

# Capacitance transient study of the metastable $M$ center in $n$ -type $4H$ -SiC

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The metastable  $M$  center in  $n$ -type  $4H$  silicon carbide is studied in detail after it has been introduced by 2.5 MeV proton irradiation with a fluence of  $1 \times 10^{12} \text{ cm}^{-2}$ . The experimental procedures included deep-level transient spectroscopy, carrier capture coefficient and capacitance versus temperature measurements, and pulse-train measurements. The pulse-train measurements are reproduced by simulations. Three band-gap levels have previously been assigned to the  $M$  center:  $M_1$  at  $E_C - 0.42 \text{ eV}$ ,  $M_2$  at  $E_C - 0.63 \text{ eV}$ , and  $M_3$  at  $E_C - 0.83 \text{ eV}$ , where  $E_C$  is the conduction-band edge. Direct measurements of the majority-carrier capture cross sections show that the cross section values extracted from Arrhenius plots are about two orders of magnitude too large, indicating a large entropy factor. A detailed configuration diagram of the  $M$  center is presented, including charge state levels and reconfiguration barriers. Evidence in support of a fourth  $M$  center level, not explicitly observed, is presented. Isochronal and isothermal annealing experiments show that the  $M$  center anneal out between 310 and 370 °C in a process displaying first-order kinetics. The annealing process, which is shown to have an activation energy of 2.0 eV, is identified as dissociation.

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## I. INTRODUCTION

Deep-level transient spectroscopy (DLTS) on electron- and proton-irradiated  $n$ -type  $4H$  silicon carbide shows that many defect levels are generated by low-dose irradiation and that annealing at room temperature or slightly above ( $< 300 \text{ °C}$ ) significantly changes the defect composition.<sup>1-4</sup> This low-dose and low-annealing temperature regime has often been neglected in other defect studies in SiC, even though this regime offers great opportunities for a fundamental understanding of point defects in silicon carbide. Most of the defects in silicon carbide have been neither studied in detail nor identified. In  $4H$  silicon carbide, the  $Z$  defect is well known and has been studied because of its presence in as-grown as well as in irradiated material.<sup>5</sup> It appears at suitable temperatures for DLTS with the  $Z_{1,2}(-/+)$  level positioned approximately 0.68 eV below the conduction-band edge  $E_C$ . The identity of the  $Z$  defect is still debated.<sup>6-8</sup> The two levels  $S_1$  at  $E_C - 0.40 \text{ eV}$  and  $S_2$  at  $E_C - 0.71 \text{ eV}$  originate from different charge states of the same defect<sup>3,9,10</sup> (the  $S$  center) and three other levels  $M_1$ ,  $M_2$ , and  $M_3$  have been assigned to a metastable defect (the  $M$  center).<sup>11</sup> Defect levels have also been observed deeper into the band gap, but these defects are inaccessible by DLTS in a low-temperature annealing study because probing these levels requires temperatures so high that the measurement itself would cause annealing.

Metastability of point defects have been reported earlier, e.g., for the carbon-carbon<sup>12,13</sup> and carbon-group-V-atom<sup>14</sup> pairs in silicon and for an unknown, tristable defect in  $6H$  silicon carbide.<sup>15</sup> As described in Ref. 11, the  $M$  center in  $4H$  silicon carbide has been observed in two configurations ( $A$  and  $B$ ). The levels  $M_1$  and  $M_3$  belong to configuration  $A$  and  $M_2$  to configuration  $B$ . It was also shown in Ref. 11 that there

is a one-to-one correlation between the two configurations and that the configuration of the  $M$  center can be changed reversibly. Configuration  $A$  is introduced at temperatures  $\geq 20 \text{ °C}$  only when reverse bias is applied so that the active DLTS region is depleted of charge carriers. In the depletion region, the  $M$  centers are thus prohibited from capturing electrons; and once they have become empty through emission of electrons, they will reconfigure from  $B$  to  $A$  through a thermally controlled process which has an energy barrier of 0.90 eV. The opposite transformation ( $A$  to  $B$ ) requires temperatures  $\geq 140 \text{ °C}$  and filled  $M$  centers, which are obtained by applying zero bias voltage, so that the active DLTS region is no longer depleted. The energy barrier for the reconfiguration from  $A$  to  $B$  is 1.4 eV.

Here we report on the full annealing behavior of the  $M$  center, and furthermore, we present a configuration diagram based also on filling pulse measurements and simulations of capacitance measurements during capture-emission sequences. In addition to the three observed levels  $M_{1,2,3}$ , the data strongly suggest the existence of a fourth deep level, which we have labeled  $M_4$ . This level is observed indirectly when the  $M$  center is in configuration  $B$ .

## II. EXPERIMENTAL PROCEDURE

A 20- $\mu\text{m}$ -thick, nitrogen-doped layer was grown on a Cree substrate by chemical vapor deposition at Linköping University.<sup>16</sup> A doping concentration of  $(1-2) \times 10^{15} \text{ cm}^{-3}$  was determined in the layer by capacitance-voltage measurements. High-quality Schottky diodes were prepared<sup>17</sup> by deposition of 1200 Å TiW followed by thermal annealing at 500 °C. Subsequently, the diodes were implanted with 2.5 MeV protons at the tandem accelerator at the Ångström Laboratory in Uppsala.<sup>18</sup> Several samples were implanted

with a fluence of  $1 \times 10^{12} \text{ cm}^{-2}$ . The protons had their end of range  $50 \mu\text{m}$  below the surface in the highly doped substrate. The distribution of generated defects is expected to be nearly uniform in the active DLTS region ( $1\text{--}5 \mu\text{m}$  from the surface). Irradiation with 15 MeV electrons was performed at the Alfvén Laboratory in Stockholm. Annealings were performed under a flow of  $\text{N}_2$  gas and, as no bias was applied, the monitored  $M$  centers were in configuration  $B$  during annealing.

A refined version of a constant-voltage DLTS setup described elsewhere<sup>19</sup> was employed for the capacitance measurements. The temperature range used was 77 to 350 K and for the DLTS measurements, rate windows ranged from  $(100 \text{ ms})^{-1}$  to  $(3200 \text{ ms})^{-1}$ . Depth profiling and carrier capture coefficient measurements on individual defects were performed by fixing the sample temperature at the position of the appropriate DLTS peak. In the depth profiling measurements, the steady-state reverse bias voltage was kept constant, while the DLTS signal was measured as the amplitude of the majority-carrier pulse was gradually increased. To study charge carrier capture, the DLTS signal versus filling pulse durations was measured, making it possible to deduce the carrier capture cross section directly.

If the defect concentrations are small compared to the doping concentration, the DLTS peak heights are proportional to the defect concentrations. If independent peaks are overlapping, the total DLTS signal is given by the sum of the individual peaks. This means that DLTS spectra recorded on the same sample and with the same parameters can be subtracted to reveal the DLTS signature of the defect(s) responsible for any change in the spectra caused by, e.g., an additional annealing step or a change in configuration. Since we have investigated high-quality diodes enabling measurements with a high degree of reproducibility, we could make extensive use of subtracted spectra. This has proven to be a powerful tool when dealing with the complex DLTS spectra which are recorded after low annealing temperatures.

During so-called pulse-train measurements<sup>15,20</sup> the applied bias is repeatedly changed between two levels, filling and measurements bias. During the short (50 or 300 ns) filling pulses, empty defects start to capture majority carriers. The reverse bias capacitance is measured between the pulses, and here the defects may emit carriers again. After a sufficient number of such short pulses, steady state between capture and emission is established and the charge carrier population of defects saturates at a level that depends on temperature, filling pulse duration, and repetition frequency. In our case, the initial occupation of the defects was controlled by bias and temperature, and the response of the  $M$  center levels was revealed by subtracting pulse-train measurements from the configurations  $A$  and  $B$ . For each defect, the capture and emission process was controlled by the capture and emission rates, but also by the filling pulse duration  $t_p$  and time between pulses (1.75 s). The reverse-bias capacitance is measured 50 ms after the pulse.

### III. RESULTS

#### A. The $M$ center in 4H-SiC

After annealing at  $200^\circ\text{C}$ , the upper part of the band gap is dominated by the  $Z$ ,  $M$ , and  $S$  levels, as can be seen in Fig.

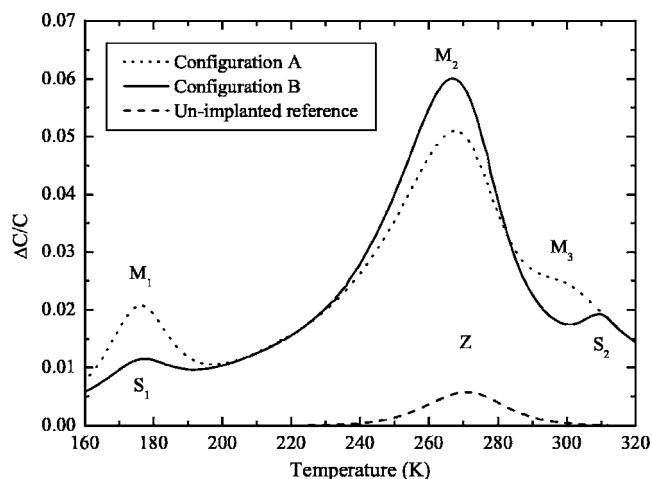


FIG. 1. DLTS temperature scan of 2.5 MeV proton-implanted 4H-SiC after annealing at  $200^\circ\text{C}$ . The solid (dotted) curve was measured when all  $M$  centers were in configuration  $A$  ( $B$ ). The DLTS spectrum for an unimplanted reference sample is shown for comparison. Rate window was  $(3.2 \text{ s})^{-1}$ .

1 for a proton-implanted sample. Spectra from an unimplanted reference sample is shown together with DLTS spectra for configurations  $A$  and  $B$  of the  $M$  center. In the latter cases, all  $M$  centers were either completely in configuration  $A$  or completely in configuration  $B$ . It is seen that the  $M_1$  and  $M_2$  levels overlap with the  $S_1$  and  $Z$  levels, respectively, but because of the opportunity to switch completely between configurations  $A$  and  $B$ , information on the  $M$  center levels can still be obtained, despite this overlap. There is also a partial overlap between  $M_3$  and  $S_2$ , as seen in Fig. 1. The  $M$  center levels can be clearly revealed by subtracting DLTS measurements which vary only in the configuration of the  $M$  center. Subtracting the two DLTS spectra for configurations  $A$  and  $B$  in Fig. 1 results in the three DLTS peaks for  $M_1$ ,  $M_2$ , and  $M_3$  shown in Fig. 2. By combining such subtracted DLTS spectra with Arrhenius plots and simultaneous

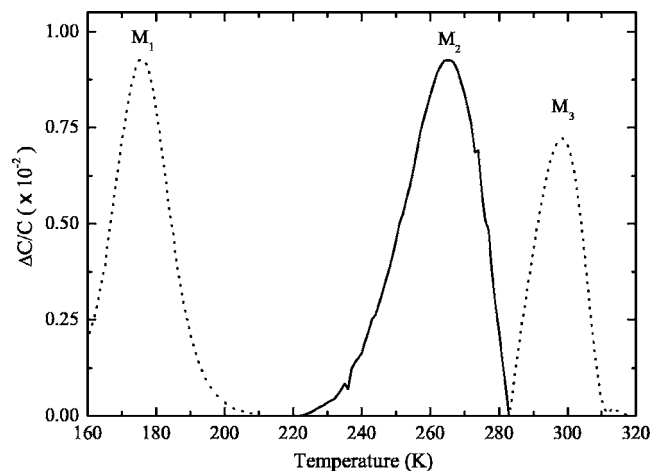


FIG. 2. DLTS signal for the three  $M$  center levels  $M_1$ ,  $M_2$ , and  $M_3$ , obtained by subtracting configuration  $A$  and configuration  $B$  spectra. The results shown here are based on the DLTS spectra in Fig. 1. Rate window was  $(3.2 \text{ s})^{-1}$ .

TABLE I. Apparent energy position below the conduction-band edge and carrier capture cross section  $\sigma$  for  $M_1$ ,  $M_2$ , and  $M_3$ . The  $\sigma_\infty$  values are extracted from Arrhenius plots whereas  $\sigma_{meas}$  refers to direct measurements. Direct measurements have been made at the indicated temperatures.

Defect level	Energy (eV)	$\sigma_\infty$ ( $\times 10^{-15}$ cm <sup>2</sup> )	$\sigma_{meas}$ ( $\times 10^{-15}$ cm <sup>2</sup> )	Temperature (K)
$M_1$	0.42	6	0.04–0.07	176, 187
$M_2$	0.63	4	0.02–0.06	244, 265, 281
$M_3$	$\sim 0.83$	$\sim 300$	$> 2$	276

curve fitting of all the DLTS rate windows,<sup>21</sup> the apparent energy positions in the band gap and extrapolated carrier capture cross sections for the  $M$  center levels were extracted with a high accuracy. The results are shown in Table I.

Figure 3 depicts the defect concentration versus depth measured with a rate window of  $(400 \text{ ms})^{-1}$  at 185.5 K. With these parameters, the total concentration of the overlapping  $M_1$  and  $S_1$  peaks is measured. In the figure, depth profiles are reported for three cases of  $M$  center configuration. In the first case, all  $M$  centers in the active DLTS region were in configuration A, while in the second case they were in configuration B. In the third case, only a low reverse bias was applied during reconfiguration heat treatment ( $50^\circ\text{C}$ ) so that the edge of the depletion region was at  $\sim 2.8 \mu\text{m}$ , yielding the A configuration below  $\sim 2.8 \mu\text{m}$  and the B configuration at larger depths.

### B. Annealing behavior

Both isochronal and isothermal annealing series have been performed. After each annealing, two DLTS spectra

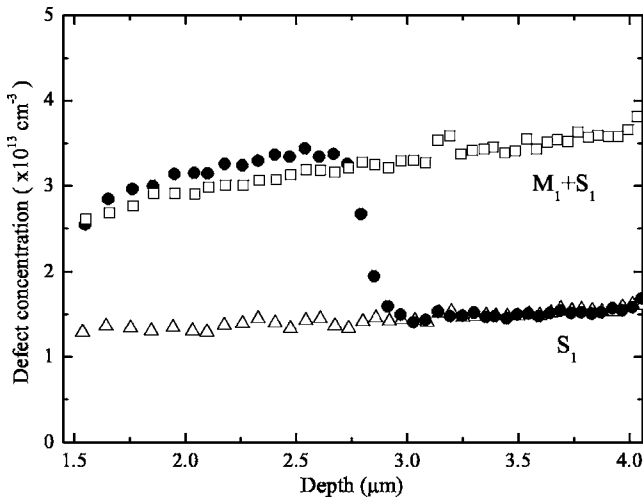


FIG. 3. Defect concentration versus depth for the overlapping defect levels  $M_1$  and  $S_1$ . Depth profiles were measured when all  $M$  centers were in configuration B and only the overlapping  $S_1$  signal was measured (triangles), when only half of the active DLTS region was depleted during reconfiguration heat treatment (circles), and when all  $M$  centers in the active region had been allowed to reconfigure from B to A (squares). Measurement temperature was 185.5 K and the rate window was  $(400 \text{ ms})^{-1}$ . The implantation fluence was  $1 \times 10^{12} \text{ cm}^{-2}$ .

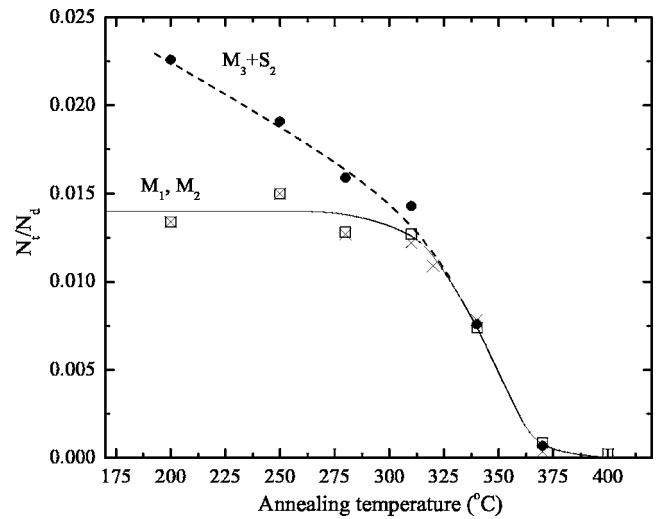


FIG. 4. Isochronal annealing (30 min). Concentration of  $M_1$ ,  $M_2$ , and the sum of  $M_3$  and  $S_2$  as a function of annealing temperature. The concentrations of  $M_1$  and  $M_2$  are deduced from the height of their DLTS peaks in subtracted spectra like the one shown in Fig. 2. The concentration is expressed as the relation between the trap concentration  $N_t$  and the background doping  $N_d$ . The  $(M_3+S_2)$  concentration was found by comparing the configuration A DLTS spectrum at each annealing temperature to the spectrum at  $400^\circ\text{C}$ . Lines are included to guide the eye.

were measured. The annealing itself, during which no bias was applied, placed all monitored  $M$  centers in configuration B. This configuration was measured by scanning the temperature from 275 to 77 and back to 320 K. During the final part of the measurement (285–320 K) the  $M$  centers gradually changed to configuration A (as described in Ref. 11). To assure a complete transformation, the bias was applied at 320 K for at least 5 min before the second DLTS spectrum (configuration A) was recorded. The concentrations of  $M_1$  and  $M_2$  in Figs. 4 and 5 were found from the DLTS peak heights in the subtracted spectrum. The results from the

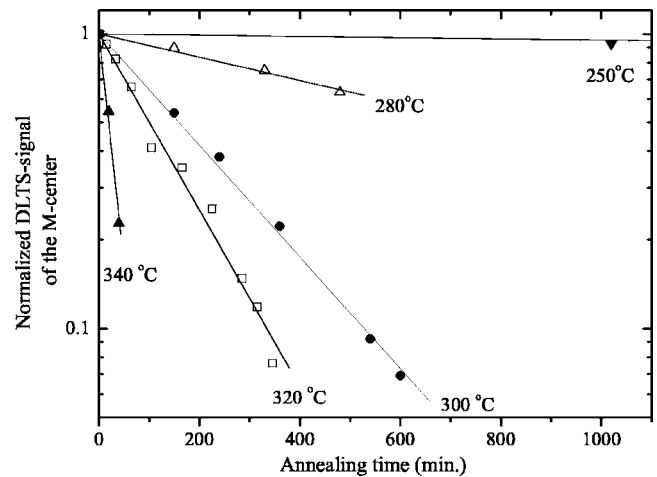


FIG. 5. Isothermal annealing. Normalized  $M$  center concentration as a function of annealing time at 250, 280, 300, 320, and  $340^\circ\text{C}$ . Determination of the rate of annealing at  $250^\circ\text{C}$  is based on four points, of which only the first one is shown.

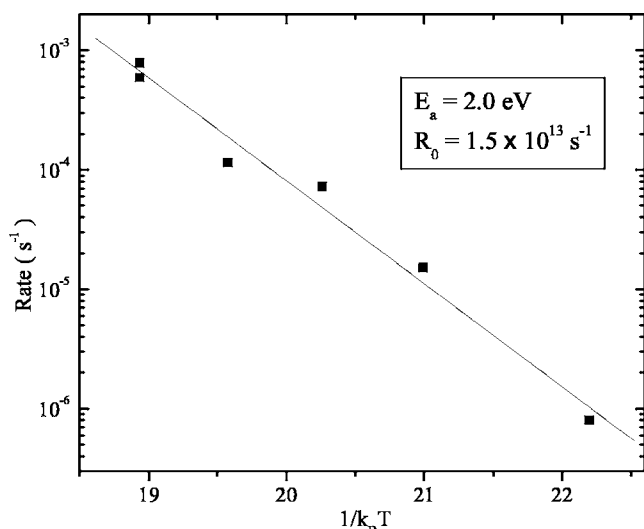


FIG. 6. Rate of  $M$  center annealing versus  $1/k_B T$ . The Arrhenius plot gives an activation energy of 2.0 eV and a prefactor of  $1.5 \times 10^{13} \text{ s}^{-1}$ . Five of the measured points come from the five isothermal annealings shown in Fig. 5, and the sixth point (at 340 °C) is extracted from the isochronal annealing data.

30 min isochronal annealing series on the same sample are shown in Fig. 4. The concentration of  $M_3$  could not be found by subtraction due to the gradual transformation at 285–320 K, but the total concentration of  $M_3$  and  $S_2$  could be found by following the development in the configuration A spectra.

The results of the isothermal annealings series are shown in Fig. 5 for five different temperatures, and first-order kinetics (exponential decay) is found. The annealing rates at these five temperatures (indicated by lines in Fig. 5 and determined by least-squares fits) are shown in Fig. 6 as a function of  $1/k_B T$ , where  $k_B$  is Boltzmann's constant and  $T$  is the absolute annealing temperature. The additional point at 340 °C was extracted from the isochronal annealing series (Fig. 4) and agrees very well with the isothermal points. The annealing rate  $R$  can be described by

$$R(T) = R_0 \exp\left(\frac{-E_a}{k_B T}\right), \quad (1)$$

where  $E_a$  is the activation energy of the process and  $R_0$  is a prefactor. A linear fit of the six points plotted in the semi-logarithmic Arrhenius graph (Fig. 6) gives  $E_a = 2.0 \text{ eV}$  and a prefactor of  $R_0 = 1.5 \times 10^{13} \text{ s}^{-1}$ . Notice that the measured annealing rates span three orders of magnitude.

### C. Capture and emission of charge carriers

The reverse-bias capacitance is always recorded concurrently with the DLTS signal as a function of temperature. A careful comparison between such reverse bias capacitance curves for the configurations A and B is shown in Fig. 7. At low ( $<180 \text{ K}$ ) and high ( $>305 \text{ K}$ ) temperatures the two curves overlap perfectly, but in between these temperatures the capacitance is higher if the  $M$  centers are in configuration A. The difference in capacitance is about 1 pF and remains

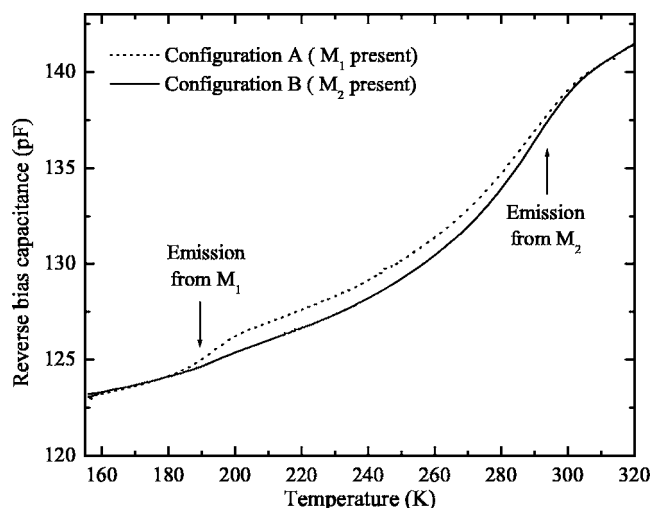


FIG. 7. Reverse-bias capacitance as a function of temperature after annealing at 300 °C. Curves from configurations A and B are shown, and a difference of about 1 pF can be seen between 200 and 275 K.

constant between 200 and 275 K. The splitting of the two curves (at  $\sim 180$ –200 K) coincides with the temperature for the  $M_1$  emission of electrons, and the rejoining (at  $\sim 275$ –305 K) coincides with the  $M_2$  emission of electrons.

To measure the charge carrier capture cross section directly, the DLTS signal was measured as a function of filling pulse duration for  $M_1$ ,  $M_2$ , and  $M_3$ . This was done in both configurations and the filling pulse curves for the three levels were deduced by subtraction. The filling pulse curves for  $M_2$  measured at 265 K with a reverse bias of 5 and 15 V are shown in Fig. 8. A theoretical expression for the filling pulse curve of a uniformly distributed deep level with a concentration well below the doping concentration is given by Pons.<sup>22</sup> Fitting the experimental data in Fig. 8 with this expression

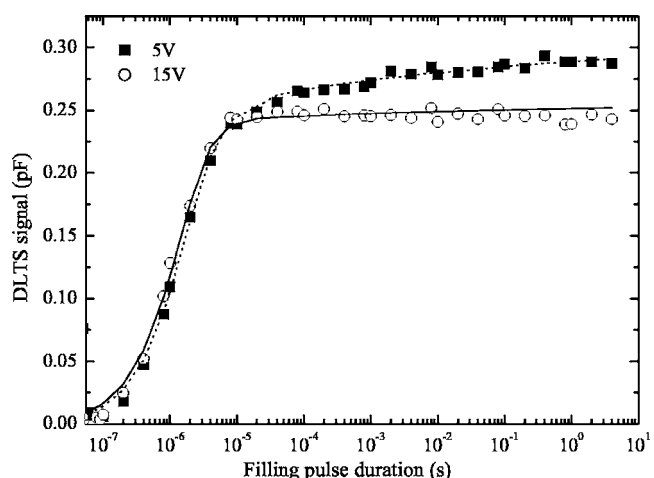


FIG. 8. The filling kinetics for  $M_2$  obtained from subtracted DLTS signal versus filling pulse duration measurements after annealing at 200 °C. Results are shown for reverse biases of 5 and 15 V together with calculated curves according to Pons (Ref. 22). The rate window used was  $(3200 \text{ ms})^{-1}$  and the measurement temperature was 265 K.



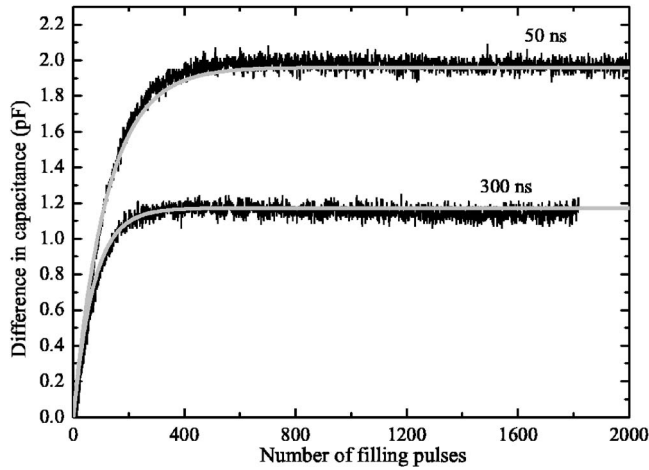


FIG. 9. Difference in reverse-bias capacitance during pulse-train measurements versus number of applied filling pulses. The difference is between identical measurements on configurations *A* and *B*. The sample temperature was 150 K [procedure (i)]. The solid line represents simulation results.

gives a capture cross section of  $4.7 \times 10^{-17} \text{ cm}^2$  (5 V) and  $5.3 \times 10^{-17} \text{ cm}^2$  (15 V) for  $M_2$  at 265 K. The results from all the measurements of the capture cross sections are summarized in Table I.

Pulse-train measurements have been performed with four different initial occupation of the defects: (i) stabilizing the temperature at 150 K, long initial filling pulse ( $>30$  s), and then a pulse-train measurement with a certain filling pulse duration, (ii) as in (i) but at 220 K, (iii) stabilizing the temperature at 220 K, long initial filling pulse followed by an emptying under reverse bias for 120 s, cooling to 150 K with reverse bias, and then a pulse-train measurement, and (iv) as in (iii) but emptying at 275 K and measurement at 220 K. For each case, pulse-train measurements were performed with different pulse durations. The results for (i) are shown in Fig. 9 for filling pulse durations of 50 and 300 ns, along with simulation results which are discussed below. Again, we stress that it is the difference between two pulse-train measurements (*A* and *B*), that is shown in Fig. 9, and because of this, only the effect of the  $M$  center levels is displayed. The corresponding experimental and simulation results for (iv) are shown in Fig. 10. The pulse-train measurements were performed on  $M$  centers generated by 15 MeV electron irradiation.

#### IV. DISCUSSION

##### A. Depth profile of the $M$ center

In the investigated region, the defects are expected to be almost uniformly distributed, but Fig. 3 shows a gradual increase with depth for both the  $S$  and  $M$  centers. The increase is not an artifact caused by, for instance, a nonuniform doping concentration. Instead, the increase can be linked to the depth distribution of the primary irradiation damage as calculated by TRIM (Ref. 23) and it is less likely to be caused by either surface-point defect interactions,<sup>24</sup> or the involvement

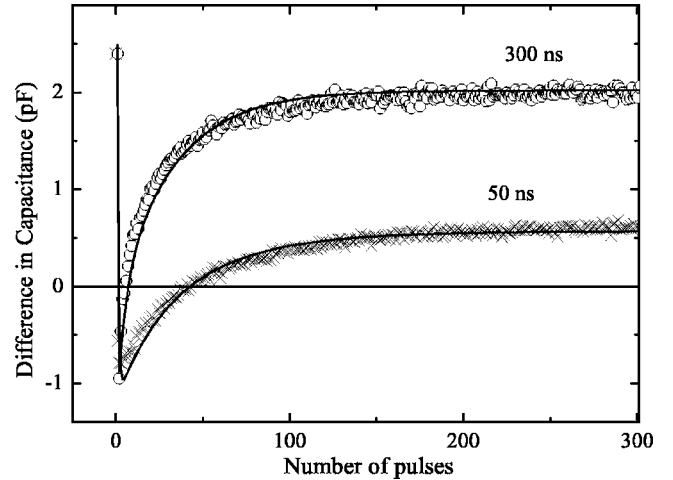


FIG. 10. Difference in reverse-bias capacitance during pulse-train measurements versus number of applied filling pulses. The difference is between identical measurements on configurations *A* and *B*. Defect levels were emptied at 275 K and kept empty until the pulse-train measurements were started at 220 K [procedure (iv)]. The first point is measured before the first pulse is applied. The solid line represents simulation results.

of a nonuniformly distributed impurity in the  $M$  center. The identity of the  $M$  center is not yet known and the use of complementary characterization techniques is needed. As the  $M$  center is introduced by both electron and proton irradiation, the implanted hydrogen atoms are not involved in the defect. Any correlation with residual impurity hydrogen cannot, however, be excluded.

##### B. Annealing behavior

According to the isochronal annealings (Fig. 4),  $M_1$  and  $M_2$  display identical behavior, and  $M_3$  is considered to be similarly affected by the annealings, as the sum of  $M_3$  and  $S_2$  disappears together with  $M_1$  and  $M_2$  between 310 and 400 °C. The decrease in the total concentration of  $M_3$  and  $S_2$  below 310 °C corresponds well with the annealing of  $S_1$  in our samples and with the annealing of the  $S$  defect reported in Ref. 10. In the subtracted spectra (Fig. 2), the  $M_3$  peak appears lower than the  $M_1$  and  $M_2$  peaks due to the gradual reconfiguration process<sup>11</sup> which takes place between 285 and 320 K. We conclude that the  $M$  center anneals out between 310 and 370 °C and Fig. 4 strongly supports the assignment of the three levels  $M_1$ ,  $M_2$ , and  $M_3$  to the same defect.

The isothermal annealing results show that the  $M$ -center loss displays first-order kinetics over more than one order of magnitude in defect concentration (300 and 320 °C in Fig. 5). This first-order behavior can be explained by three different mechanisms: (i) defect dissociation, (ii)  $M$  center migration followed by trapping at another, significantly more abundant defect, or (iii) interaction between a mobile, abundant defect and an immobile  $M$  center. The prefactor for the thermally activated process was found to be  $\sim 1.5 \times 10^{13} \text{ s}^{-1}$  (Fig. 6) which is, within the experimental accuracy, identical to a theoretical estimate<sup>25</sup> of the lattice vibration frequency in 4H-SiC at 300 °C,  $\sim 1.6 \times 10^{13} \text{ s}^{-1}$ . Hence,

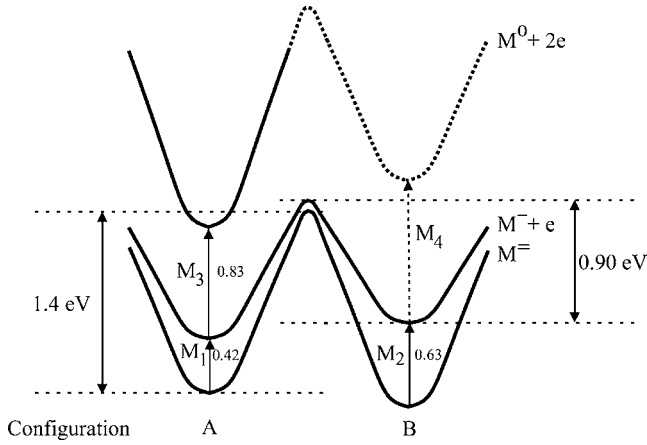


FIG. 11. Suggested configuration diagram for the  $M$  center in 4H-SiC.

this strongly favors a pure dissociation process with negligible back reaction (association). For mechanisms (ii) and (iii), which involve defect or impurity migration, substantially lower prefactors are anticipated, typically  $\leq 10^{10} \text{ s}^{-1}$  assuming a trap concentration of  $\leq 10^{16} \text{ cm}^{-3}$  and diffusion prefactor of  $\leq 1 \text{ cm}^2/\text{s}$ . Thus, (ii) and (iii) are ruled out as the main annealing mechanisms for the  $M$  center, and dissociation dominates.

The temperature range of annealing is similar to what Itoh *et al.*<sup>26</sup> reported for the intrinsic T6 and T7 defects in 3C-SiC. These defects have, however, only been seen in  $p$ -type material and no metastability has yet been reported. The identity of the  $M$  center is still unresolved.

### C. Charge states and configuration diagram

In Fig. 11, a configuration diagram for the  $M$  center is suggested. The diagram is consistent with all our results, as discussed in the following. The  $M_1$  and  $M_2$  levels are assigned to the same charge state transition for two reasons. First, at temperatures below 180 K both  $M_1$  and  $M_2$  are filled and the total amount of charge in the depletion region is the same, irrespectively of the  $M$  center configuration (see Fig. 7). Figure 7 also shows that the total amount of (positive) charge in the depletion region is increased (seen by the increase in reverse-bias capacitance) when  $M_1$  and  $M_2$  emit their trapped electrons in configurations A and B, respectively. The splitting between the two capacitance curves in Fig. 7 occurs because  $M_1$  ( $E_C - 0.42 \text{ eV}$ ) is shallower than  $M_2$  ( $E_C - 0.63 \text{ eV}$ ). This means that  $M_1$  is empty and  $M_2$  filled between 200 and 275 K. It should be mentioned that the rejoining of the capacitance curves at 275–305 K is assisted by the gradual transition from configuration B to A, but it cannot be explained by the reconfiguration alone. Second, the direct measurements on  $M_1$  and  $M_2$  revealed very similar carrier capture cross sections and this indicates that  $M_1$  and  $M_2$  belong to transitions between the same charge states. Indications of the absolute charge states can be deduced from the measured carrier capture cross section values. The values for  $M_1$  and  $M_2$  ( $\sigma \approx 5 \times 10^{-17} \text{ cm}^2$ ) suggest a  $(=/-)$  transition. Further, because no peaks are observed be-

tween  $M_1$  and  $M_3$  in configuration A and because the DLTS peak amplitudes of  $M_1$  and  $M_3$  are the same,  $M_3$  is assigned to a  $(-/0)$  transition. This is also consistent with the higher capture cross section ( $> 2 \times 10^{-15} \text{ cm}^2$ ) for  $M_3$ .

It should be mentioned that no Poole-Frenkel effect has been observed for  $M_1$  and  $M_2$ —indicating acceptor-type levels, but the absence of such an effect cannot be used to conclude strongly on the charge state of a defect.<sup>27</sup>

Table I shows that the carrier capture cross sections extracted from the Arrhenius plot using  $T^2$  corrections are much larger than the measured ones for  $M_1$  and  $M_2$ . This discrepancy is normally attributed to a large change in entropy,  $\Delta S$  for the defect as it emits the electron.<sup>28</sup> Assuming that the capture cross sections are independent of temperature,  $\Delta S$  becomes approximately  $5k_B$  for  $M_1$  and for  $M_2$ .

Compelling evidence for the existence of a second level, labeled  $M_4$ , for configuration B is provided by Fig. 7. Below  $\sim 180 \text{ K}$ , where both  $M_1$  and  $M_3$  are filled, configurations A and B display the same capacitance values showing that the two configurations accommodate the same amount of charge. That is, for configuration B, the  $M_2$  level is not sufficient but one additional state must exist, and it is deeper than  $M_2$  since the two capacitance curves merge above  $\sim 295 \text{ K}$  where  $M_2$  is empty and  $M_3$  still (partly) populated. This is also consistent with the observations that the merge of the curves cannot be accounted for only by the reconfiguration from B to A. Further evidence for the fourth charge state will be discussed below.

Reconfiguration from B to A has a barrier of 0.9 eV and takes place when  $M_2$  is empty—hence the placement of the 0.9 eV barrier in Fig. 11. It should be pointed out that thermal carrier emission from  $M_2$  is not the limiting factor when it comes to the transition from  $B^=$  to  $B^-$  to  $A^-$ . At 300 K, the first process takes place on a subsecond time scale whereas the reconfiguration process has a time scale of several minutes. It may look striking that  $M_3$  emission and B to A reconfiguration have similar activation energies, but the two processes are uncorrelated as the change is *from B to A* and the time scale for  $M_3$  emission is on the order of a few seconds at 300 K.

When the reconfiguration barrier for the transformation from A to B was determined<sup>11</sup> to 1.4 eV, the temperatures and samples used were such that both  $M_1$  and  $M_2$  were filled, i.e., below the Fermi level. This gives the 1.4 eV barrier between  $A^=$  and  $B^=$  in Fig. 11.

### D. Simulations of reverse-bias capacitance during filling pulse train measurements

The simulations of the pulse-train measurements are based on a model where the difference in reverse bias capacitance is given by

$$\Delta C_{rev} \approx \text{const} \times (Q_A - Q_B) \quad (2)$$

assuming that all other defects are unaffected by the configuration of the  $M$  center, and also that the concentration of defects is low compared to the doping concentration.  $Q_A$  and  $Q_B$  are the charges from the  $M$  centers contributing to the depletion region capacitance, in configurations A and B, re-

spectively. Three charge states ( $=/-/0$ ) are considered for both configurations and it is assumed that the sum of the corresponding three occupation fractions  $f$  is unity. The transition  $B^- \leftrightarrow B^0$  has not been explicitly observed experimentally, but it is included in the model due to the discussion about  $M_4$  that followed Fig. 7. Capture and emission rates for the levels  $M_1$ ,  $M_2$ ,  $M_3$ , and  $M_4$  are used as input parameters in the simulations. Measurements undertaken at 150 K [case (i), initially filled levels] are shown in Fig. 9. When the  $M$  centers are all in configuration  $B$ , the  $M_2$  (and  $M_4$ ) levels are all filled because the emission rate for  $M_2$  is extremely low at 150 K (see Fig. 2). In configuration  $A$ , the  $M_1$  (and  $M_3$ ) levels are also filled initially, but the emission rate is not negligible so the  $M_1$  defects will partly fill during each pulse and partly empty during each measurement interval, until steady-state conditions are established. Figure 9 shows that in the beginning, where defects in either configuration of the  $M$  center are filled,  $\Delta C_{rev} \approx 0$ , and  $M_1$  and  $M_2$  must therefore be transitions between the same charge states. As the occupation fraction  $f(A^-)$  drops from 1 toward its steady-state value, then  $\Delta C_{rev}$  increases and even more so for shorter filling pulses (50 versus 300 ns). The experimental data in Fig. 9 were reproduced by an emission rate of  $0.004 \text{ s}^{-1}$  and a capture rate of  $2 \times 10^4 \text{ s}^{-1}$ ; these values are close to those expected from an extrapolation of the DLTS results for  $M_1$ .

In fact, using reasonable input parameters, the model could account for all the experimental observations using different initial filling conditions [(i) to (iv)]. This was impossible if  $M_1$  and  $M_2$  were assigned to different charge state transitions. Absolute charge states of  $=/-/0$  were assumed but using charge states of  $=/0/+$  would yield identical simulation results. As discussed earlier, however, the direct measurements of the capture cross sections favor ( $=/-$ ) and ( $=/0$ ) for  $M_1$  and  $M_3$ , respectively.

Finally, it should be emphasized that also the simulations strongly support the existence of a single acceptor state  $M_4$  for configuration  $B$ . In Fig. 10,  $\Delta C_{rev}$  is positive *before* the first filling pulse, but substantially negative *after* the first

pulse. This is attributed to partial emptying of the single negative charge state in configuration  $B$  ( $M_4$ ) and almost complete emptying in configuration  $A$  ( $M_3$ ) at 275 K, with a rapid capture for  $M_3$  at 220 K. Further, the capture rate for  $M_4$  was much larger than that of  $M_2$ , consistent with assigning  $M_4$  to a ( $=/0$ ) transition, while the emission rate for  $M_4$  was somewhat lower than that of  $M_3$ . This places the  $M_4$  level inside the band gap at a position deeper, but not much deeper, than  $M_3$ . Hence,  $M_4$  escapes detection by DLTS as the  $M$  center changes configuration from  $B$  to  $A$  (at  $\sim 300 \text{ K}$ ) before the temperatures needed to observe  $M_4$  are reached.

## V. CONCLUSIONS

The irradiation-induced, metastable  $M$  defect in  $4H$ -SiC has been studied in detail. Three levels  $M_1$ ,  $M_2$ , and  $M_3$  are directly observed in DLTS measurements and compelling indirect evidence is obtained for a fourth level  $M_4$ , located deeper in the band gap than  $M_3$ . On the basis of an extensive set of experimental data (DLTS, capacitance versus temperature, pulse-train measurements) together with simulations of charge carrier capture and emission, a detailed configuration diagram for the  $M$  center is presented, where  $M_1$  and  $M_3$  correspond to a doubly and singly negative charge state of the  $M$  center in configuration  $A$ , while  $M_2$  and  $M_4$  correspond to a doubly and singly negative charge state in configuration  $B$ . The  $M$  center is observed to anneal out between 310 and 370 °C, with first-order kinetics and a rate given by  $(1.5 \times 10^{13} \text{ s}^{-1})[\exp(-2.0 \text{ eV})/k_B T]$ , strongly suggesting that dissociation is the main annealing mechanism.

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