Raman Scattering and Carrier Diffusion Study in Heavily Co-doped 6H-SiC Layers

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Abstract. Thick 6H-SiC epilayers were grown using the fast sublimation method on low-off-axis substrates. They were co-doped with N and B impurities of \( \approx 10^{19} \text{ cm}^{-3} \) and \((4 \cdot 10^{16} - 5 \cdot 10^{18}) \text{ cm}^{-3}\) concentration, respectively. The epilayers exhibited donor–acceptor pair (DAP) photoluminescence. The micro-Raman spectroscopic study exposed a compensated \( n \)-6H-SiC epilayer of common quality with some 3C-SiC inclusions. The compensation ratio of B through 200 \( \mu \text{m} \) thick epilayer varied in 20-30% range. The free carrier diffusivity was studied by transient grating technique at high injection level. The determined ambipolar diffusion coefficient at RT was found to decrease from 1.15 cm²/s to virtually 0 cm²/s with boron concentration increasing by two orders.

1. Introduction
It is known that efficiency of the radiative DAP recombination can increase dramatically by introducing large quantities of donors and acceptors in the indirect band gap of 6H-SiC. It is desirable for the co-doped impurities to maintain uniform distribution through the whole thickness of the epilayer, which can reach several hundred microns, and occupy optimal energy states in the 6H-SiC band gap. The emitted DAP light has broad spectrum which, combined with a ultraviolet light excitation from LED of III-V nitrides, can make a preferable white light emitting device with high colour rendering parameters [1]. To solve this problem there is a need to grow SiC on low-off-axis substrates to match GaN and SiC lattice. Unfortunately, under such conditions 3C polytype of SiC also tends to grow. The challenge is to optimise growth conditions in such a way that to avoid 3C-SiC formation and to achieve electronic parameters of 6H-SiC preferable for DAP emission. In this work, some highly co-doped B-N 6H-SiC epilayers were investigated and their characterisation was performed in order to study basic requirements for light emitting co-doped 6H-SiC epilayers.

2. Experimental
The epilayers of 6H-SiC were obtained by the fast sublimation growth [2]. The process was performed using (0001) 6H-SiC substrates with the off-orientation angle of 1.4° toward [11 \( \overline{2} \) 0] direction. The
The distance between source and substrate was adjusted to be 1 mm. Polycrystalline SiC plates, doped with different concentrations of B and N, were used as a source material. The nitrogen incorporation was enhanced by growing samples in nitrogen atmosphere. According to secondary ion mass spectrometry profiles (SIMS), the concentrations of N and B in different samples vary in the range of \((9 – 13) \times 10^{18} \text{ cm}^{-3}\) and \((0.04 – 8) \times 10^{18} \text{ cm}^{-3}\), respectively. The epilayers parameters are presented in the Table 1. The backside of each sample was polished to allow ordinary absorption measurements. Some samples were cut into stripes with cross section of \(\approx (200 \times 500) \mu \text{m}^2\) and length of 5-7 mm. Then both cut edges were carefully polished to allow depth-resolved optical measurements.

### Table 1. The parameters of epilayers: doping N, B (SIMS), defects: *a) carbon inclusions; *b) polycrystalline inclusions, ambipolar diffusion coefficient \(D\) (TG).

| Sample No. | Thickness (µm) | N (cm\(^{-3}\)) | B (cm\(^{-3}\)) | \(N_D - N_A\) (cm\(^{-3}\)) | Defects (cm\(^{-2}\)) | \(D\) (cm\(^2\)/s) at \(3 \times 10^{18} \text{ cm}^{-3}\) |
|------------|----------------|----------------|----------------|--------------------------|----------------------|------------------------|
| ELS 117    | 45             | \(9.0 \times 10^{18}\) | \(4.4 \times 10^{18}\) | \(4.6 \times 10^{18}\) | -                     | 0.1                    |
| ELS 118    | 45             | \(9.2 \times 10^{18}\) | \(5.2 \times 10^{18}\) | \(4.0 \times 10^{18}\) | -                     | -                      |
| ELS 296    | 200            | \(1.3 \times 10^{19}\) | \(2.1 \times 10^{18}\) | \(\approx 1.1 \times 10^{19}\) | \(10^1 \text{ a)}\) | 0 ± 0.05               |
| ELS 297    | 200            | \(1.1 \times 10^{19}\) | \(4.0 \times 10^{16}\) | \(\approx 1.1 \times 10^{19}\) | \(10^6 \text{ b)}\) | 1.15                   |
| RF 18      | 130            | \(4 \times 10^{18}\) | \(2.5 \times 10^{18}\) | \(1.5 \times 10^{18}\) | \(10^{-2} \text{ a)}\) | -                      |
| RF 04      | 110            | \(8 \times 10^{18}\) | \(2.2 \times 10^{18}\) | \(5.8 \times 10^{18}\) | \(10^{-7} \text{ b)}\) | -                      |

Unpolarized micro-Raman spectra was collected in the backward direction with the *NanoFinder* confocal system (LOTIS-TII, Belarus - Japan) using excitation of polarized 473 nm solid state cw-laser focused to the spot of \(\approx 0.5 \mu \text{m}\) diameter on the surface. The excitation power was 8 mW and the exposition time 20 s. The ordinary (depth-integrated) absorption was measured using *Shimadzu* UV spectrometer. The depth-resolved absorption was studied by probing across the epilayer \((k \parallel c)\) with a focused 1300 nm cw-laser beam. Carrier lifetime and diffusivity measurements were performed by transient grating (TG) technique at the excitation geometry of \(k \parallel c\) [3]. The excitation was accomplished by 355 nm and 25 ps pulsed laser. The estimated absorption depth for such wavelength is 11 µm. The period \(\Lambda\) of the TG was varied between 2 and 8 µm. Lifetime \(\tau_e\) and ambipolar carrier
diffusivity $D$ were extracted from the plot of inverse TG erasure time $\tau_g$ versus square of inverse TG period: $1/\tau_g = 1/\tau_R + 4\pi^2 D/\Lambda^2$ [3]. All measurements were performed at RT.

3. Results and Discussion

The selected Raman spectra are given in figure 1 with measurement geometries shown in the inset. All samples exhibit Raman spectra similar in appearance. Everyone consists of one transverse optical TO$_0$ and two folded TO: FTO$_{2/6}$ and FTO$_{6/6}$ as well as one longitudinal optical LO$_0$ modes. The position of planar optics Raman modes for the excitation geometry of $k||c$ and ratio of their magnitude are in close agreement with the data in the available literature [4-6]. In the 3C inclusion (figure 1e, dashed line) the only TO$_0$ mode at 796 cm$^{-1}$ was observed as was reported in [4,5]. The axial optics LO$_0$ mode suffers small shifts from 966 cm$^{-1}$ to 967.3 cm$^{-1}$ and a usual broadening with increasing N doping as evident by comparing figures 1a and 1b with 1c and 1d. This broadening, however, is not affected by B doping (note a close similarity between figure 1c and 1d). Larger Raman shift was observed for samples excited from lateral polished side (excitation geometry of $k\perp c$, figure 1e). Moreover, in this case FTO$_{6/6}$ mode disappears due to anisotropy of SiC.

The absorption spectra are shown in Figure 2. All co-doped epilayers exhibit two broad absorption bands at 1.98 eV and 2.8 eV below the band gap (3.0 eV), as in the case of $n$-type 6H-SiC substrate (N of about 10$^{18}$ cm$^{-3}$). These bands are related to well-known vertical free-carrier-absorption (FCA) transition into two upper conduction band branches. A broad absorption in the infrared region (below 1.0 eV) is caused by phonon-assisted FCA. The value of absorption in different epilayers and substrate tends to be directly proportional to $(N_D - N_A)$ (see Table 1). A small deviation from this tendency at energies between FCA peaks, where absorption is reduced, could be associated with an error in the determination of the epilayer absorption from absorption of epilayer with substrate and absorption of substrate alone. Such behavior of FCA implies that free carrier concentration is determined by $(N_D - N_A)$ and all B atoms serve as compensating impurity. The inset of figure 2 shows depth-resolved absorption at 1300 nm (see A and B points on a vertical line at 0.96 eV), which was recorded by passing light through the lateral polished sides of the sample. Absorption is the highest on the top of the epilayer and gradually decreases towards the substrate by 20-30 %. This trend manifests change of compensation during the process of the epilayer growth.

![Figure 2](image_url)

**Figure 2.** Absorption spectra of different co-doped samples and a substrate. Dashed vertical line marks probe laser energy at 1300 nm. A and B points mark the thickness-averaged absorption in ELS 297 and 296, respectively, while in the inset the absorption depth-distribution coefficient for these samples is shown.

The inset of the figure 3 shows the examples of diffraction efficiency kinetics at different injection fluencies in the sample ELS 296. When excited carrier concentration exceeds the $(N_D - N_A)$ (curve 3 and curve 4), the fast diffraction efficiency component exceeding an order of magnitude has appeared. In the sample ELS 117 this signal is halved and in the sample ELS 297 it is not observed at all. The
data from Table 1 led us to propose that the fast signal is largely dependent on the B concentration and could be tentatively attributed to B atom assisted Auger recombination. However, the two-step absorption through the deep B levels could be also considered as a possible cause. Analysis of this fast signal is out of the scope of the present work and will be treated elsewhere.

The recombination lifetime, $\tau_R$, and ambipolar diffusion coefficient, $D$, obtained by dynamic TG technique for three samples versus the injected carrier concentration is presented in Figure 3 (a, b). The values of measured parameters for the injection level of $3 \times 10^{18}$ cm$^{-3}$ are also included in the Table 1. For all samples both $\tau_R$ and $D$ are significantly dependent on the B concentration. For the samples with high B concentration the ambipolar diffusion coefficient is very close to zero (ELS 296, see Table 1 at injection $3 \times 10^{18}$ cm$^{-3}$) or is quite small (ELS 117, see figure 3 b). Whereas in the sample with the lowest amount of B (ELS 297) $D$ is substantial. It steeply increases after injection crossing the B concentration level, to value 1.15 cm$^2$/s at about $3 \times 10^{18}$ cm$^{-3}$ and further to value 1.6 cm$^2$/s at the injection of $10^{19}$ cm$^{-3}$. This diffusion coefficient increase is not governed by a change in the degeneracy statistics since this effect (in undoped samples 4H-SiC) becomes sufficient at room temperature only at higher injection level above $10^{19}$ cm$^{-3}$ [10]. We attribute observed trend of diffusion to negatively charged B states that also immobilise holes by trapping them. Consequently, at low injection, both minority holes and majority electrons are strictly hindered by the acceptor-induced space-charge field. Correspondingly, with injection increasing above B concentration, the space-charge field becomes reduced gradually by screening and diffusivity increases to the common values of a free-carrier ambipolar plasma diffusion states [11].

From Fig. 3a is clear the opposite trend occurs with $\tau_R$. In the sample ELS 297 with the lowest amount of B lifetime drops at injection level approaching B concentration. At $\Delta n \geq 10^{17}$ cm$^{-3}$ $\tau_R = 0.5$ ns and is independent of injection. For two other samples with high B concentration the carrier lifetime reaches 20 ns and decreases with injection level approaching or above B concentration. It is

Figure 3. a) Carrier lifetime and b) ambipolar diffusion coefficient versus excited carrier concentration in co-doped 6H-SiC samples at RT. The inset shows carrier diffraction efficiency, $\eta$, kinetics at increasing excitation fluencies from 0.2 to 12 mJ/cm$^2$ (1 to 4) in the sample ELS 296.
noteworthy that in the undoped 6H-SiC for similar injection level \((3\times10^{18} \text{ cm}^{-3})\) the ambipolar diffusion coefficient and lifetime were determined to be \(D = 2.7 \text{ cm}^2/\text{s}\) and \(\tau_R \approx 0.4 \text{ ns}\) [7].

The opposite relationship of diffusivity and lifetime versus injected carrier concentration suggests that carrier lifetime is determined by diffusion-limited recombination times at extended defects. This behaviour is quite common for high band gap compound semiconductors, and is observed in GaN epilayers [8]. It is a consequence of the same effect described above; at low injection and high B concentration diffusivity is restricted due to coulombic attraction of minority holes to negatively charged B traps. At high injection holes fill most of B traps and recharge them. Ambipolar diffusivity starts to increase with an increase of the hole and electron concentration providing favourable access of pairs to non-radiative recombination centers. This process compete with more slower channel through N traps which is involved in DAP emission and which is responsible for a hundred \(\mu\text{s}\)-long lifetimes at RT [see Manolis et al. in this issue]. This assumption supports the experimental finding that DAP radiative emission at low injection can be steeply enhanced in co-doped 6H-SiC epilayers with \(N > B > 4\times10^{18} \text{ cm}^{-3}\) [9].

4. Conclusions

In this study the physical properties of fluorescing 6H-SiC were investigated in order to improve the growth technology of such co-doped layers and to find optimal conditions for the increasing of DAP photoluminescence. The micro-Raman and absorption measurements showed that N-B co-doping does not degrade the quality of crystal structure up to the doping of \(10^{19} \text{ cm}^{-3}\). Performing research of the free carriers’ diffusivity and their lifetime shows that they both are dependent on B concentration and behave in the opposite way versus injected carrier concentration. Thus, the feasible condition as a contributory factor for DAP emission can be obtained for co-doped 6H-SiC with high B concentration but smaller than that of N concentration. In this case, the restricted diffusivity (most probably due to induced space-charge field) is limiting carrier recombination through nonradiative centres, thus multiple trapping of electrons to N traps stimulates a further radiative emission to deep B levels.

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