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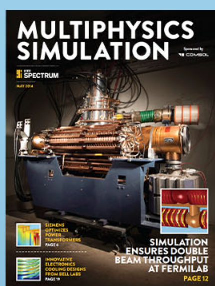

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Resolving the $EH_{6/7}$ level in 4H-SiC by Laplace-transform deep level transient spectroscopy

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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 correlation[4] 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 ($\sim 10^{-13}\,\mathrm{cm}^2$) (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 Svensson[11] 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 Kimoto[4] 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:

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

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 $1 \times 10^{16}\,\mathrm{cm}^{-3}$) was irradiated with a dose of $3 \times 10^{18}\,\mathrm{cm}^{-2}$ and annealed at 950 °C for 30 min while the second set (b) ($N_D \sim 7 - 8 \times 10^{15}\,\mathrm{cm}^{-3}$) was irradiated with four different doses: 5×10^{16}, 5×10^{17}, 2×10^{18}, $5 \times 10^{18}\,\mathrm{cm}^{-2}$. 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

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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-LDLTS, 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 LDLTS 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 LDLTS 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 LDLTS 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 LDLTS peaks but also to increase the accuracy of our measurements because, as Dobaczewski *et al.*[15] have pointed out, the energy resolution of LDLTS is inversely proportional to the temperature at which the measurement is performed. The second feature regards the magnitude of the EH_7 peak. The LDLTS 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 $\sim 5 \times 10^{-16}$ cm^2 while for EH_7, we obtained $E_C - 1.49 \pm 0.06$ eV and $\sim 4 \times 10^{-15}$ cm^2, 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

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

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

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

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 LDLTS 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

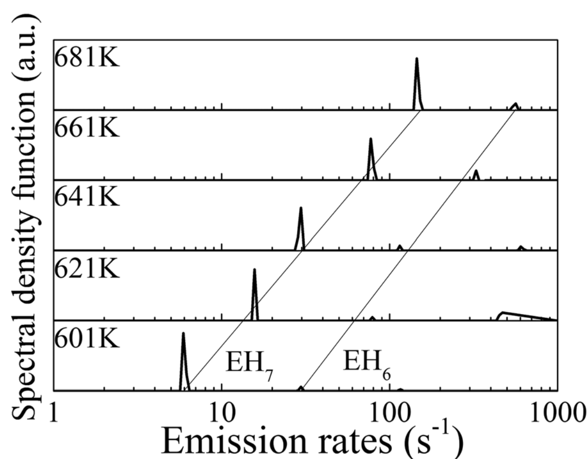

FIG. 1. Typical Laplace transform DLTS spectra showing the emission rates of EH_6 and EH_7, estimated at 601, 621, 641, 661, and 681 K. The spectra were computed by employing CONTIN.

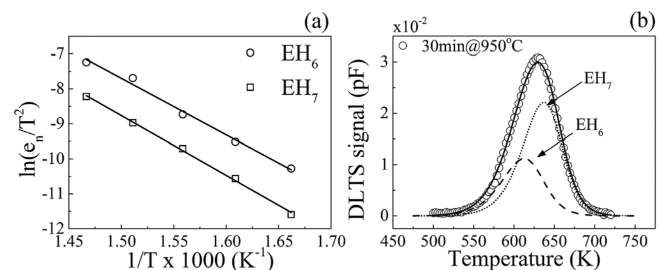

FIG. 2. (a) Arrhenius dependence of the emission rates of EH_6 and EH_7 obtained by LDLTS and (b) simulation of the EH_6 and EH_7 DLTS peaks with the energy position and capture cross section values obtained by the Arrhenius plot. The solid line represents the fit for the experimental data (circles)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

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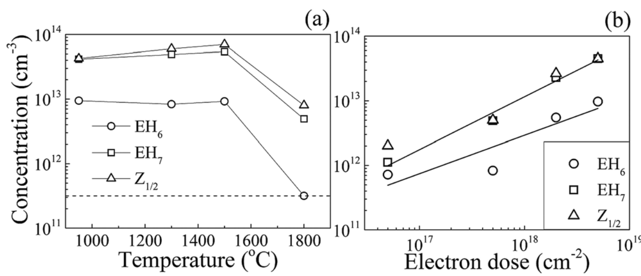

FIG. 3. (a) Annealing behavior in the 950-1800 °C temperature range for a 4H-SiC epilayer irradiated with 116 keV and a dose of 5×10^{18} cm^{-2}. (b) Electron dose dependence of the EH_6, EH_7, and $Z_{1/2}$ levels in 116 keV irradiated samples.

annealing behavior of EH_6, EH_7, and $Z_{1/2}$ in the 950-1800 °C range for the 5×10^{18} 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 cluster[6] 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, $V_{P1} = -2$ V, $V_{P2} = -1$ V, $V_{P1} = -3$ V, $V_{P2} = -2$ V, and $V_{P1} = -4$ V, $V_{P2} = -3$ V, corresponding to electric fields of decreasing intensity. Since this measurement consists in the application of two filling 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.

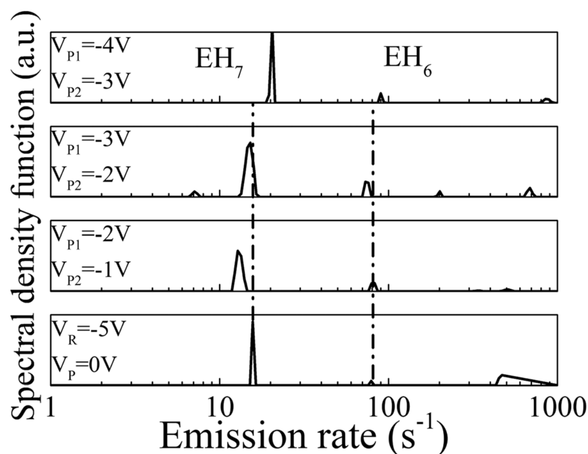

FIG. 4. Double-LDLTS spectra measured at 621 K for pulse voltages $V_{P1} = -2$ V, $V_{P2} = -1$ V; $V_{P1} = -3$ V, $V_{P2} = -2$ V; $V_{P1} = -4$ V, $V_{P2} = -3$ V. The reverse bias (V_R) is set to -5 V.

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 behavior[20] 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 Kimoto[21] 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 5×10^{11} cm^{-3} and from 9×10^{12} to 1×10^{12} 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

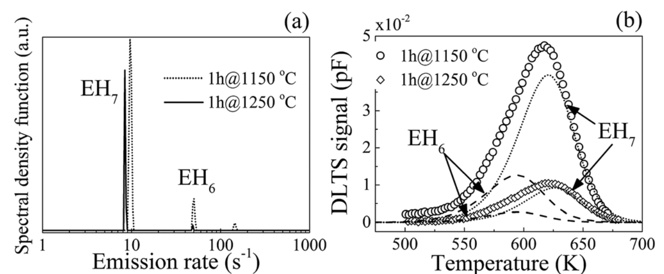

FIG. 5. (a) LDLTS spectrum for the 1150 and 1250 °C oxidized samples, measured at 621 K and (b) DLTS spectrum of the $EH_{6/7}$ level after oxidization at 1150 and 1250 °C with the simulated EH_6 and EH_7 levels.

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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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