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DEEP-LEVEL DEFECTS IN EPITAXIAL 4H-SiC IRRADIATED WITH LOW-ENERGY ELECTRONS

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Deep level transient spectroscopy (DLTS) has been applied to study defect centers in epitaxial layers of nitrogen-doped *n*-type 4H-SiC before and after irradiation with a dose of $1.0 \times 10^{17} \text{ cm}^{-2}$ of 300-keV electrons. It is shown that the minority carrier lifetime in the as-grown epilayers is predominantly affected by the $Z_{1/2}$ center concentration. The capture cross-section of the $Z_{1/2}$ center for holes is found to be $\sim 6.0 \times 10^{-14} \text{ cm}^2$. We have tentatively attributed the center to the divacancy $V_C V_{Si}$ formed by the nearest neighbor silicon and carbon vacancies located in different (*h* or *k*) lattice sites. The substantial increase in the $Z_{1/2}$ center concentration induced by low-energy electron irradiation is likely to be dependent on both the residual concentration of silicon vacancies and nitrogen concentration in the as-grown material. Four irradiation-induced deep electron traps with the activation energies of 0.71, 0.78, 1.04 and 1.33 eV have been revealed. The 0.71-eV trap, observed only in the epilayer with a higher nitrogen concentration of $4.0 \times 10^{15} \text{ cm}^{-3}$, is tentatively identified with the complex defect involving a dicarbon interstitial and a nitrogen atom. The 0.78-eV and 1.04-eV traps are assigned to the carbon vacancy levels for $V_C (2-/)$ and $V_C (-/0)$, respectively. The 1.33-eV trap is proposed to be related to the dicarbon interstitial.

Keywords 4H-SiC, DLTS, electron traps, point defects

Głębokie centra defektowe w warstwach epitaksjalnych 4H-SiC napromieniowanych

elektronami o niskiej energii

Niestacjonarną spektroskopię pojemnościową (DLTS) zastosowano do badania centrów defektowych w domieszkowanych azotem warstwach epitaksjalnych 4H-SiC typu *n* przed oraz po napromieniowaniu dawką elektronów o energii 300 keV, równą $1,0 \times 10^{17} \text{ cm}^{-2}$. Pokazano, że czas życia mniejszościowych nośników ładunku w warstwach nienapromieniowanych jest zależny głównie od koncentracji centrów $Z_{1/2}$. Stwierdzono, że przekrój czynny na wychwyt dziur przez te centra wynosi $\sim 6 \times 10^{-14} \text{ cm}^2$. W oparciu o dyskusję wyników badań przedstawionych w literaturze zaproponowano konfigurację atomową centrów $Z_{1/2}$. Stwierdzono, że centra te są prawdopodobnie związane z lukami podwójnymi $V_C V_{Si}$ utworzonymi przez znajdujące się w najbliższym sąsiedztwie luki węglowe (V_C) i luki krzemowe (V_{Si}) zlokalizowane odpowiednio w węzłach *h* i *k* lub *k* i *h* sieci krystalicznej 4H-SiC. Otrzymane wyniki wskazują, że przyrost koncentracji centrów $Z_{1/2}$ wywołany napromieniowaniem elektronami o niskiej energii zależny jest zarówno od koncentracji luk krzemowych, jak i od koncentracji azotu w materiale wyjściowym. Wykryto cztery pułapki elektronowe, charakteryzujące się energią aktywacji 0,71 eV, 0,78 eV, 1,04 eV i 1,33 eV, powstałe w wyniku napromieniowania. Pułapki o energii aktywacji 0,71 eV, które wykryto tylko w warstwie epitaksjalnej o większej koncentracji azotu, równej $4 \times 10^{15} \text{ cm}^{-3}$, są prawdopodobnie związane z kompleksami złożonymi z atomów azotu i dwóch międzywęzłowych atomów węgla. Pułapki o energii aktywacji 0,78 eV i 1,04 eV przypisano lukom węgl-

wym znajdującym się odpowiednio w dwóch różnych stanach ładunkowych $V_C(2/-)$ i $V_C(-/0)$. Pułapki o energii aktywacji 1,33 są prawdopodobnie związane z aglomeratami złożonymi z dwóch międzywęzłowych atomów węgla.

Słowa kluczowe: 4H-SiC, DLTS, pułapki elektronowe, defekty punktowe

I. INTRODUCTION

Epitaxial 4H-SiC is an important material for the next generation of high power devices. Taking advantage of the physical properties of 4H-SiC, at present Schottky and *p-i-n* diodes are recognized to be the most promising power device structures. The performance, stability and reliability of these devices depend, however, on the properties and concentrations of various deep-level defects, which are formed during the epitaxial growth and post-growth cooling, as well as during the device fabrication and operation [1, 2]. In contrast to shallow impurities, controlling the type and magnitude of conductivity, the deep centers act as carrier traps and recombination centers and determine the rate of non-radiative recombination of the charge carriers. Moreover, the deep-level defects are responsible for the phenomenon of recombination-enhanced point defect migration that can play an important role in device degradation observed under high current density injection conditions [3, 4]. Thus, knowledge of the properties of deep-level defects and their microscopic structure is of great importance for improving the quality of epitaxial 4H-SiC.

Deep level transient spectroscopy (DLTS) is a very effective tool to determine both the activation energies for thermal emission of electrons or holes from deep defect states and their capture cross-sections, as well as the concentrations of these states [5, 6]. According to recent results [7-12], the predominant deep electron trap in as-grown epitaxial 4H-SiC is the well-known $Z_{1/2}$ center with activation energy for electron emission of $\sim 0.60 - 0.70$ eV. Although a number of studies have been performed, the microscopic structure of this center is still unclear. Moreover, there are many contradictory experimental results indicating the various identifications of the structure of the defect center. On one hand, it has been shown that increasing the C/Si ratio during chemical vapor deposition enhances the $Z_{1/2}$ center formation [8]. This means that as the deviation from the stoichiometric composition of the vapor phase tends towards a C-rich environment, the concentration of the $Z_{1/2}$ center increases, there-

by suggesting that this center is related to a carbon interstitial or a native defect located in the silicon sublattice. On the other hand, there are experimental results showing that epitaxial growth at higher values of the C/Si ratio causes a decrease in the $Z_{1/2}$ center concentration [9-12]. In other words, the shift of the vapor phase composition towards C-rich conditions leads to a suppression of the $Z_{1/2}$ center formation. So, the center would be expected to be related to a native defect in the carbon sublattice, such as a carbon vacancy (V_C) or silicon antisite (Si_C) [9, 10]. Furthermore, there are also experimental results indicating the involvement of nitrogen dopants in $Z_{1/2}$ center formation [8, 13]. Such contradictory results have hindered the identification of the microscopic structure of the $Z_{1/2}$ center, but theoretical modeling based on first-principles calculations indicates that this center could arise from a complex containing an interstitial-nitrogen and interstitial carbon [14].

In this work, we used DLTS to study deep-level defects formed in epitaxial 4H-SiC due to the 300-keV electron irradiation with a dose of 1×10^{17} cm⁻². Our work is motivated by the recent experimental results [15] indicating that the different atomic masses of C and Si atoms, give the ability to form selectively the associated vacancies, V_C and V_{Si} , via controlling the energy of the bombarding electrons. In particular, at the 300-keV electron irradiation, mostly C atoms are displaced and carbon vacancies formed. The objective of our work is to find how the concentration of the $Z_{1/2}$ center changes after various irradiation conditions and to determine the properties and concentrations of deep-level defects related to point defects created in the carbon sublattice.

II. EXPERIMENTAL DETAILS

Epitaxial layers were grown in an Aixtron/Epigress VP508 horizontal hot-wall chemical vapor deposition reactor using silane (SiH_4 , 2% in H_2) and propane (C_3H_8) as precursors, with palladium-purified hydrogen used as a carrier gas. The epitaxial layers were grown on standard *n*-type 4H-SiC substrates with a net donor concentration of $\sim 10^{18}$ cm⁻³ that were oriented 8° off the (0001) plane toward [11-20]. The substrates were quartered and the epitaxial growth was carried out at a constant temperature and pressure of 1580°C and 100 mbar, respectively. The films were intentionally doped using ultra-high purity N_2 source gas. While the nitrogen gas flow was varied from sample to sample to incorporate dif-

ferent levels of nitrogen concentration, the C/Si ratio was maintained for all growth processes at 1.55. The epitaxial layers consisted of an initial 5 μm thick n^+ ($\sim 1 \times 10^{18} \text{ cm}^{-3}$) buffer layer grown at 5 $\mu\text{m/h}$, followed by a 20 μm thick layer grown at 10 $\mu\text{m/h}$. Deep defect centers were studied in the layers obtained in two selected epitaxial processes labeled as C1061215 (epilayer A) and C1070714 (epilayer B).

Schottky diodes for DLTS measurements were prepared by evaporating a 20-nm film of Cr and a 300-nm film of Au on the surface of the epitaxial 4H-SiC. The Schottky contacts were deposited through a metal shadow mask with a diameter of 0.5 mm. Large-area Ohmic Al contacts were deposited on the back side of the wafer by electron beam evaporation. The sample with the contacts was cut into chips of $5 \times 5 \text{ mm}^2$ in area that were subsequently used for measurements of the capacitance-voltage (C-V) characteristics and for DLTS experiments. The DLTS spectra were taken between 150 and 700 K at a reverse bias $V_R = -10 \text{ V}$, a filling pulse amplitude $V_F = 10 \text{ V}$ and a filling pulse duration time $t_c = 100 \mu\text{s}$. The measurements were carried out using as-grown samples, as well as those subjected to the bombardment with 300-keV electrons, performed in a van de Graff accelerator at room temperature with a dose of $\sim 1 \times 10^{17} \text{ cm}^{-2}$. The DLTS system used in the present work and the procedures used for determination of the trap activation energy, apparent capture cross-section and concentration have been described elsewhere [5]. The net donor concentrations obtained from the C-V measurements on as-grown epilayers A and B were equal to 1.0×10^{15} and $3.5 \times 10^{15} \text{ cm}^{-3}$, respectively. The residual nitrogen concentrations in the epilayers, determined by Secondary Ion Mass Spectroscopy (SIMS), were 1.1×10^{15} and $4.0 \times 10^{15} \text{ cm}^{-3}$, respectively.

Charge carrier lifetime measurements were performed via microwave photoconductance decay (μ -PCD). The 355-nm line of a tripled Nd:YAG pulsed laser was used to excite electron hole pairs within the epitaxial layer, while the lifetime was determined through the measurement of the time constant of the exponential decay of the reflected microwave signal power. Lifetime mapping on the wafer was performed using a Semilab WT-85 lifetime scanner where the excitation pulse width is 10 ns and the frequency of the reflected microwave signal is in the range of 10.0 - 10.6 GHz.

III. RESULTS AND DISCUSSION

A. Deep-level defects in as-grown material

DLTS spectra typical of the as-grown epilayers A and B, with the nitrogen concentrations of 1.1×10^{15} and $4 \times 10^{15} \text{ cm}^{-3}$, respectively, are presented in Fig. 1 and the images illustrating the distributions

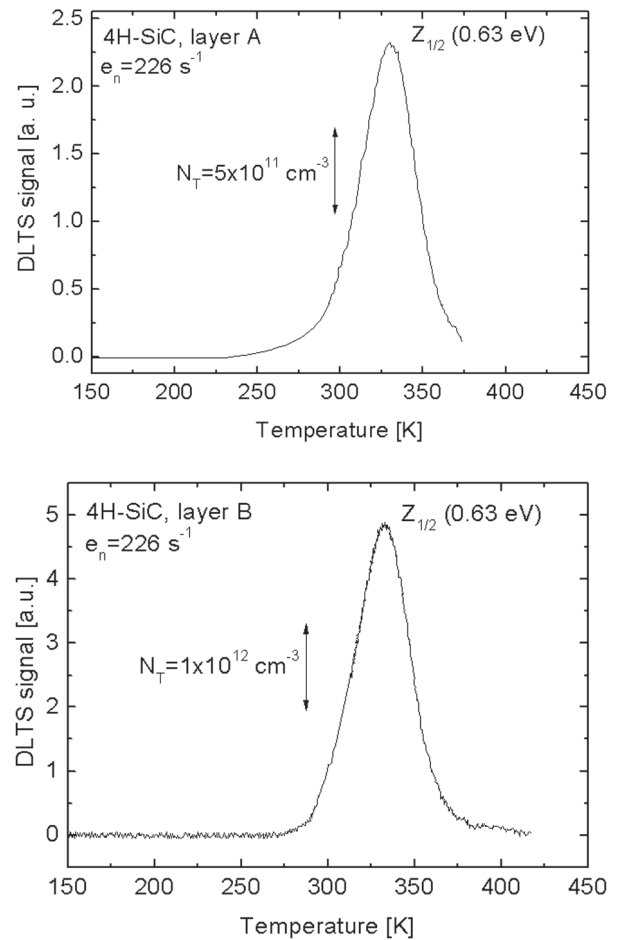


Fig. 1. DLTS spectra typical of the as-grown epilayers A (left) and B (right) with the nitrogen concentrations $1.1 \times 10^{15} \text{ cm}^{-3}$ and $4.0 \times 10^{15} \text{ cm}^{-3}$, respectively.

Rys. 1. Widma DLTS typowe dla warstw epitaksjalnych z grupy A (strona lewa) oraz z grupy B (strona prawa), w których koncentracja azotu wynosiła odpowiednio $1,1 \times 10^{15} \text{ cm}^{-3}$ i $4,0 \times 10^{15} \text{ cm}^{-3}$.

of minority carrier lifetime in various regions of the epilayers are shown in Fig. 2. According to the DLTS results, in the both epilayers only the $Z_{1/2}$ center is observed. The concentrations of this center in the epilayers A and B are found to be 1.8×10^{12} and $3.4 \times 10^{12} \text{ cm}^{-3}$, respectively. As seen in Fig. 2, the minority carrier lifetime for approximately 60% of the epilayer A area is $\sim 970 \text{ ns}$ and for around 70%

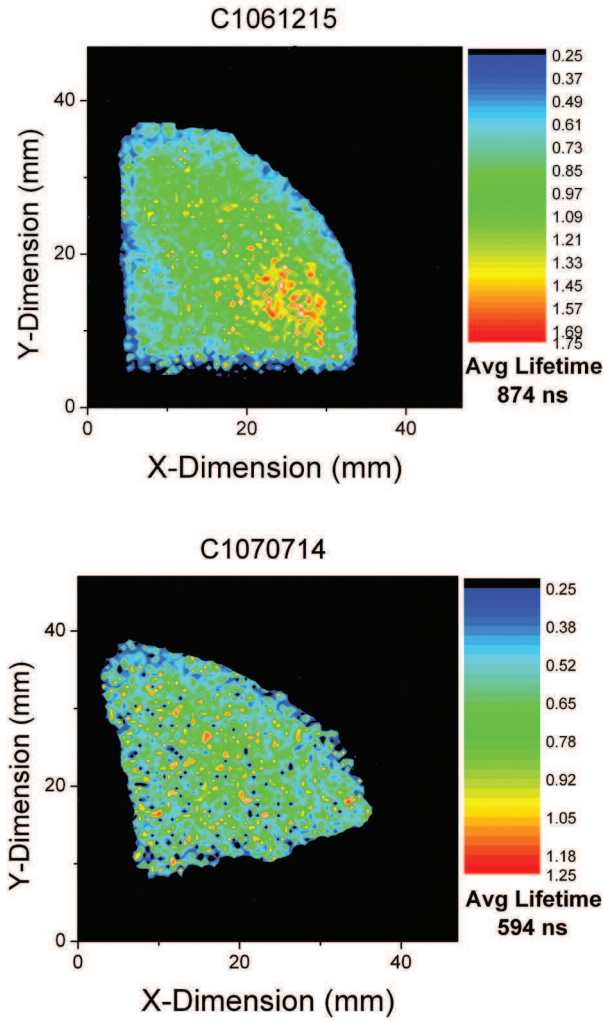


Fig. 2. Images of the minority carrier lifetime distributions for the as-grown epilayers A (left) and B (right) with the nitrogen concentrations $1.1 \times 10^{15} \text{ cm}^{-3}$ and $4.0 \times 10^{15} \text{ cm}^{-3}$, respectively.

Rys. 2. Obrazy ilustrujące rozkład wartości czasu życia mniejszościowych nośników ładunku bezpośrednio po procesie wzrostu w warstwie epitaksjalnej z grupy A (strona lewa) oraz w warstwie epitaksjalnej z grupy B (strona prawa) o koncentracji azotu odpowiednio $1.1 \times 10^{15} \text{ cm}^{-3}$ i $4.0 \times 10^{15} \text{ cm}^{-3}$.

of the epilayer B area is $\sim 520 \text{ ns}$. In view of the previous results [1, 16], the $Z_{1/2}$ center is recognized to be the main lifetime killer in the epitaxial 4H-SiC. So, the minority carrier lifetime can be written as

$$\tau_p = \frac{1}{[Z_{1/2}]\sigma_p \langle v_p \rangle} \quad (2)$$

where $[Z_{1/2}]$ denotes the $Z_{1/2}$ center concentration, σ_p is the capture cross-section of the $Z_{1/2}$ center for holes and $\langle v_p \rangle$ is the mean thermal velocity of holes. Equation (1) indicates that the lifetime is inversely proportional to the $Z_{1/2}$ center concentration. Therefore,

the ratio of the lifetime values for the epilayers A and B should be equal to the ratio of the values of the $Z_{1/2}$ center concentrations in the epilayers B and A. Taking into account the above mentioned data, the former is equal to 1.87 and the latter is equal to 1.89. Thus, our results are consistent with the earlier experimental data showing that the minority carrier lifetime in epitaxial 4H-SiC is predominantly affected by the $Z_{1/2}$ center concentration [1, 11 - 12, 16]. However, according to the results demonstrated by Danno *et al.* [11] and Kimoto *et al.* [12], the measured value of the lifetime can be significantly affected by surface recombination and recombination in the substrate when the trap concentration is lower than $1 \times 10^{13} \text{ cm}^{-3}$. In our studies these effects have not occurred and we managed to observe the decrease in the minority carrier lifetime due to increasing the $Z_{1/2}$ center concentration from 1.8×10^{12} to $3.4 \times 10^{12} \text{ cm}^{-3}$. It is worth adding that the μ -PCD measurements mentioned in Refs. 11 and 12 were carried out at the microwave signal frequency of 26 GHz, whereas our measurements were performed at $\sim 10 \text{ GHz}$. The capture cross-section of the $Z_{1/2}$ center for holes at 300 K, calculated from Eq. (1), is $\sim 6 \times 10^{-14} \text{ cm}^2$. It should be noted that $Z_{1/2}$ defect is an amphoteric, negative- U center having the donor level ($0/+$) located closer to the bottom of the conduction band than the acceptor level ($-/0$) [8, 14]. The large value of σ_p indicates that the hole capture by the $Z_{1/2}$ center is enhanced by attractive Coulombic potential. Thus, the acceptor level of the center seems to be the dominant recombination level.

The DLTS spectra (Fig. 1) show that the $Z_{1/2}$ center concentration increases almost two times with increasing the nitrogen concentration from 1.1×10^{15} to $4 \times 10^{15} \text{ cm}^{-3}$. This experimental fact is consistent with the results reported by Pintilie *et al.* [8] revealing that the concentration of $Z_{1/2}$ center is not only positively correlated with the N donor concentration, but is also enhanced with the higher C/Si ratio. In view of these results, Eberlein *et al.* [14] proposed a model for the microscopic structure of the $Z_{1/2}$ center, based on first-principles calculations performed using spin-polarized density functional theory (DFT). According to this model, the $Z_{1/2}$ center is presumably a complex defect composed of a dicarbon interstitial and an interstitial-nitrogen atom. However, the direct nitrogen involvement in the $Z_{1/2}$ center formation was contradicted by subsequent studies from Storasta *et al.* [13, 17] that indicated that the concentration of the $Z_{1/2}$ center in electron irradiated 4H-SiC epilayers can exceed the nitrogen concentration by one order of magnitude. Thus, the microscopic structure of this center is still not fully understood, although there are

indications that it is related to a native defect whose formation is strongly affected by the composition of the gas phase during the CVD processes [1, 8, 18].

Assuming that the $Z_{1/2}$ center is associated with a native defect, like a carbon vacancy, as has been reported by Danno and Kimoto [19], we propose an alternative explanation of the doping level effect on the center concentration. It should be noted that the increase in the donor concentration results in the rise of the Fermi energy in relation to the valence band maximum. Since increase in the Fermi energy lowers the formation energy of native acceptors, the higher N concentration leads to the enhancement of the generation of these point defects during the epitaxial growth [14]. Thus, the concentrations of native point defects with multiple negative charge states strongly increase when the Fermi level shifts towards the conduction band minimum [20]. Hence, the observed rise in the $Z_{1/2}$ center concentration may be explained by an indirect effect of the increase in the N concentration.

The reported [8, 18], seemingly opposite, dependences of the $Z_{1/2}$ center concentration on the C/Si ratio can therefore be understood, if we tentatively attribute this center to the divacancy $V_C V_{Si}$ that consists of nearest-neighbor silicon (V_{Si}) and carbon (V_C) vacancies formed due to the removal of the Si and C atoms from different lattice sites – hexagonal (h) and cubic (k) or cubic (k) and hexagonal (h), respectively. According to DFT calculations [21], only the divacancies composed of vacancies located at different lattice sites ($V_C^h V_{Si}^k$) or ($V_C^k V_{Si}^h$) will exhibit such a negative- U behavior in 4H-SiC. Moreover, such divacancies are characterized by high thermal stability, similar to that observed for the $Z_{1/2}$ center. It is worth noting that initially the $Z_{1/2}$ center was suggested to be associated with such a $V_C V_{Si}$ divacancy by Dalibor *et al.* [22].

On the grounds of the theory of relative native- and impurity-defect abundances in compound semiconductors and the factors that influence them [23], we can assume that at low C/Si values (~ 0.4), the divacancy concentration is limited by the concentration of the silicon vacancies. In this case the residual concentration of the carbon vacancies is much higher (by more than one order of magnitude) than that of silicon vacancies. It should be noted, however, that a part of carbon vacancies can be involved in the formation of silicon antisites (Si_C). In addition, silicon vacancy-silicon antisite pairs ($V_{Si} Si_C$) may also be formed.

At high C/Si values ($\sim 1.5 - 3$), the divacancy concentration is limited by the carbon vacancy concentration, however the significantly higher

concentration of the silicon vacancies can be reduced through the formation of carbon antisites (C_{Si}). Apart from that, the complexes $V_C C_{Si}$ can be also created. Thus, the influence of the C/Si ratio on the $Z_{1/2}$ center concentration follows that on the $V_C V_{Si}$ concentration. In other words, the $Z_{1/2}$ center can be formed during the epitaxial growth either at lower values of the C/Si ratio, or at higher values of the C/Si ratio. So, there should be an optimal value of the C/Si ratio allowing for the minimization of the $Z_{1/2}$ center concentration. This conclusion is consistent with the experimental results showing that the dependence of the $Z_{1/2}$ center concentration on the C/Si ratio follows such a trend [8, 18].

B. Deep-level defects in as-irradiated material

Fig. 3 shows the DLTS spectra representative of the epilayers A and B after irradiation with low-energy electrons. It is easily seen that the irradiation resulted in the formation of additional electron traps, labeled as TI2, TI3, TI4 and TI5. It is interesting to note that the $Z_{1/2}$ center is not observed in these spectra. This is due to the fact that after the irradiation, the capacitance of the depletion region in the Schottky diodes on epilayers A and B, measured at zero bias at the temperature of 300 K, dropped from 10.5 to 4.4 pF and from 19.6 to 6.0 pF, respectively. In other words, the shallow donors in the both epilayers were almost fully compensated with the $Z_{1/2}$ acceptors that arose during the irradiation. On the other hand, at the temperature of 350 K, the capacitance values were nearly such as at 300 K before the irradiation. Taking into account that in the range of 300 – 350 K the thermal emission rate of electrons trapped at $Z_{1/2}$ centers increases from ~ 77 to ~ 3416 s⁻¹, we can assume that the capacitance changes observed with increasing the temperature are due to the change in the charge state of the $Z_{1/2}$ centers induced in the both epilayers by the low-energy electron irradiation. Thus, at 300 K, the vast majority of the centers are occupied by electrons and being negatively charged compensate positively charged nitrogen donors. At 350 K, the centers are mostly neutral and compensation almost disappears, as the thermal emission rate of electrons is sufficiently high.

As it seen in Fig. 3, the trap TI2, with the activation energy of 0.71 eV, only was observed in the epilayer B, which had a higher nitrogen concentration equal to 4.0×10^{15} cm⁻³. For all the traps detected in as-irradiated epilayers, the plots of $\log(T^2/e_n)$ versus $1/kT$, where e_n is the electron thermal emission rate and k is the Boltzmann constant, are presented in

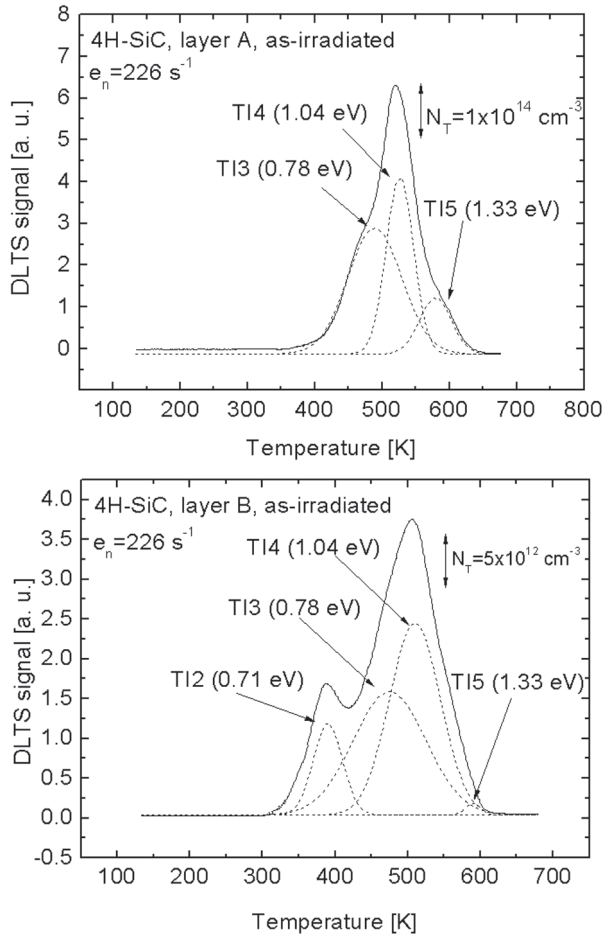


Fig. 3. DLTS spectra typical of nitrogen-doped epilayers A (left) and B (right) after irradiation with a dose of $1.0 \times 10^{17} \text{ cm}^{-2}$ of 300-keV electrons.

Rys. 3. Widma DLTS typowe dla warstw epitaksjalnych z grupy A (strona lewa) oraz z grupy B (strona prawa) po napromieniowaniu dawką elektronów o energii 300 keV, równą $1,0 \times 10^{17} \text{ cm}^{-2}$.

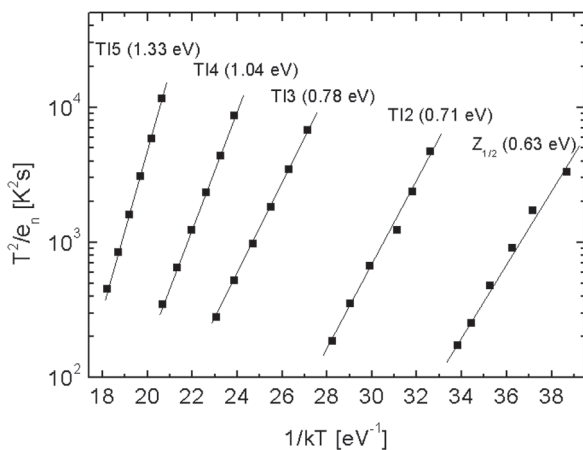


Fig. 4. Arrhenius plots for deep electron traps detected in as-irradiated, nitrogen-doped epilayers A and B of 4H-SiC.

Rys. 4. Wykresy Arrheniusa dla pułapek elektronowych wykrytych w domieszkowanych azotem warstwach epitaksjalnych 4H-SiC z grupy A oraz z grupy B.

Fig. 4. The values of the thermal emission activation energy E_a and apparent electron capture cross-section σ_n , calculated from the slope and intercept of each line, are listed in Table I.

Table I. Summary of activation energies and capture cross-sections for deep electron traps detected the 4H-SiC epilayers A and B before and after 300-keV electron irradiation.

T a b l e I .

Trap label	Activation energy E_a [eV]	Capture cross-section σ_n [cm ²]	E p i - layer	Remarks
$Z_{1/2}$	0.63 ± 0.05	1.3×10^{-14}	A, B	observed in as-grown and irradiated material, $V_{Si}V_C$
TI2	0.71 ± 0.05	4.2×10^{-15}	B	irradiation induced, S2 in Ref. 24, $N_i(C_i)_2$
TI3	0.78 ± 0.05	4.1×10^{-16}	A, B	irradiation induced, EH4 in Ref. 7, $V_C (-/-)$
TI4	1.04 ± 0.05	4.8×10^{-15}	A, B	irradiation induced, EH5 in Ref. 7, $V_C (-/0)$
TI5	1.33 ± 0.05	1.3×10^{-13}	A, B	irradiation induced, EH6 in Ref. 19, $(C_i)_2$

Fig. 5 shows the comparison of the $Z_{1/2}$ center concentrations after the irradiation, as well as the concentrations of irradiation-induced traps TI2, TI3, TI4 and TI5 in the epilayers A and B. It should be added that the $Z_{1/2}$ center concentrations were calculated from the capacitance changes observed in the temperature range of 300 – 350 K. The results indicate that the $Z_{1/2}$ center concentrations, induced in the epilayers A and B by 300-keV electron irradiation, are 8.25×10^{14} and $3.17 \times 10^{15} \text{ cm}^{-3}$, respectively. It is interesting to note that according to the results of Danno and Kimoto [19], for 4H-SiC epilayers with $N_D - N_A$ ranging from 8.0×10^{14} to $1.6 \times 10^{16} \text{ cm}^{-3}$ before the irradiation, the $Z_{1/2}$ center concentration induced by the irradiation with 300-keV electrons is $\sim 1 \times 10^{15} \text{ cm}^{-3}$. The results shown in Fig. 5 indicate that the $Z_{1/2}$ center is the predominant electron trap induced in the epilayers A and B by the electron irradiation at 300 keV and a dose of $1 \times 10^{17} \text{ cm}^{-2}$. Compared to as-grown material, the increase in the

center concentration in the both epilayers is found to be nearly by three orders of magnitude.

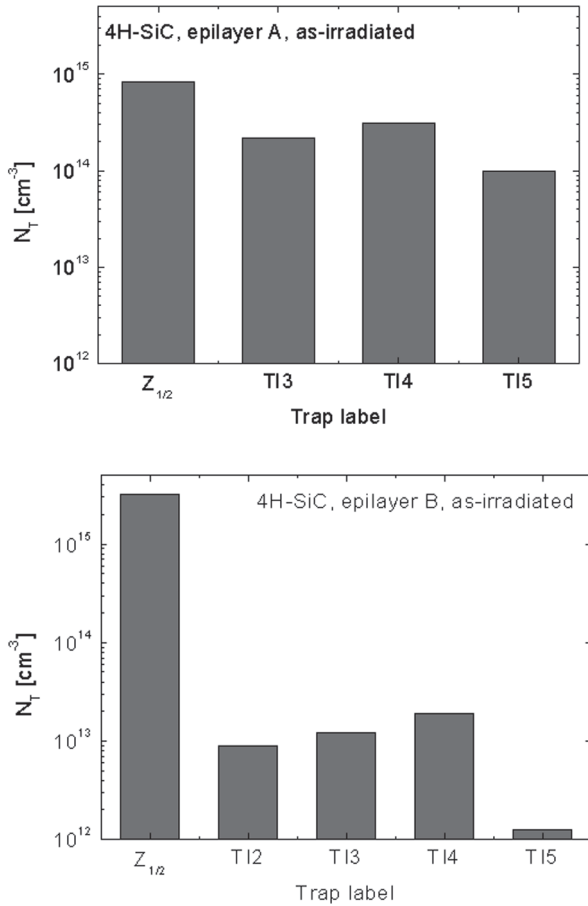


Fig. 5. Concentrations of deep-level defects detected in the epilayers A (left) and B (right) with the nitrogen concentrations of $1.1 \times 10^{15} \text{ cm}^{-3}$ and $4.0 \times 10^{15} \text{ cm}^{-3}$, respectively, after irradiation with a dose of $1.0 \times 10^{17} \text{ cm}^{-2}$ of 300-keV electrons.

Rys. 5. Ilustracja graficzna wartości koncentracji głębokich centrów defektowych, wykrytych w warstwach epitaksjalnych z grupy A oraz z grupy B po napromieniowaniu dawką elektronów o energii 300 keV, równą $1,0 \times 10^{17} \text{ cm}^{-2}$. Koncentracja azotu w warstwach wynosi odpowiednio $1,1 \times 10^{15} \text{ cm}^{-3}$ i $4,0 \times 10^{15} \text{ cm}^{-3}$.

In view of the results obtained by measurements of the positron lifetimes [15], C atoms are predominantly displaced when irradiated with low energy (300 keV) electrons, giving rise to Frenkel pairs: V_C and C_i . Silicon atoms can be displaced at higher energies (500 keV) and irradiation with 2.5-MeV electrons results in divacancy ($V_{Si}V_{Si}$) formation. Thus, we can assume that the increase in the $Z_{1/2}$ center concentration seen in Fig. 5, as well as the formation of deep electron traps TI2 (0.71 eV), TI3 (0.78 eV), TI4 (1.04 eV) and TI5 (1.33 eV), are mainly due to the radiation damage on the carbon sublattice. This fact enables us to explain the sub-

stantial rise in the $Z_{1/2}$ center concentration and give a tentative identification for the irradiation-induced deep-level defects.

On the grounds of the discussion given above for the as-grown material, we have attributed the $Z_{1/2}$ center to the divacancy $V_C V_{Si}$. In other words, the formation of this center requires both carbon and silicon vacancies. Thus, the increase in the concentration of $Z_{1/2}$ center after the low-energy electron irradiation that can only displace C atoms is limited by the V_{Si} concentration. Therefore, we can assume that there are high residual V_{Si} concentrations in the as-grown epilayers A and B. This assumption is fully justified, for the both epilayers were grown at the high C/Si ratio equal to 1.55. In other words the gas phase during the CVD processes was significantly carbon rich. The concentrations of the traps TI2 (0.71 eV), TI3 (0.78 eV), TI4 (1.04 eV) and TI5 (1.33 eV), arising from the formation of the Frenkel pairs on the carbon sublattice, are significantly lower.

The electron trap TI2 (0.71 eV) was only observed in the epilayer B which exhibited the higher nitrogen concentration ($4 \times 10^{15} \text{ cm}^{-3}$). This fact suggests that a nitrogen atom may be involved in the formation of this trap. In view of calculations performed using DFT numerical procedures [14], this trap is likely to be attributed to the complex of $N_i(C_i)_2$ that is composed of an interstitial-nitrogen - and dicarbon interstitial and was proposed earlier as a possible structure for the $Z_{1/2}$ center. It is worth adding that the parameters of the trap TI2 given in Table I are very close to those of the electron trap S2 in Ref. 24, which occurs in epitaxial 4H-SiC with $N_D - N_A = 5 \times 10^{15} \text{ cm}^{-3}$ after the electron irradiation at an energy of 15 MeV with a dose of $2 \times 10^{14} \text{ cm}^{-2}$.

The concentrations of traps TI3 (0.78 eV) TI4 (1.04 eV) and TI5 (1.33 eV) are substantially higher in the epilayer A that had a lower nitrogen concentration ($N_D - N_A = 1.0 \times 10^{15} \text{ cm}^{-3}$). This fact can be explained by taking into account that the $Z_{1/2}$ center concentration after the irradiation is much lower in this epilayer than in the epilayer B. In other words, much less carbon vacancies was captured by silicon vacancies to form the $Z_{1/2}$ centers. Thus, a higher concentration of these vacancies was involved in the formation of other defects.

Moreover, the parameters of traps TI3 and TI4 are close to those of traps EH4 and EH5, respectively, which have been observed earlier (Ref. 7) in epitaxial 4H-SiC with $N_D - N_A = (0.3 - 1) \times 10^{15} \text{ cm}^{-3}$ after the electron irradiation at an energy of 2.5 MeV with doses ranging from 5×10^{13} to $1 \times 10^{15} \text{ cm}^{-2}$. It should also be noted

that the proportions of the TI3-trap concentration to the TI4-trap concentration in the both epilayers are very similar being close to 0.7 with an error less than 10%. Furthermore, the activation energies of these traps match up very well with the energy levels $E_v + (1.65\text{--}2.21)$ eV and $E_v + (1.90\text{--}2.09)$ eV that are calculated by DFT for $V_c(2/-)$ and $V_c(-/0)$, respectively [25]. Experimental results obtained from photo-EPR measurements also indicate that the level corresponding to $V_c(-/0)$ is located at $\sim E_c - 1.1$ eV [26]. Thus, the traps TI3 and TI4 are likely to be attributed to the two acceptor states of the carbon vacancy.

The parameters of trap TI5 indicate that this may be the same trap as the EH_6 center that was detected by Danno and Kimoto in epitaxial 4H-SiC by deconvolution the broad DLTS peak corresponding to the known $EH_{6/7}$ center [19]. The significant concentration of the EH_6 center, equal to 1.3×10^{13} cm⁻³, was observed after the electron irradiation at an energy of 116 keV with a dose of 3×10^{17} cm⁻³ and annealing at 950 °C for 30 min. In view of recent results obtained by low-temperature photoluminescence microspectroscopy of electron-irradiated epitaxial 4H-SiC, combined with calculations of local vibration mode energies of C interstitial clusters [27], the trap TI5 seems to be related to the dicarbon interstitial. It has been shown that C interstitials are extremely mobile and under the conditions associated with electron irradiation, interstitial carbon aggregates are formed [27]. The formation of dicarbon interstitials supports the fact that in the epilayer A, which had a lower N concentration, the concentration of trap TI5 (Fig. 5) is approximately two times lower than the concentrations of traps TI3 and TI4 which are assigned to carbon vacancies. In the epilayer B, the concentration of trap TI2 represents approximately a half of the concentrations of traps TI3 and TI4, for the vast majority of the dicarbon interstitials are captured by nitrogen atoms. Therefore, the concentration of the irradiation induced TI5 centers, equal to 1.25×10^{12} cm⁻³, is very low compared to the concentrations of the other traps detected in the epilayer B after the irradiation.

IV. CONCLUSIONS

The low-energy electron irradiation has been used as a tool for identification of electron traps in epitaxial 4H-SiC observed by the DLTS technique. The effect of the nitrogen content on the properties and concentrations of the deep-level defects is shown. On

the grounds of our experimental results, as well as by taking into account the earlier reported dependences of the $Z_{1/2}$ center concentration on the C/Si ratio, we have tentatively attributed the center to the divacancy V_cV_{Si} formed by the nearest neighbor silicon and carbon vacancies located in different (h or k) lattice sites. It is shown that the minority carrier lifetime in n -type epitaxial 4H-SiC is predominantly affected by the $Z_{1/2}$ center concentration. In particular, we demonstrate that when the $Z_{1/2}$ center concentration goes up from 1.8×10^{12} to 3.4×10^{12} cm⁻³ the carrier lifetime decreases from 970 to 520 ns. This result completes the experimental data presented in Refs. 11 and 12 showing the decrease in the lifetime for the $Z_{1/2}$ center concentrations higher than 10^{13} cm⁻³. The capture cross-section of the $Z_{1/2}$ center for holes is found to be $\sim 6.0 \times 10^{-14}$ cm². The substantial increase in the $Z_{1/2}$ center concentration induced by the low-energy electron irradiation is observed. The concentration of this center seems to be dependent either on the residual concentration of silicon vacancies in the as-grown material, or on the nitrogen concentration. Four irradiation-induced deep electron traps with the activation energies of 0.71, 0.78, 1.04 and 1.33 eV have been revealed. The 0.71-eV trap, observed only in the epilayer with a higher nitrogen concentration, is tentatively identified with the complex defect arising from the capture of a dicarbon interstitial by a nitrogen atom. The 0.78-eV and 1.04-eV traps are assigned to the carbon vacancy levels for $V_c(2/-)$ and $V_c(-/0)$, respectively, whereas the 1.33-eV trap is proposed to be related to the dicarbon interstitial.

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