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Resolving the $EH_{6/7}$ level in 4H-SiC by Laplace-transform deep level transient spectroscopy

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We show that Laplace transform deep level transient spectroscopy (LDLTS) is an effective technique for the separation of the overlapping emission rates of the EH_6 and EH_7 levels, which are known to constitute $EH_{6/7}$, a mid-gap level in *n*-type 4H-SiC. The analysis of the electron irradiation dose, electric field dependence, and the effects of carbon interstitials injection on the emission rates of EH_6 and EH_7 shows that EH_7 is dominant over EH_6 and confirms that their nature is related to a carbon vacancy. © 2013 AIP Publishing LLC [<http://dx.doi.org/10.1063/1.4802248>]

The development of SiC bipolar devices is attractive for the industry because these devices are more suitable than unipolar ones for high-voltage applications (>6 kV), due to lower on-resistance owing to the effect of conductivity modulation.¹ A crucial issue for the development of such devices is the presence of deep-level defects which, acting as recombination centers, affect the lifetime of charge carriers in lightly doped epilayers. Since deep levels play an important role in the development of SiC-based electronics, much effort has been devoted in the past for their characterization.^{2–7}

In 4H-SiC, a well-known lifetime-killer is the $Z_{1/2}$ located at 0.6–0.7 eV below the minimum of the conduction band (E_C). This level is present in the as-grown as well as low/high energy electron irradiated or ion implanted epilayers and it is a very efficient electron trap due to its negative-U property that allows the capture of two electrons.⁸ A recent study has shown that it has a rather elementary nature involving a carbon vacancy (V_C).⁹

Apart from $Z_{1/2}$, another prominent level in 4H-SiC is the $EH_{6/7}$, located at ~ 1.5 – 1.6 eV below E_C , that can also be found in as-grown, electron irradiated and implanted 4H-SiC. The $EH_{6/7}$ level has a one-to-one correlation⁴ with the $Z_{1/2}$ that has lead researchers to believe that these two levels may be two different charge states of the same defect (V_C).¹⁰ The broad features of the deep level transient spectroscopy (DLTS) peak associated to the $EH_{6/7}$ level together with its large capture cross section ($\sim 10^{-13}$ cm²) (Refs. 2 and 4) are clear hints that it may originate from two overlapping peaks and many attempts were carried out in order to separate the two emission rates related to $EH_{6/7}$.

One way to achieve this is by employing either low energy irradiation or low-dose ion implantation and annealing: By performing an electron irradiation energy dependence study, Storasta *et al.*³ have shown that the EH_7 can be detected at $E_C - 1.54$ eV while Wong-Leung and Svensson¹¹ have found that the application of an electric field can lead to the detection of EH_7 at $E_C - 1.44$ eV, in *N*-implanted 4H-SiC epilayers. On the other hand, Danno and Kimoto⁴ have resolved EH_6 and EH_7 by simulating the Fourier-transform DLTS peak of $EH_{6/7}$ and reported an energy position of $E_C - 1.35$ and $E_C - 1.50$ eV for EH_6 and EH_7 , respectively. A further attempt was done by depositing different metals on

the epilayer surface in order to change the Schottky barrier height. By this method, Reshanov *et al.*¹² reported an energy position of $E_C - 1.39$ and $E_C - 1.53$ eV, for EH_6 and EH_7 , respectively, while Zippelius *et al.*¹³ reported $E_C - 1.20$ and $E_C - 1.58$ eV for EH_6 and EH_7 , respectively.

Due to the attention of the scientific community for this topic, we employed Laplace-transform DLTS (LDLTS)¹⁴ in order to separate the emission rates of EH_6 and EH_7 . This technique has been successfully employed in the past in a number of semiconductors,¹⁵ including 6H-SiC,¹⁶ and consists in the solution of the following integral:

$$f(t) = \int_0^\infty F(\lambda, t) s(\lambda) d\lambda + A + \varepsilon, \quad (1)$$

where $f(t)$ is the measured capacitance transient, $F(\lambda, t)$ is a known function, A is the constant background, ε is the noise component and $s(\lambda)$ is the solution. In the case of DLTS, the $F(\lambda, t)$ is chosen as $e^{-\lambda t}$ and the solution $s(\lambda)$ becomes a sum of delta functions corresponding to the emission rates of the deep levels and the inverse Laplace transform of the capacitance transient results in a spectrum of delta-like peaks for a multi- or mono-exponential transient.

In the following, we show how, by employing LDLTS, it is possible to clearly resolve the emission rates of EH_6 and EH_7 and by analyzing the annealing behavior, electron dose and electric field dependence of the emission rates, we show that the EH_7 and the $Z_{1/2}$ level can be directly correlated providing further evidence that they belong to two different charge states of the V_C .

For our study, we employed two sets of *n*-type 4H-SiC epilayers irradiated with 116 keV electrons. The first set (a) (net donor concentration, N_D , ranging from 8×10^{14} to 1×10^{16} cm⁻³) was irradiated with a dose of 3×10^{18} cm⁻² and annealed at 950 °C for 30 min while the second set (b) ($N_D \sim 7 - 8 \times 10^{15}$ cm⁻³) was irradiated with four different doses: 5×10^{16} , 5×10^{17} , 2×10^{18} , 5×10^{18} cm⁻². Schottky diodes were formed by deposition of Ni on the epilayer surface by thermal evaporation, and Fourier transform DLTS (FT-DLTS)¹⁷ was then carried out on each sample with a reverse bias of -5 V and a pulse voltage of 0 V. The LDLTS investigation was performed as follows: Capacitance

transients were recorded at 601, 621, 641, 661, and 681 K, by keeping the temperature stability within ± 0.02 K and by applying a reverse bias of -5 V and a pulse voltage of 0 V. Each capacitance transient consisted of 1024 points and was obtained by averaging a total of five-hundred capacitance transients, in order to increase the signal-to-noise ratio. The Laplace transform was then computed from the averaged transient by using CONTIN,¹⁸ a software that employs Tikhonov regularization.

Once the EH_6 and EH_7 emission rates were resolved, the annealing behavior of EH_6 and EH_7 in the 1000 – 1800 °C range (time step 15 min) and the electron-dose dependence of their concentration were investigated, by employing the (b) set 4H-SiC epilayers. Thermal treatments were carried out in Ar ambient, either by a rapid thermal annealing furnace (RTA) or a chemical vapor deposition (CVD) furnace. A carbon cap was deposited on the epilayer surface for temperatures above 1100 °C (so to minimize the effects of surface decomposition)¹⁹ and was later removed by a dry oxidation process (1 h at 800 °C). The electric field dependence study of the emission rates was investigated on set (a) samples by double- $DLTS$, that is, applying a constant bias voltage and two filling pulses of different magnitudes. In addition, the effects of dry oxidation of the epilayer surface on the concentration of EH_6 and EH_7 was also studied, by oxidizing set (a) samples at 1150 °C and 1250 °C for 1 h in 100% oxygen ambient.

Fig. 1 shows a typical $DLTS$ spectrum measured at five different temperatures. As it can be seen, two peaks can be detected and assigned to the emission rates of EH_6 and EH_7 , respectively. Two features can be noted: First is the appearance of extra $DLTS$ peaks (see at $500 - 600$ s⁻¹ in Fig. 1). The presence of spurious peaks can be attributed to the nature of the inverse Laplace transform and, for this reason, it is important to carefully examine the $DLTS$ spectrum in order to avoid any misinterpretation of the nature of the calculated peaks. To do this, the measurement of the averaged transient was repeated twenty times at each temperature T and the resulting emission rate, of both EH_6 and EH_7 , was taken as the average of twenty values. This procedure was carried out not only to recognize fake $DLTS$ peaks but

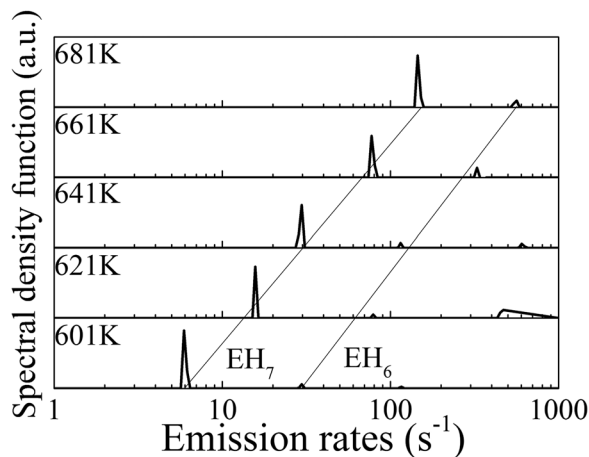


FIG. 1. Typical Laplace transform $DLTS$ spectra showing the emission rates of EH_6 and EH_7 , estimated at 601, 621, 641, 661, and 681 K. The spectra were computed by employing CONTIN.

also to increase the accuracy of our measurements because, as Dobaczewski *et al.*¹⁵ have pointed out, the energy resolution of $DLTS$ is inversely proportional to the temperature at which the measurement is performed. The second feature regards the magnitude of the EH_7 peak. The $DLTS$ peak associated to this level is greater than that associated to the EH_6 ; therefore, it can be predicted that the EH_7 $DLTS$ peak may be dominant over EH_6 .

Once the emission rates are obtained at each temperature, the Arrhenius dependence is plotted and shown in Fig. 2(a). For EH_6 , we obtained an energy position in the band gap of $E_C - 1.3 \pm 0.08$ eV and a capture cross section of $\sim 5 \times 10^{-16}$ cm² while for EH_7 , we obtained $E_C - 1.49 \pm 0.06$ eV and $\sim 4 \times 10^{-15}$ cm², in good agreement with the data reported by Danno and Kimoto.⁴ The experimentally obtained values of the energy position in the band gap and capture cross section of EH_6 and EH_7 are employed to fit the $EH_{6/7}$ the FT- $DLTS$ peak, by using

$$S = \frac{N_T C_{st}}{T_W N_D} (e^{-T_W/\tau} - 1) \frac{2\pi/T_W}{1/\tau^2 + (2\pi/T_W)^2}, \quad (2)$$

where S , N_T , C_{st} , and T_W are the $DLTS$ signal, the trap concentration, the steady capacitance under reverse bias condition, and the period width, respectively. τ is defined as

$$\tau = \frac{1}{\sigma v_{th} N_C} \exp\left(\frac{E_C - E_T}{kT}\right), \quad (3)$$

with σ , v_{th} , N_C , E_T , k are the capture cross section, thermal velocity, effective density of states in the conduction band, energy position of the deep level, and Boltzmann constant, respectively. The N_T of both EH_6 and EH_7 was considered as a free parameter so that the sum of their amplitudes could reproduce the $EH_{6/7}$ peak. Fig. 2(b) shows the $EH_{6/7}$ $DLTS$ peak ($\sim 3.4 \times 10^{13}$ cm⁻³) together with the simulated EH_6 and EH_7 peaks. As it was previously suggested by the analysis of the $DLTS$ spectrum, the EH_7 is dominant with respect to the EH_6 $DLTS$ peak and, by employing the above described fitting procedure, we extracted the values of the concentrations of both EH_6 and EH_7 , finding a ratio of roughly 1:3.

In order to find a correlation between the $Z_{1/2}$ and the two resolved levels, we analyzed their annealing behavior and the electron dose dependence. Fig. 3(a) displays the

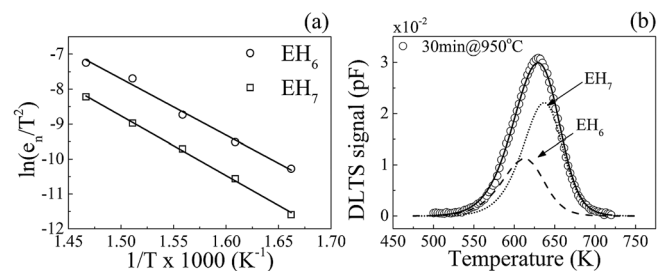


FIG. 2. (a) Arrhenius dependence of the emission rates of EH_6 and EH_7 obtained by $DLTS$ and (b) simulation of the EH_6 and EH_7 $DLTS$ peaks with the energy position and capture cross section values obtained by the Arrhenius plot. The solid line represents the fit for the experimental data (circles) of the $EH_{6/7}$ level measured after annealing at 950 °C of a n -type 4H-SiC epilayer.

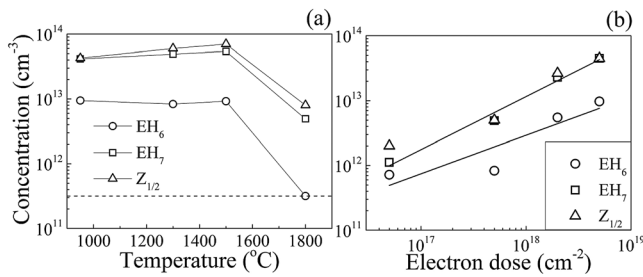


FIG. 3. (a) Annealing behavior in the 950-1800 °C temperature range for a 4H-SiC epilayer irradiated with 116 keV and a dose of $5 \times 10^{18} \text{ cm}^{-2}$. (b) Electron dose dependence of the EH_6 , EH_7 , and $Z_{1/2}$ levels in 116 keV irradiated samples.

annealing behavior of EH_6 , EH_7 , and $Z_{1/2}$ in the 950-1800 °C range for the $5 \times 10^{18} \text{ cm}^{-2}$ irradiated sample and the annealing behavior of EH_7 is very similar to that of $Z_{1/2}$. Although the EH_6 also exhibit high thermal stability, it was almost annealed out after annealing at 1800 °C. This suggests that the nature of EH_7 is similar to that of $Z_{1/2}$, with EH_7 being a positive charge state of the carbon vacancy, V_C .¹⁰ This is further confirmed by the electron dose dependence results shown in Fig. 3(b) in which both EH_7 and $Z_{1/2}$ are found to follow the same linear trend with a slope close to unity (0.8 ± 0.06), while EH_6 possess a more moderate slope (0.6 ± 0.2). We point out that the concentration of $Z_{1/2}$ is half of that measured by DLTS, due to the negative-U property of this center.⁸ Unlike EH_7 , the annealing behavior and electron dose dependence of EH_6 are different from that of $Z_{1/2}$, suggesting that these two levels may have a different nature. The question regarding the nature of EH_6 is still a matter of dispute but it has been put forward the possibility that EH_6 may be related to a higher-order cluster⁶ or to a complex containing a V_C .¹³

In order to find evidence for the donor character of EH_7 , we examined the electric field dependence of the emission rates of EH_6 and EH_7 by double-LDLTS (Fig. 4) at 621 K, by using the sample of set (a). We employed three sets of pulse voltages, that is, $V_{P1} = -2 \text{ V}$, $V_{P2} = -1 \text{ V}$, $V_{P1} = -3 \text{ V}$, $V_{P2} = -2 \text{ V}$, and $V_{P1} = -4 \text{ V}$, $V_{P2} = -3 \text{ V}$, corresponding to electric fields of decreasing intensity. Since this measurement consists in the application of two filling

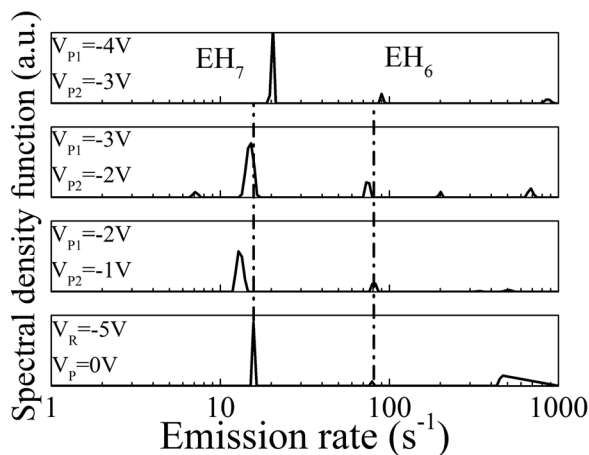


FIG. 4. Double-LDLTS spectra measured at 621 K for pulse voltages $V_{P1} = -2 \text{ V}$, $V_{P2} = -1 \text{ V}$; $V_{P1} = -3 \text{ V}$, $V_{P2} = -2 \text{ V}$; $V_{P1} = -4 \text{ V}$, $V_{P2} = -3 \text{ V}$. The reverse bias (V_R) is set to -5 V .

pulses of different magnitudes, V_{P1} and V_{P2} , we measured two thousand transients for each filling pulse value in order to maximize the signal-to-noise ratio.

As Fig. 4 shows, no clear electric field dependence of the emission rates of both EH_6 and EH_7 can be seen. If on one hand, these results confirm the conclusions of Zippelius *et al.*¹³ who found that the emission rate of the EH_6 center is independent of the electric field, on the other it can be argued that they may be in contrast with the results of Hornos *et al.*¹⁰ who suggested that EH_6 and EH_7 are the singly and doubly positive charge states of V_C . Indeed, although the presence of the Poole-Frenkel effect is a strong hint for the determination of a donor-like character of a defect, its absence does not necessarily imply an acceptor-like behavior²⁰ and, as recent electron paramagnetic resonance (EPR) results have shown,⁹ the EH_7 has been assigned to the singly positive charge state of V_C . These results trigger the question relative to the presence of the doubly positive charge state of V_C , as predicted from theory. The answer to this question is beyond the aim of the present study, but a possible candidate for this may be the P1 level, a midgap level found by Danno *et al.* at 1.49 eV above the valence band maximum.⁷

Last, we examined the effect of oxidation on EH_6 and EH_7 levels. As Hiyoshi and Kimoto²¹ have reported, by thermal oxidation in the 1150-1300 °C range, the concentration of $Z_{1/2}$ and $EH_{6/7}$ drops to below the detection limit, due to the injection of carbon interstitials (C_i) that, by diffusing, recombine with V_C . Fig. 5(a) shows the LDLTS spectra of the irradiated sample oxidized for 1 h at 1150 and 1250 °C measured at 621 K and, as it can be seen, the signal of both EH_6 and EH_7 drops after annealing at higher temperature. This indicates a possible decrease of the concentrations for both levels occurring after oxidation at 1250 °C and, in fact, the concentration of the $EH_{6/7}$ level decreases by one order of magnitude after oxidization at 1150 and 1250 °C. By simulating the EH_6 and EH_7 DLTS peaks, we found that the concentrations of EH_6 and EH_7 decrease from 4×10^{12} to $5 \times 10^{11} \text{ cm}^{-3}$ and from 9×10^{12} to $1 \times 10^{12} \text{ cm}^{-3}$, respectively, by 1250 °C oxidation, further confirming the involvement of V_C in the microscopic nature of EH_6 and EH_7 .

To summarize, we showed that LDLTS is an effective technique for the resolution of the emission rates of the EH_6 and EH_7 levels. The Arrhenius dependence of these emission rates reveals an energy position in the band gap of 1.30 and 1.49 eV below the conduction band minimum for EH_6 and EH_7 , respectively. Analysis of the annealing behavior, electron dose, and electric field dependence of the emission rates

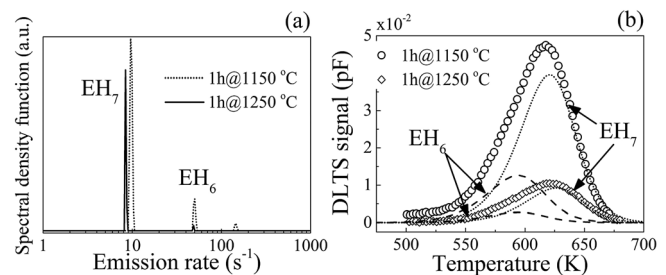


FIG. 5. (a) LDLTS spectrum for the 1150 and 1250 °C oxidized samples, measured at 621 K and (b) DLTS spectrum of the $EH_{6/7}$ level after oxidization at 1150 and 1250 °C with the simulated EH_6 and EH_7 levels.

confirm that EH_7 is related to the $Z_{1/2}$ level with which shares the same elementary nature (V_C), while EH_6 may be related to a complex involving V_C .

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