

Effects of Nitrogen Impurity Concentration on Nitrogen-Vacancy Center Formation in 4H-SiC

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Abstract. Spin defects of which states can be manipulated in Silicon Carbide (SiC) have drawn considerable attention because of their applications to quantum technologies. The single negatively-charged pairs of V_{Si} and nitrogen atom (N) on an adjacent C site ($N_C V_{Si}^-$ center) in SiC is suitable for them. This paper reports the formation of $N_C V_{Si}^-$ centers on 4H-SiC epilayers with different nitrogen concentrations using light/heavy ion irradiation and subsequent thermal annealing. The formation of $N_C V_{Si}^-$ centers is characterized by the near infrared photoluminescence (PL) spectroscopy. It is shown that the PL intensity from $N_C V_{Si}^-$ centers depends on the N concentration and the ion irradiation conditions. The PL intensity increases monotonically with increasing the N concentration when the N concentration is above $2.6 \times 10^{16} \text{ cm}^{-3}$, whereas no linear correlation between them does not appear below that N concentration. Although the PL intensity increases with increasing defects induced by ion irradiation, the PL quenching due to neighboring residual defects appear at above the areal vacancy concentration of 10^{17} vac/cm^2 and the broad Raman scattering spectra originated from vibration modes of amorphized regions hinder the PL from $N_C V_{Si}^-$ centers at above 10^{18} vac/cm^2 . The formation mechanism and the charge state stability of $N_C V_{Si}^-$ centers are discussed based on the obtained results.

Introduction

Point defects which have electronic spin (spin defects) in wide band-gap semiconductors have attractive attention because of their potential applications to quantum computing, quantum telecommunication and quantum sensing [1-3]. Silicon carbide (SiC) is one of the suitable materials for quantum technology applications because of the availability of high quality wafers with relatively large size and the mature device fabrication technology. It has been reported that spin defects in SiC such as single negatively charged silicon vacancy (V_{Si}^-) [4] and neutral divacancy ($V_{Si} V_C^0$) [5] were manipulated using the optically detected magnetic resonance (ODMR) technique. In addition to these spin defects, it has been recently reported that negatively-charged pairs of V_{Si} and nitrogen atom (N) on an adjacent C site ($N_C V_{Si}^-$ center) in SiC [6,7] have similar electronic structure to NV centers in diamond [8] which can be optically polarizable spin triplet ($S=1$). Unlike NV centers in diamond which show red photoluminescence (600-800 nm), the $N_C V_{Si}^-$ centers show near infrared (NIR) PL centered at around 1300 nm at room temperature (RT). The NIR-PL emission characteristics is especially suitable for life-science applications such as *in vivo* imaging and sensing, since the NIR light can penetrate biological tissues such as skin and blood more efficiently than visible light. Although high density $N_C V_{Si}^-$ center formation is crucial to improve sensitivity of imaging/sensing without increasing the volume, the method to control the formation of $N_C V_{Si}^-$ centers has not been established yet. It is known that $N_C V_{Si}^-$ centers are formed by ion irradiation and subsequent thermal

annealing [6]. Recently, we have reported intensity variations of the PL from $N_C V_{Si}^-$ centers formed by different ion species and fluences and thermal annealing temperatures [9], whereas effects of the N impurity concentration on $N_C V_{Si}^-$ center formation remain to be elucidated.

Here we show NIR-PL properties of $N_C V_{Si}^-$ centers formed in 4H-SiC epilayers with different N impurity concentrations and clarify the relationship between the N concentration and the $N_C V_{Si}^-$ center formation. Ion irradiation and thermal annealing were performed for the creation of $N_C V_{Si}^-$ centers in 4H-SiCs and the formation mechanism of $N_C V_{Si}^-$ centers is discussed.

Experimental

Samples used in this study were intentionally nitrogen (N) doped 4H-SiC epilayers grown on n-type 4H-SiC substrates (4° off, Si-face). The N impurity concentrations in the epilayers were 4.9×10^{15} , 7.5×10^{15} , 2.6×10^{16} , 2.1×10^{17} , and 3.5×10^{18} cm^{-3} . Here, these samples are represented as [N]4.9E15, [N]7.5E15, [N]2.6E16, [N]2.1E17, and [N]3.5E18, respectively. The samples were irradiated with 240 keV-hydrogen (H), 4 MeV-silicon (Si), and 7 MeV-iodine (I) ions at RT at the Takasaki Advanced Radiation Research Institute, National Institutes for Quantum and Radiological Science and Technology. These ion energies were chosen so that the peak defect concentrations appeared at 1.5~2.0 μm in depth from the sample surface. The irradiated fluence ranges and their corresponding areal vacancy concentrations are summarized in Table 1. The areal vacancy concentration was calculated by the Monte Carlo Simulation Code, TRIM [10]. After ion irradiation, thermal annealing was performed at 1000 $^\circ\text{C}$ for 30 min under Ar atmosphere with an infrared heating furnace. It was revealed from our previous study that the optimal annealing temperature for the $N_C V_{Si}^-$ center formation was 1000 $^\circ\text{C}$ [9]. It was also confirmed that the annealing time longer than 30 min did not affect the $N_C V_{Si}^-$ center formation in the case of high N impurity concentration. PL measurement at 293 K (RT) and 80 K was performed through 1064 nm excitation with HORIBA LabRAM HR Evolution (micro-PL measurement system). The laser spot diameter and the net laser power were 1.4 μm and 160.5 mW at 293 K, and 2.6 μm and 74.8 mW at 80 K, respectively. Since the ideal depth resolution of measurement system was estimated to be more than 5 μm when the refractive index of SiC was 2.6, all the regions in which vacancies were induced by irradiations were observed and the vacancy profile along the depth direction was not considered in the measurement system of this study. Consequently, we used the unit of vacancies per area (vac/cm^2) instead of vacancy concentration (vac/cm^3) to evaluate the amount of vacancies induced by irradiations [9].

Table 1. The ion irradiation conditions in this study. The areal vacancy concentration (vac/cm^2) was calculated by TRIM.

Ion species	Fluence (cm^{-2})	Vacancies per area (vac/cm^2)
240 keV-H	$1.0 \times 10^{16} \sim 5.0 \times 10^{16}$	$1.3 \times 10^{17} \sim 6.5 \times 10^{17}$
4 MeV-Si	$2.5 \times 10^{12} \sim 2.5 \times 10^{15}$	$8.8 \times 10^{15} \sim 8.8 \times 10^{18}$
7 MeV-I	$6.0 \times 10^{11} \sim 6.0 \times 10^{14}$	$1.7 \times 10^{16} \sim 1.7 \times 10^{19}$

Results and Discussion

Figure 1 shows PL spectra of the [N]3.5E18 sample irradiated with 4 MeV-Si ions at the areal vacancy concentration of 8.8×10^{17} vac/cm^2 . A broad PL spectrum centered at around 1300 nm was observed at RT, whereas four sharp peaks at 1173.7 nm, 1179.7 nm, 1223.7 nm, and 1243.8 nm were observed at 80 K. These peaks corresponded to zero phonon lines (ZPLs) of $N_C V_{Si}^-$ centers reported previously [11]. We conclude from the comparison of PL spectra at RT to 80 K that the broad peak observed at RT is attributable to the PL from $N_C V_{Si}^-$ centers. Note that the fringe appeared at 1350-1450 nm is due to absorption water in air.

Figure 2 shows PL spectra at RT of the [N]2.6E16 sample irradiated with 7 MeV-I at different fluences. While similar PL spectra as Fig. 1 was observed in the areal vacancy concentration of 1.7×10^{16} vac/cm² and 1.7×10^{17} vac/cm², the broadening of PL spectrum appeared at 1.7×10^{18} vac/cm² and extra broad peaks centered at around 1150 nm and 1500 nm appeared at 1.7×10^{19} vac/cm². The similar trend was also found from the [N]7.5E15 and [N]4.9E15 samples, being not found from the [N]2.1E17 and [N]3.5E18 samples. The distortion of PL spectra observed at high areal vacancy concentrations can be explained by the radiation induced amorphization of SiC crystal. The amorphization of SiC crystal starts to occur when irradiation fluence exceeds a critical dose. Once the amorphization occurs, the recrystallization is no longer expected by thermal annealing at 1000 °C and the formation of $N_C V_{Si}^-$ centers is also unexpected. According to Ref. [9], the critical dose of amorphization of 4H-SiC is around 10^{17} vac/cm² in the case of 7 MeV-I irradiation. Unlike the Raman scattering of phonon modes in SiC crystal, broad vibration modes generally appear from the amorphized region. It has been reported that two broad peaks at 200-400 cm⁻¹ and 400-600 cm⁻¹ due to Si-Si vibration modes, one broad peak at 600-1000 cm⁻¹ due to Si-C vibration modes, and two broad peaks at 1000-1200 cm⁻¹ and 1200-1600 cm⁻¹ due to C-C vibration modes appeared after high dose ion irradiation [12]. Wang *et al.* has also reported that Raman shift of graphite called G and 2D bands appeared at around 1650 cm⁻¹ and 2730 cm⁻¹ [13]. Considering the Raman shift of 1064 nm excitation wavelength, these reported peaks were good agreement with the peaks observed in our experimental data at 1.7×10^{19} vac/cm². Hence, it was concluded that the distortion of PL spectra was caused by the Raman scattering from the amorphized region. Also, the distortion of PL spectra was not observed at the [N]2.1E17 and [N]3.5E18 samples, since the PL intensity originated from $N_C V_{Si}^-$ centers were far higher than the Raman scattering from the amorphized region.

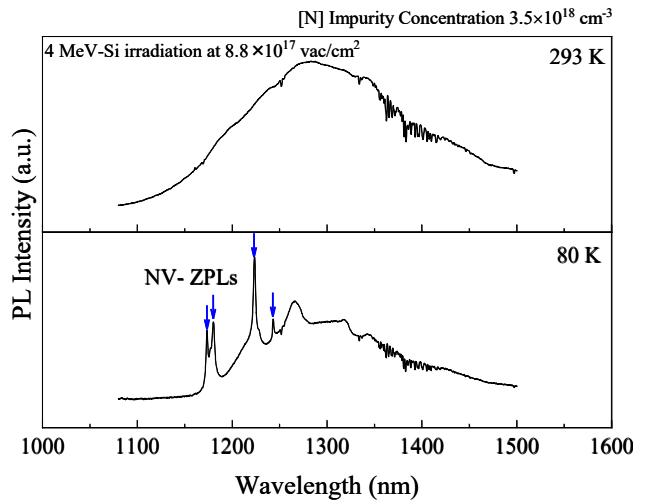


Fig. 1. NIR-PL spectra at 293 K (top) and at 80 K (bottom) of the sample [N]3.5E18 irradiated with 4 Me-Si at the areal vacancy concentration of 8.8×10^{16} vac/cm². Arrows in the bottom figure denote four ZPL lines of $N_C V_{Si}^-$ centers.

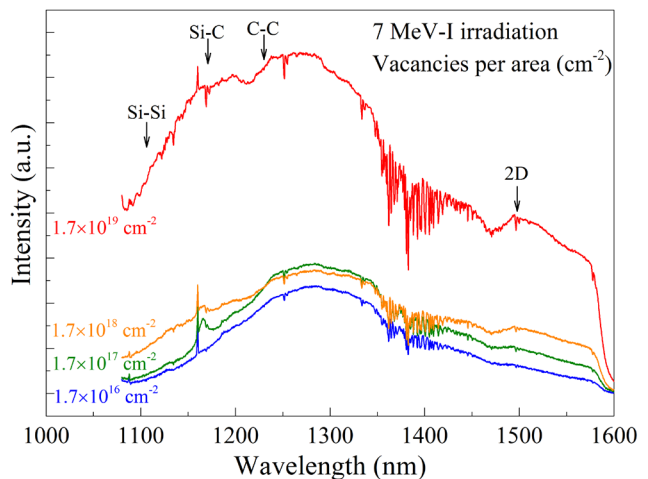


Fig. 2. NIR-PL spectra at 293 K of the 4H-SiC epilayer with N concentration of 2.1×10^{16} cm⁻³ after 7 MeV-I irradiation. The four arrows show Raman scattering originated from SiC and graphite for 1064 nm laser excitation.

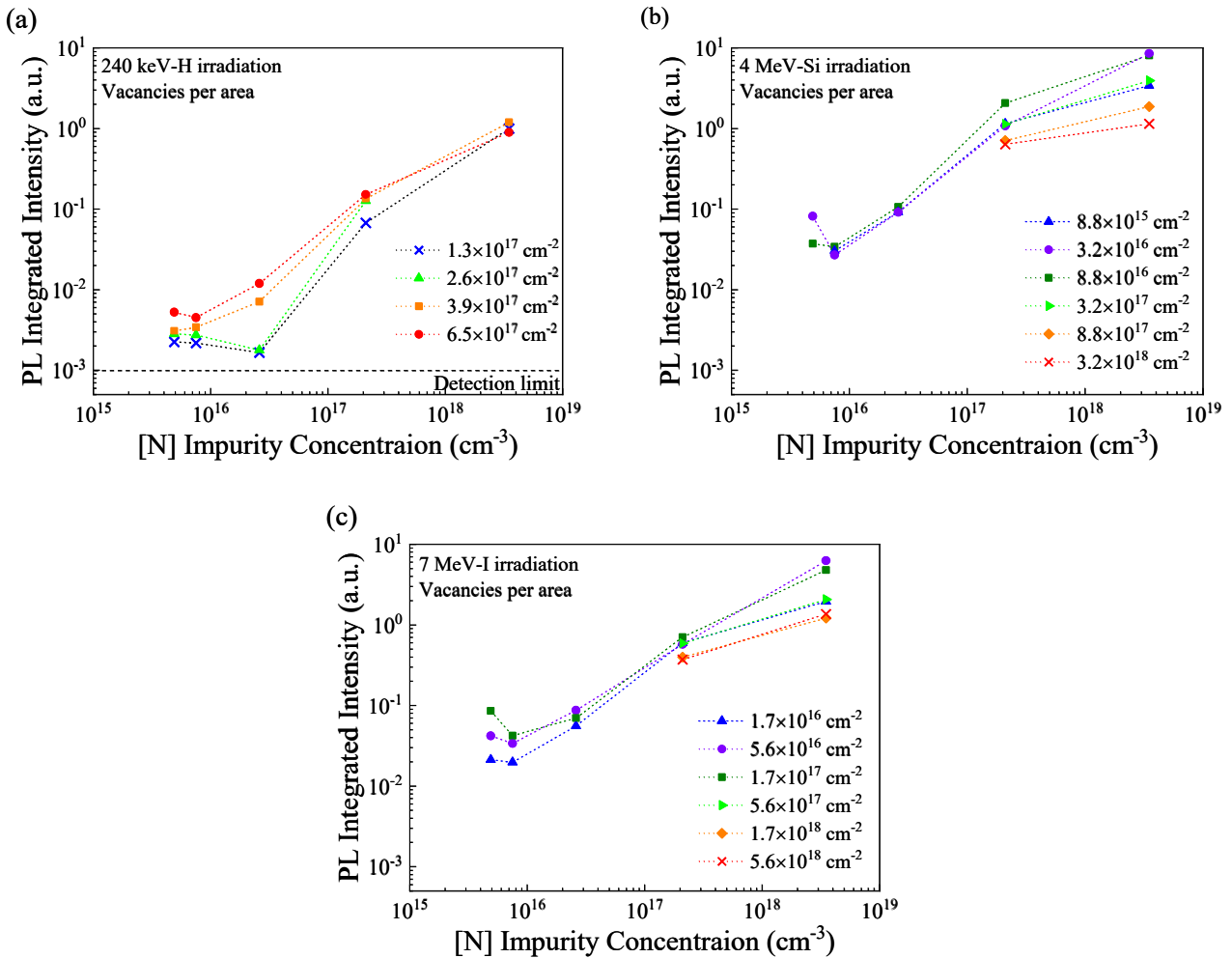


Fig. 3. The N concentration dependence of PL integrated intensity of $\text{N}_\text{C}\text{V}_{\text{Si}}^-$ centers. Ion species which irradiated to the 4H-SiC epilayer is 240 keV-H (top left), 4 MeV-Si (top right), and 7 MeV-I (bottom). PL integrated intensity were normalized value at $[\text{N}] = 3.5 \times 10^{18} \text{ cm}^{-3}$, 240 keV-H fluence at $1.0 \times 10^{16} \text{ cm}^{-2}$ to 1. All the PL spectra was integrated from 1150 nm to 1450 nm. For micro PL spectroscopy used this time, detection limit to measure PL emission is around 10^3 .

Figure 3 shows the N impurity concentration dependence of the PL integrated intensity of 240 keV-H, 4 MeV-Si, and 7 MeV-I irradiated samples. The ordinate shows PL intensity integrated from 1150 nm to 1450 nm which are normalized by the value of the $[\text{N}] = 3.5 \times 10^{18} \text{ cm}^{-3}$ sample irradiated with 240 keV-H at $1.3 \times 10^{17} \text{ vac/cm}^2$. The PL integrated intensity increased with increasing N concentration for all ion species. In the case of 240 keV-H irradiation (Fig. 3(a)), the PL integrated intensity seemed to saturate around 10^{17} vac/cm^2 at all the N concentrations. In the cases of 4 MeV-Si and 7 MeV-I irradiations (Figs. 3(b) and (c)), the PL integrated intensities showed maximum at around 10^{17} vac/cm^2 independent of N concentrations and then decreased when exceeds 10^{17} vac/cm^2 . Note that the PL integrated intensities for the N concentration below $2.6 \times 10^{16} \text{ cm}^{-3}$ at the vacancy concentration above 10^{17} vac/cm^2 were not successfully characterized in the cases of 4 MeV-Si and 7 MeV-I irradiations because of overlapping of the Raman scattering from amorphous regions. The reduction of PL integrated intensity above 10^{17} vac/cm^2 is thought to be induced by the quenching due to residual defects after 1000 °C thermal annealing. We have reported that the thermal annealing at 1000 °C was optimal for the formation of $\text{N}_\text{C}\text{V}_{\text{Si}}^-$ centers, although the temperature more than 1500 °C was required to remove the residual defects completely [14]. When focusing on the vacancy concentration around 10^{17} vac/cm^2 , the PL integrated intensities of 4 MeV-Si and 7 MeV-I irradiated samples were higher than that of 240 keV-H irradiated samples. This fact implies that cascade damage, *i.e.*, localized dense defect regions contribute to the efficient formation of $\text{N}_\text{C}\text{V}_{\text{Si}}^-$ centers [9].

No linear correlation between the PL intensity and the N concentration might be due to the formation mechanism of $N_C V_{Si}^-$ centers and their charge stability. Here we discuss the formation mechanism including defect charge states. Two formation processes of $N_C V_{Si}^-$ centers are suggested: One is the direct formation process by the combination of V_{Si} and N_C ($N_C + V_{Si} \rightarrow N_C V_{Si}$) and the other is the indirect process via nitrogen-carbon split interstitial ($(NC)_C$) and divacancy ($(NC)_C + V_C V_{Si} \rightarrow N_C V_{Si}$). According to the theoretical calculation by Gerstmann *et al.*, the indirect process is more dominant than the direct process because of the lower activation energy (3.5 eV for the direct process and 0.2 eV for the indirect process) [14]. However, the charge state of these defects has not been discussed despite the fact that the defect charge state played a significant role in defect kinetics. Bratus *et al.* have reported that the charge state of $(NC)_C$ was normally +1 because $(NC)_C$ was formed by combination of carbon interstitials ($(CC)_C^0$) and N_C^+ [15], while Bockstedte *et al.* have reported that $(NC)_C$ was neutral for intrinsic 4H-SiC but was -1 for n-type 4H-SiC [16]. It has been also reported that the most stable charge state of $V_C V_{Si}$ was neutral for intrinsic 4H-SiC but was negative (-1 or -2) for n-type 4H-SiC [17]. These results suggest that one or two extra electrons have to be supplied from donors or other defects to form negatively charged $N_C V_{Si}$ and the stability of charge state of $N_C V_{Si}^-$ centers should be considered in the case of intrinsic (or low N concentration) 4H-SiC. This effect might appear in results obtained from samples with N concentrations below 10^{16} cm^{-3} shown in Fig. 3. While the charge state of divacancy and its conversion have been clarified recently [18], no result has been reported regarding $N_C V_{Si}^-$ centers, to our best knowledge. Further investigation is necessary to clarify the charge state conversion of $N_C V_{Si}^-$ centers and the effects of donor concentration on it. Not only PL studies but also ESR (Electron Spin Resonance) studies should be performed for understanding the defect formation process.

Summary

We investigated NIR-PL properties of $N_C V_{Si}^-$ centers in the n-type 4H-SiC epilayers formed by 240 keV-H, 4 MeV-Si, and 7 MeV-I ion irradiations and subsequent thermal annealing at 1000 °C for 30 min. The broad emission peak centered at 1300 nm at RT and four ZPL lines of 1173.7 nm, 1179.7 nm, 1223.7 nm, and 1243.8 nm at 80 K were attributed to the PL from $N_C V_{Si}^-$ centers. The PL intensity increased with increasing N concentration when the N concentration was above $2.6 \times 10^{16} \text{ cm}^{-3}$, although no linear correlation between them did not appear below that concentration. This result might be originated from the instability of charge state of $N_C V_{Si}$ defects and their different charge state formation. We conclude that the high N impurity concentration is preferable to obtain efficient formation of the $N_C V_{Si}^-$ centers.

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