to 1 only for the pristine material, being equal to 2.7 for the annealed material. This result fully corresponds to the data shown in Figure 5, illustrating the temperature dependences of the excess charge carriers' lifetime. According to the Laplace spectral fringes (Figure 3), the $Z_2^{+/-}$ transitions occur at temperatures close to 380 K, at which the carriers' lifetime in the annealed material is $\sim 7 \times 10^{-9}$ s, while the $Z_2^{+/0}$ transitions are observed at temperatures near 330 K, when the lifetime is by a factor of ~ 2.5 shorter. This phenomenon results in the accordingly lower excess electron concentration to be captured by the Z_2^+ defects [20].

The most important result of this work is the demonstration that as a result of the heat treatment at 1400 °C, the Z_1 and Z_2 defects' concentrations in the semi-insulating material go up from 2.1×10^{13} to $2.2 \times 10^{14} \text{ cm}^{-3}$ and from 1.2×10^{13} to $2.7 \times 10^{14} \text{ cm}^{-3}$. This finding is in line with the postulate that the Z_1 and Z_2 defects can be attributed to the $V_C V_{Si}$ complexes consisting of the nearest-neighbor V_C and V_{Si} residing at k and h as well as h and k sites, respectively. This postulate is based on the results of first-principles calculations for divacancy defects in 4H-SiC, revealing their formation energies and stability, their ionization levels, and symmetry point groups corresponding to neutral and charged states [15,23]. According to these results, the divacancies possess a remarkably high binding energy of ~ 4 eV, and there is a strong dependence of the formation energies on the sites in which the nearest-neighbor silicon and carbon monovacancies are located [15]. It is worth stressing that these results, derived from the calculations based on the density functional theory (DFT), prove that a negative- U behavior leading to the $1+/1-$ charge state transitions occurs only for the divacancies involving the V_C and V_{Si} located in the nearest neighborhood at the hk and kh lattice sites, respectively [15]. Furthermore, it has been shown that the formation energy of the $V_C(h)-V_{Si}(k)$ complex is ~ 0.3 eV lower than that of the $V_C(k)V_{Si}(h)$ one [15]. By assuming that the Z_2 defect is attributed to the $V_C(h)V_{Si}(k)$, it is possible to understand why this defect is predominant in the n -type epitaxial 4H-SiC used for the studies described in this work as well as in Ref. [4]. Moreover, the impact of the C/Si ratio during the epitaxial growth on the Z_2 defect's concentration can also be explained. For a long time, this concentration has been hidden in that of the artificial $Z_{1/2}$ defect [5,7]. At the low C/Si values (0.4–1), the $[V_C]$ dominates, and the Z_2 defect concentration is limited by the $[V_{Si}]$. On the other hand, at the most frequently used C/Si values in the middle range of (1.5–3), the $[V_{Si}]$ increases, and the $[V_C]$ contributing to the Z_2 defect formation may be additionally increased by the irradiation with low-energy

particles [7–9]. At a C/Si value of six, the $[Z_2]$ was found to drop by a factor of four compared to that at the C/Si = 3 [5]. In this case, the $[V_C]$ significantly decreases, and V_{Si} is likely to be transformed into the carbon-related antisite–vacancy (CAV) pair, being an isomer of the V_{Si} in the form of the $C_{Si}V_C$ complex [21].

Attributing the Z_1 and Z_2 defects to the $V_C(k)V_{Si}(h)$ and $V_C(h)V_{Si}(k)$ divacancies, respectively, allows us to understand two facts established in this work. The first says that as a result of the heat treatment, the defects' concentrations in the HPSI 4H-SiC increase by an order of magnitude. During annealing, both V_C and V_{Si} become mobile, and, to be bound, their migration paths should exceed the distance between them. Assuming that the activation energy for V_C migration is 3.6 eV and the pre-factor $D_0 = 0.54 \text{ cm}^2/\text{s}$ [16,27], the V_C diffusion coefficient at 1400 °C (D) equals $7.8 \times 10^{-12} \text{ cm}^2/\text{s}$, and the diffusion length $L_D = 2(Dt)^{1/2}$ for $t = 3 \text{ h}$ is $\sim 6 \text{ }\mu\text{m}$. According to the reported data [19], the $[V_C]$ and $[V_{Si}]$ concentrations in HPSI 4H-SiC crystals are $\sim 1 \times 10^{15} \text{ cm}^{-3}$, which means that the average distance between the vacancies is $\sim 0.08 \text{ }\mu\text{m}$. Thus, the interactions leading to the divacancy formation are very likely [24,26]. The second phenomenon is that the Z_1 and Z_2 defects' concentrations after the heat treatment become approximately equal. This means that due to the mutual interactions between the isolated vacancies, the $[V_C]$ and $[V_{Si}]$ tend to equalize, and the h and k lattice sites become equally occupied by the vacancies [23].

It is worth stressing that there are interesting results obtained through photoluminescence (PL), EPR, and positron annihilation spectroscopy (PAS) showing the unique properties of divacancies in HPSI 4H-SiC [25,26,28–31]. The neutral $(V_C V_{Si})^0$ divacancy optical properties have been widely investigated through PL measurements, and the photon energies corresponding to the zero-phonon lines (ZPLs), labeled PL1, PL2, PL3, and PL4, have been precisely determined [28,29]. The energies indicated by the distinct PL peaks' positions for these lines are 1.095, 1.096, 1.119, and 1.150 eV, respectively [29]. By correlating these energies with theoretical values derived from hybrid density functional theory, equal to 1.056, 1.044, 1.081, and 1.103 eV, respectively, the PL1 and PL2 lines have been attributed to the divacancy in the axial hh and kk configurations, respectively, while the PL3 and PL4 lines have been assigned to the divacancy in the basal kh and hk configurations, respectively [28,29]. Furthermore, the PL1–PL4 lines have also been attributed to the P6/P7 centers ($S = 1$) detected in the EPR spectra measured for as-grown and electron-irradiated HPSI 4H-SiC [25,26]. The spectra were measured at 77 K using the magnetic field parallel to the c axis and the sample illumination with photons, whose energy was in the 2.0–2.8 eV range. Based on the first principles calculations results, which enabled the parameters of hyperfine (HF) interactions to be found, as well as the results of the angular dependence and intensity of the HF lines' measurements, the P6/P7 centers were identified with the $(V_C V_{Si})^0$ divacancy in the four configurations, including the hh and kk ones, with the C_{3v} symmetry, as well as the kh and hk ones, with the C_{1h} symmetry [25,26]. The divacancies in the former two configurations were observed in the EPR spectra as the P6b and P6'b centers, respectively [25,26]. The defects in the latter two configurations are known as the P7'b and P7b centers, respectively [25,26]. Thus, the PL1, PL2, PL3, and PL4 zero-phonon lines attributed to the $(V_C V_{Si})^0$ in the hh , kk , kh , and hk configurations are also assigned to the P6b, P6'b, P7'b, and P7b centers observed in the EPR spectra, respectively [25,26,29]. The positron annihilation studies of vacancy-type defects in SI 4H-SiC have shown that the material contains vacancy clusters, and the positron trapping to the clusters is enhanced by annealing for 1 h at 1600 °C in H_2 ambient [30]. Interesting results obtained through the positron lifetime measurements are presented in Ref. [31]. It has been shown that after annealing the SI 4H-SiC samples for 1 h at 1600 °C in H_2 ambient, the material resistivity drops from 2×10^9 to $1 \times 10^8 \text{ }\Omega\text{cm}$, but the concentration of V_{Si} -related defects, being in the pristine material $\sim 6 \times 10^{16} \text{ cm}^{-3}$, increases by nearly 10%, while the concentration of Si vacancy clusters decreases from 8×10^{15} to $6 \times 10^{15} \text{ cm}^{-3}$ and the number of vacancies in the cluster rises from 5 to 16 [31]. This fact indicates that silicon vacancies are mobile during the annealing and they diffuse either outwards of the cluster or inside the cluster.

The mobile Si vacancies can also form more stable complexes, such as $V_C C_{Si}$ or divacancies, which act as compensating centers after the thermal treatment [31].

5. Conclusions

The electronic properties and concentrations of the Z_1 and Z_2 defects have been experimentally studied in the lightly nitrogen-doped n -type epitaxial 4H-SiC layers and HPSI 4H-SiC wafers using high-resolution techniques, such as LDLTS and LPITS, respectively. The thermal electron emission from both defects was well-resolved, and the activation energies and electron capture cross-sections for the separated defects were determined. By means of the electrical trap-filling process, only the thermal two-electron emission from each defect was observed in the epitaxial material, and the activation energies of 587 and 645 meV for the Z_1 and Z_2 defects were determined. The defects' concentrations were found to be 6.03×10^{11} and $2.64 \times 10^{12} \text{ cm}^{-3}$, which indicates that the $[Z_2]/[Z_1]$ ratio was 4.48.

For the first time, the negative- U properties and the concentrations of the Z_1 and Z_2 defects in semi-insulating wafers of high-purity 4H-SiC were revealed. For each defect, the thermal one-electron emission as well as the thermal two-electron emission has been perfectly resolved. It is found that the former corresponds to the $Z_1^{0/+}$ and $Z_2^{0/+}$ transitions with the activation energies of 514 and 432 meV, respectively. The latter is associated with the $Z_1^{-/+}$ and $Z_2^{-/+}$ transitions with the activation energies of 592 meV and 650 meV, respectively. In view of these results, the Z_1 and Z_2 defects display amphoteric properties, behaving like donors, when they capture or emit one electron, as well as like acceptors, capturing or emitting two electrons. Because the two-electron capture by the positively charged defects is strongly affected by the Coulombic interaction, the $Z_1^{0/+}$ and $Z_2^{0/+}$ transitions are not observed in the epitaxial material using the conventional trap-filling process during the LDLTS experiment.

The Z_1 and Z_2 defects' concentrations have been found to increase after the heat treatment of HPSI 4H-SiC samples at 1400 °C for 3 h in Ar ambience. The concentrations of these defects rise from 2.1×10^{13} to $2.2 \times 10^{14} \text{ cm}^{-3}$ and from 1.2×10^{13} to $2.7 \times 10^{14} \text{ cm}^{-3}$, respectively. This finding is consistent with the theoretical results showing that the migration length of V_C during annealing can be sufficiently long to induce the interactions between V_C and V_{Si} and enhance the formation of $V_C V_{Si}$ pairs. It is postulated that the Z_1 and Z_2 centers can be identified with the $V_C(k)V_{Si}(h)$ and $V_C(h)V_{Si}(k)$ divacancies. Taking into account the fact that in view of the reported DFT calculations results, the formation energy of the latter is lower than that of the former and that the Z_2 centers are predominant in epitaxial 4H-SiC, the Z_1 and Z_2 centers are presumably related to the $V_C(k)V_{Si}(h)$ and $V_C(h)V_{Si}(k)$ pairs, respectively. The theoretical results indicate that only in these configurations the divacancies exhibit the negative- U properties.

The closely spaced energy levels of the Z_1 and Z_2 defects were revealed using the high-resolution experimental techniques, such as LDLTS and LPITS. They proved to be very useful, particularly for the characterization of point defects in 4H-SiC crystals, where, due to the occupation of the k and h lattice sites, the defects' properties only slightly differ.

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References

- Hemmingsson, C.G.; Son, N.T.; Ellison, A.; Zhang, J.; Janzén, E. Negative- U centers in 4H silicon carbide. *Phys. Rev. B* **1998**, *58*, R10119. [\[CrossRef\]](#)
- Harris, R.D.; Newton, J.L.; Watkins, G.D. Negative- U defect: Interstitial boron in silicon. *Phys. Rev. B* **1987**, *36*, 1094–1103. [\[CrossRef\]](#)
- Taguchi, A.; Kageshima, H. Atomic configuration of oxygen negative- U center in GaAs. *Mater. Sci. Forum* **1997**, *258–263*, 873–878. [\[CrossRef\]](#)
- Capan, I.; Brodar, T.; Coutinho, J.; Ohshima, T.; Markevich, V.P.; Peaker, A.R. Acceptor levels of the carbon vacancy in 4H-SiC: Combining Laplace deep level transient spectroscopy with density functional modelling. *J. Appl. Phys.* **2018**, *124*, 245701. [\[CrossRef\]](#)
- Litton, C.W.; Johnstone, D.; Akarca-Biyikli, S.; Ramaiah, K.S.; Bhat, I.; Chow, T.P.; Kim, J.K.; Schubert, E.F. Effect of C/Si ratio on deep levels in epitaxial 4H-SiC. *Appl. Phys. Lett.* **2006**, *88*, 121914. [\[CrossRef\]](#)
- Storasta, L.; Tsuchida, H. Reduction of traps and improvement of carrier lifetime in 4H-SiC epilayers by ion implantation. *Appl. Phys. Lett.* **2007**, *90*, 062116. [\[CrossRef\]](#)
- Danno, K.; Hori, T.; Kimoto, T. Impact of growth parameters on deep levels in n -type 4H-SiC. *J. Appl. Phys.* **2007**, *101*, 053709. [\[CrossRef\]](#)
- Kawahara, K.; Trinh, X.T.; Son, N.T.; Janzén, E.; Suda, J.; Kimoto, T. Investigation of origin $Z_{1/2}$ center in SiC by deep level transient spectroscopy and electron paramagnetic resonance. *Appl. Phys. Lett.* **2013**, *102*, 112106. [\[CrossRef\]](#)
- Kawahara, K.; Trinh, X.T.; Son, N.T.; Janzén, E.; Suda, J.; Kimoto, T. Quantitative comparison between $Z_{1/2}$ center and carbon vacancy in 4H-SiC. *J. Appl. Phys.* **2014**, *115*, 143705. [\[CrossRef\]](#)
- Son, N.T.; Trinh, X.T.; Løvile, L.S.; Svensson, B.G.; Kawahara, K.; Suda, J.; Kimoto, T.; Umeda, T.; Isoya, J.; Makino, T.; et al. Negative- U system of carbon vacancy in 4H-SiC. *Phys. Rev. Lett.* **2012**, *109*, 187603. [\[CrossRef\]](#)
- Provencher, S.W. CONTIN: A general purpose constrained regularization program for inverting noisy linear algebraic and integral equations. *Comput. Phys. Commun.* **1982**, *27*, 229–242. [\[CrossRef\]](#)
- Zajac, M.; Kamiński, P.; Kozłowski, R.; Litwin-Staszewska, E.; Piotrkowski, R.; Grabiańska, K.; Kucharski, R.; Jakiela, R. Formation of grown-in nitrogen vacancies and interstitials in highly Mg-doped ammonothermal GaN. *Materials* **2024**, *17*, 1160. [\[CrossRef\]](#)
- Ciuk, T.; Kozłowski, R.; Romanowska, A.; Zagojski, A.; Piętak-Jurczak, K.; Stańczyk, B.; Przyborowska, K.; Czołak, D.; Kamiński, P. Defect-engineered graphene-on-silicon-carbide platform for magnetic field sensing at greatly elevated temperatures. *Carbon Trends* **2023**, *13*, 100303. [\[CrossRef\]](#)
- Balberg, I.; Albin, D.; Noufi, R. Mobility-lifetime products in CuGaSe₂. *Appl. Phys. Lett.* **1989**, *54*, 1244–1247. [\[CrossRef\]](#)
- Torpo, L.; Staab, T.E.M.; Nieminen, R.M. Divacancy in 3C- and 4H-SiC: An extremely stable defect. *Phys. Rev. B* **2002**, *65*, 085202. [\[CrossRef\]](#)
- Etzelmüller Bathen, M.; Linnarsson, M.; Ghezellou, M.; Ul Hassan, J.; Vines, L. Influence of carbon cap on self-diffusion in silicon carbide. *Crystals* **2020**, *10*, 752. [\[CrossRef\]](#)
- Rogal, J.; Divinski, S.V.; Finnis, M.W.; Glensk, A.; Neugebauer, J.; Perepezko, J.H.; Schuwalow, S.; Sluiter, M.H.F.; Sundman, B. Perspectives on point defect thermodynamics. *Phys. Status Solidi B* **2014**, *251*, 97–129. [\[CrossRef\]](#)
- Darling, R.B. Electrostatic and current transport properties of $n+$ /semi-insulating GaAs junctions. *J. Appl. Phys.* **1993**, *74*, 4571–4589. [\[CrossRef\]](#)
- Son, N.T.; Carlsson, P.; Ul Hassan, J.; Magnusson, B.; Janzén, E. Defects and carrier compensation in semi-insulating 4H-SiC substrates. *Phys. Rev. B* **2007**, *75*, 155204. [\[CrossRef\]](#)
- Zhang, J.; Liang, X.; Min, J.; Zhang, J.; Zhang, D.; Jin, C.; Liang, S.; Chen, P.; Ling, L.; Chen, J.; et al. Effect of point defects trapping characteristics on mobility-lifetime ($\mu\tau$) product in CdZnTe crystals. *J. Cryst. Growth* **2019**, *519*, 41–45. [\[CrossRef\]](#)
- Coutinho, J. Theory of the thermal stability of silicon vacancies and interstitials in 4H-SiC. *Crystals* **2021**, *11*, 167. [\[CrossRef\]](#)
- Wang, R.; Huang, Y.; Yang, D.; Pi, X. Impurities and defects in 4H silicon carbide. *Appl. Phys. Lett.* **2023**, *122*, 180501. [\[CrossRef\]](#)
- Yan, X.; Li, P.; Kang, L.; Wei, S.-H.; Huang, B. First-principles study of electronic and diffusion properties of intrinsic defects in 4H-SiC. *J. Appl. Phys.* **2020**, *127*, 085702. [\[CrossRef\]](#)
- Evwaraye, A.O. Phonon-assisted tunneling from Z_1/Z_2 in 4H-SiC. *J. Electron. Mater.* **2010**, *39*, 751–755. [\[CrossRef\]](#)
- Son, N.T.; Carlsson, P.; Ul Hassan, J.; Janzén, E.; Umeda, T.; Isoya, J.; Gali, A.; Bockstedte, M.; Morishita, N.; Ohshima, T.; et al. Divacancy in 4H-SiC. *Phys. Rev. Lett.* **2006**, *96*, 069902. [\[CrossRef\]](#)
- Son, N.T.; Shafizadeh, D.; Ohshima, T.; Ivanov, I.G. Modified divacancies in 4H-SiC. *J. Appl. Phys.* **2022**, *132*, 025703. [\[CrossRef\]](#)

27. Bathen, M.E.; Coutinho, J.H.M.; Ayedh, H.M.J.; Ul Hassan, J.; Farkas, I.; Öberg, S.Y.K.; Frodason, Y.K.; Svensson, B.G.; Vines, L. Anisotropic and plane-selective migration of the carbon vacancy in SiC: Theory and experiment. *Phys. Rev. B* **2019**, *100*, 014103. [[CrossRef](#)]
28. Falk, A.L.; Buckley, B.B.; Greg Calusine, G.; Koehl, W.F.; Dobrovitski, V.V.; Alberto Politi, A.P.; Zorman, C.A.; Philip, X.-L.; Feng, P.X.-L.; Awschalom, D.D. Polytype control of spin qubits in silicon carbide. *Nat. Commun.* **2013**, *4*, 1819. [[CrossRef](#)]
29. Davidsson, J.; Ivády, V.; Armiento, R.; Son, N.T.; Gali, A.; Abrikosov, I.A. First principles predictions of magneto-optical data for semiconductor point defect identification: The case of divacancy defects in 4H-SiC. *New J. Phys.* **2018**, *20*, 023035. [[CrossRef](#)]
30. Aavikko, R.; Saarinen, K.; Magnusson, B.; Janzén, E. Clustering of vacancies in semi-insulating SiC observed with positron spectroscopy. *Mater. Sci. Forum* **2006**, 527–529, 575–578. [[CrossRef](#)]
31. Aavikko, R.; Saarinen, K.; Tuomisto, F.; Magnusson, B.; Son, N.T.; Janzén, E. Clustering of vacancy defects in high-purity semi-insulating SiC. *Phys. Rev. B* **2007**, *75*, 085208. [[CrossRef](#)]

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