The role of defects in fluorescent silicon carbide layers grown by sublimation epitaxy

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Abstract. Donor-acceptor co-doped SiC is a promising light converter for novel monolithic all-semiconductor white LEDs due to its broad-band donor-acceptor pair luminescence and potentially high internal quantum efficiency. Besides sufficiently high doping concentrations in an appropriate ratio yielding short radiative lifetimes, long nonradiative lifetimes are crucial for efficient light conversion. The impact of different types of defects is studied by characterizing fluorescent silicon carbide layers with regard to photoluminescence intensity, homogeneity and efficiency taking into account dislocation density and distribution. Different doping concentrations and variations in gas phase composition and pressure are investigated.

1. Introduction

Donor-acceptor co-doped SiC was first recognized as a potential light converter for a novel monolithic all-semiconductor white LED by Kamiyama et al. in 2006 [1]. Since then, considerable research efforts have been made. However, the internal quantum efficiency (IQE) of typical samples lags far behind the theoretically predicted high efficiencies, even though a large range of doping concentrations and ratios has been studied. This suggests that the IQE is severely affected by short nonradiative lifetimes.

The layers are commonly grown by the Fast Sublimation Growth Process (FSGP) [2] which is highly suitable for the growth of high quality thick epitaxial layers with reasonable growth rate. According to XRD measurements, the epitaxial layers grown by FSGP may even show an improved crystalline quality with regard to the substrate [2] and the charge carrier lifetime is usually quite high, typically about 2 µs [3]. As the considerations above indicate that short nonradiative lifetimes may be a critical issue for the light conversion efficiency of f-SiC layers, this work will focus on the role of different types of defects in fluorescent silicon carbide.

2. Experimental

2.1. Growth of N-B co-doped 6H-SiC layers by sublimation epitaxy

Fluorescent silicon carbide layers were grown by the FSGP with 30 min growth time and 1850 °C growth temperature on 1.4 degree off-axis 6H-SiC substrates, yielding a layer thickness of 85 ± 10 µm. A polycrystalline monolithic source co-doped with nitrogen and boron was employed.

The source material was grown by physical vapour transport (PVT) and is described more in detail elsewhere [4].

Using the FSGP, both nitrogen and boron can be introduced by applying a co-doped monolithic silicon carbide source while nitrogen can alternatively or additionally be introduced via the ambient. Different process conditions, namely gas phase compositions and pressures (hereafter referred to as *growth ambient*) were applied as follows. Prior to each growth run, the reactor was evacuated for at least 15 h to remove adsorbed gases from the crucible and graphite insulation. In the conventional process, which will be denoted as *static RT*, the valve to the vacuum pump is closed at room temperature before starting temperature ramp-up. For nitrogen doping via the ambient, the reactor was filled with nitrogen after evacuation and pumped-down to the desired pressure. This will be denoted as nitrogen ambient accompanied by the actual pressure value. Note that there are two different pressure values: the pressure set at room temperature, and the pressure measured when reaching the growth temperature.

In order to further reduce the amount of gases adsorbed at the graphite parts of the reactor compared to static RT conditions, two new variants of static vacuum were tested. In contrast to static RT, pumping is continued during temperature ramp-up until a certain temperature is reached, namely either $1000\,°C$ or $1250\,°C$. These two process conditions will be denoted as *static 1000 °C* and *static 1250 °C*, respectively.

Besides the different process conditions described above, the concentrations of the dopants and their ratio in the source material were varied. Process conditions and source doping for the series of samples used in this work are summarized in Table 1. As determined by Secondary Ion Mass Spectrometry (SIMS) measurements, a nitrogen flux of 8 sccm during source growth yields a nitrogen concentration of 1.5×10^{19} cm^{-3} ± 2.3×10^{18} cm^{-3} in the source material. 10 ppm, 50 ppm and 100 ppm B in the PVT source powder yield a source material boron concentration of 3.37×10^{17} cm^{-3} ± 5.1×10^{16} cm^{-3}, 1.47×10^{18} cm^{-3} ± 2.2×10^{17} cm^{-3}, and 3.00×10^{18} cm^{-3} ± 4.5×10^{17} cm^{-3}, respectively.

Table 1. Experimental conditions of series A. The given concentration of B corresponds to the amount of B_4C in the SiC source powder used in source growth by PVT while the amount of N is the nitrogen flow flux during source growth.

Sample (series A)	335	336	337	338	339	340	341	342	343
B [ppm]	50	50	50	50	50	50	50	50	50
N [sccm]	4	2	1	4	2	1	4	2	1
Ambient	Static RT	Static RT	Static RT	5×10^{-4} N_2	5×10^{-4} N_2	5×10^{-4} N_2	5×10^{-3} N_2	5×10^{-3} N_2	5×10^{-3} N_2

Sample (series B)	374	375	376	377	378	379	386	387	388
B [ppm]	10	10	50	50	50	50	100	100	100
N [sccm]	8	8	8	8	4	4	8	8	8
Ambient	Static RT	Static $1000\,°C$	Static RT	Static $1000\,°C$	Static RT	Static $1000\,°C$	Static RT	Static $1000\,°C$	Static $1250\,°C$

2.2. Characterization of fluorescent 6H-SiC layers

The f-SiC layers were characterized with regard to their photoluminescence intensity using room-temperature photoluminescence (PL) for series A and fluorospectrometry for series B.

In case of series A, the internal quantum efficiencies were determined. A half integration sphere was used for IQE determination with a 355 nm excitation laser yielding an excitation power density of 1.27 W/cm^2 (hereafter termed low excitation power density) and 25.5 W/cm^2 (hereafter termed high

excitation power density), respectively. An estimated light extraction efficiency of 5 % was used for deducing IQE from the measurement. Charge carrier lifetimes where determined by microwave detected photoconductivity.

Series B was additionally characterized using room-temperature photoluminescence maps for studying luminescence homogeneity. After recording the PL maps, defect-selective etching was performed on one half of each sample of series B by dipping it into a KOH melt at 530 °C for 5 min. The etched samples were investigated using optical microscopy with regard to dislocation density.

3. Results and Discussion

In the following, photoluminescence and IQE measurements will be discussed with respect to the influence of defects on the internal quantum efficiency of f-SiC. Note that IQE of donor-acceptor pair luminescence depends on both radiative lifetime τ_r and nonradiative lifetime τ_{nr} as follows [3]:

$$IQE = \frac{1}{1+\frac{\tau_r}{\tau_{nr}}} \qquad (1)$$

The radiative lifetime is determined by doping concentrations whereas the nonradiative lifetime depends on the concentration of defect energy levels providing nonradiative recombination paths. Thus, it is necessary to consider both doping and defect concentrations. Estimates of optimum doping concentrations and appropriate ratio of donors and acceptors in f-SiC are detailed elsewhere [5].

3.1. Photoluminescence maps and defect selective etching

Room-temperature photoluminescence maps in conjunction with optical microscopy maps of the sample after defect-selective etching show that a correlation of decreased luminescence intensity with dislocation density is observed only in areas of extremely high dislocation density. No difference in PL intensity is observed e.g. for the two insets A and B in Fig. 1 and 2 with dislocation densities of $15.4 \times 10^4 \text{ cm}^{-2}$ and $6.2 \times 10^4 \text{ cm}^{-2}$, respectively. This indicates that the nonradiative lifetime is not dominated by dislocation density in most areas of the sample. This observation supports the conjecture that the nonradiative carrier lifetime in f-SiC is determined primarily by intrinsic defects or defect complexes.

3.2. The influence of doping concentrations and growth ambient on light conversion efficiency

For each of the source doping concentration used, the same trend was observed when varying the growth ambient (Fig. 3 and 4): All samples grown applying static 1000 °C show higher photoluminescence intensities than the corresponding static RT reference sample. Static 1250 °C yielded even higher luminescence intensity. This indicates that the adsorbed gases at the graphite parts cause some kind of defect that decreases the nonradiative lifetime. Total charge carrier lifetimes of samples 335 (high source nitrogen content, low nitrogen pressure in FSGP) and 343 (low source nitrogen content, high nitrogen pressure in FSGP) are 6.5 µs and 4 µs, respectively. This also supports that (nonradiative) charge carrier lifetime decreases if nitrogen is added to the growth ambient.

Similar conclusions can be drawn from the IQE measurements of the 4 sccm samples (Fig. 5) grown using different ambient nitrogen pressures which also show a decrease in efficiency with increasing nitrogen pressure in FSGP. The generally lower IQE at high excitation density conditions is attributed to the fact that filled donor and acceptor states result in enhanced nonradiative recombination. In contrast to the 4 sccm samples, the samples grown with 1 sccm and 2 sccm, respectively, do not show a clear tendency of IQE. This is most likely because the nitrogen ambient generally affects both radiative and nonradiative lifetime due to the increase in nitrogen doping and defect concentration, respectively. At very low source nitrogen doping, the decrease of radiative lifetime compensates for the decrease of nonradiative lifetime to an observable extent.
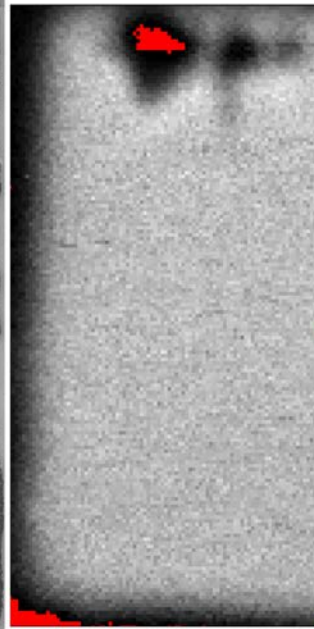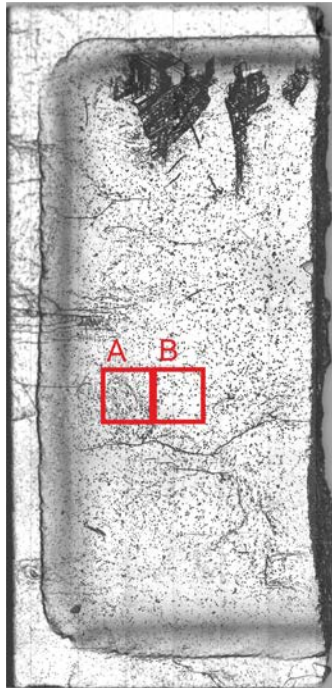
Fig. 1 Microscope map of sample ELS375 after defect-selective etching with the corresponding RTPL map (legend shows PL intensity in arbitrary units). The dark areas at the upper edge of the samples are inclusions of 3C-SiC.
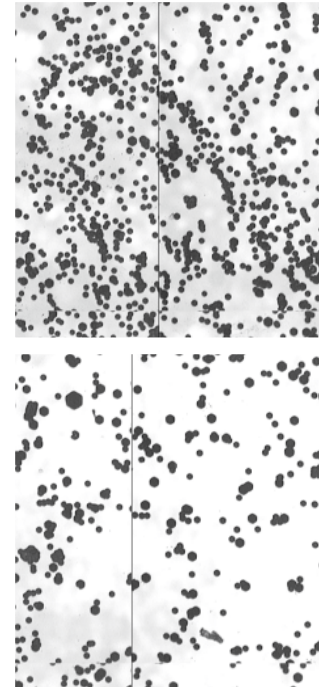

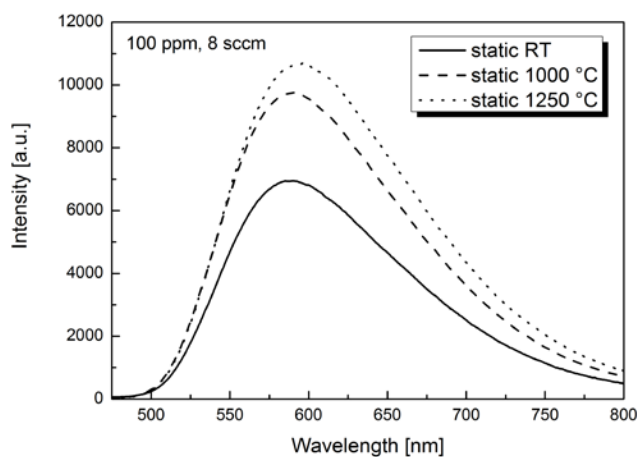**Fig. 2** Microscope images of the insets A (top) and B (bottom) marked in Fig. 5

Fig. 3 PL spectra obtained by fluorospectrometry. The samples grown from 100 ppm B, 8 sccm N_2 are displayed as an example. Samples of different doping concentration show the same trend of increasing luminescence intensity if applying static RT and 1000 °C, as can be seen from the RTPL measurements shown in Fig. 4.
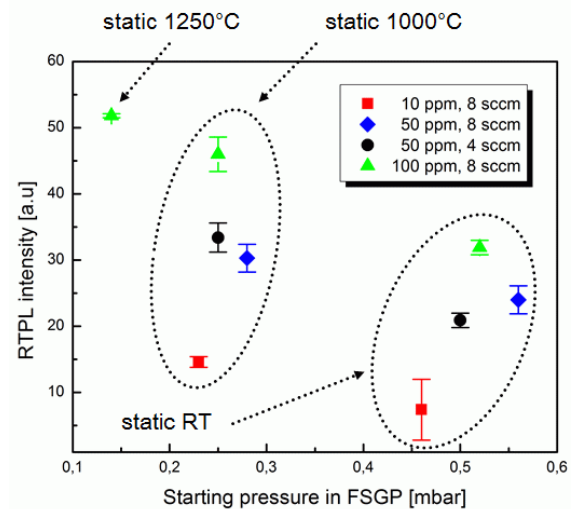

Fig. 4 Room temperature PL peak intensity as a function of starting pressure in sublimation epitaxy for samples grown from differently doped sources. Static vacuum modification used is indicated.
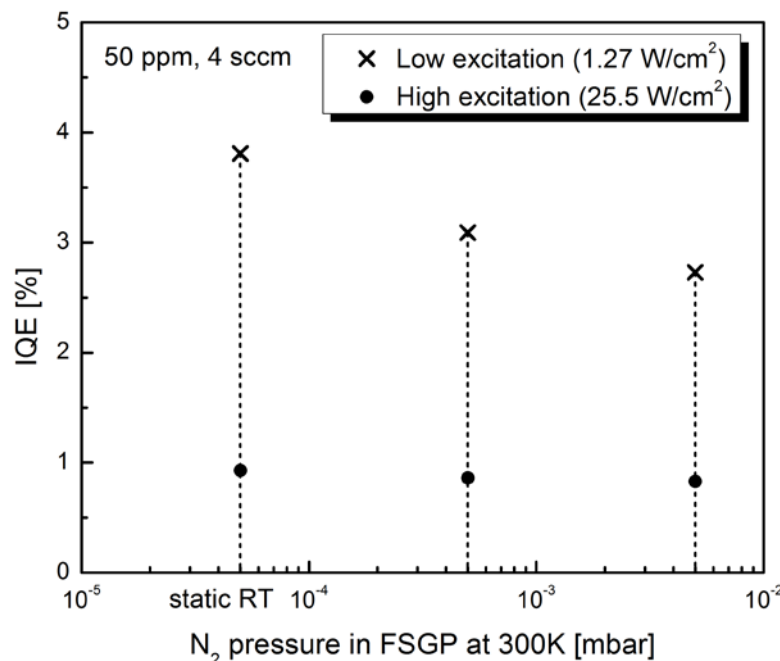
Fig. 5 Internal quantum efficiency of the 4 sccm samples of series A, for both low and high excitation.

The effect is not observed when increasing the pressure by introducing argon prior to growth, thus, it depends on the nature of the gas species and is not a general effect of slightly higher total pressure.

As the adsorbate is introduced from the air (when opening the reactor between growth runs), the possible influence of both nitrogen and oxygen needs to be considered. Experiments conducted with additional nitrogen pressure show a further decreasing luminescence intensity and internal quantum efficiency with increasing nitrogen pressure, indicating that nitrogen is likely to have the dominating influence. Interestingly it is not a matter of total nitrogen doping concentration in the epilayer, since the decrease in luminescence with increasing nitrogen pressure in the growth ambient is observed even at very low nitrogen doping concentrations in the source with an increase in source nitrogen doping still leading to considerably higher luminescence. Thus, nitrogen doping from the source (dispersed in atomic form within the source) and molecular nitrogen from the ambient must have a different effect on DAP luminescence efficiency, namely on the formation of defects that cause nonradiative recombination.

Considering that the bond dissociation energy of nitrogen is more than 50 times larger than the thermal energy at growth temperature, nitrogen can be assumed to be present primarily in molecular form in the growth ambient. Since the nature of the lifetime-limiting defect in f-SiC is not yet known for sure, one can only speculate on the mechanism of molecular nitrogen assisted defect formation. As common lifetime-limiting defects in silicon carbide are vacancy-related defects (such as the E_1E_2 in 6H-SiC and the $Z_{1/2}$ center in 4H-SiC) [6], one can suspect that adsorbed nitrogen molecules impede the incorporation of growth species into the lattice and hereby assist the formation of vacancy-related defects. The nitrogen molecule is expected to dissociate after adsorption since the energy of the N-N bond is significantly lowered by adsorption [7], however, it may be present as an adsorbed molecule for an average time sufficient to influence the incorporation of growth species, especially at high growth rates like in the FSGP. This assumption appears reasonable since nitrogen is also known to influence polytype stability [8]. Taking into account the model of nitrogen adsorption on the Si-face of (0001) 4H-SiC reported by Ashman et al. [9], it seems plausible that adsorbed nitrogen molecules may

hinder the incorporation of carbon and hereby induce the formation of carbon vacancies or a defect complex containing a carbon vacancy.

4. Conclusion

The influence of growth ambient on the light conversion efficiency of N-B co-doped 6H-SiC layers grown by sublimation epitaxy was studied for samples grown from differently doped source material. The results confirm that high nitrogen and boron concentrations are needed for efficient photoluminescence, as discussed previously in [2]. However, adding nitrogen to the FSGP growth ambient results in a decrease of photoluminescence intensity and internal quantum efficiency for a broad range of source doping concentrations. Additionally, an effect of dislocation density on photoluminescence intensity is observed only in regions of exceptionally high dislocation density. These two findings strongly indicate that some kind of intrinsic defect or defect complex plays a dominating role in the internal quantum efficiency of fluorescent silicon carbide. The precise nature of the defect limiting the nonradiative lifetime is still to be determined and its nitrogen-assisted formation mechanism remains a matter of discussion.

References

[1]   Kamiyama S, Maeda T, Nakamura Y, Iwaya M, Amano H, Akasaki I, Kinoshita H, Furusho T, Yoshimoto M, Kimoto T, Suda J, Henry A, Ivanov I G, Bergman J P, Monemar B, Onuma T and Chichibu S F 2006 *J. Appl. Phys.* **99** 093108

[2]   Syväjärvi M, Yakimova R, Tuominen M, Kakanakova-Georgieva A, MacMillan M, Henry A, Wahab Q and Janzén E 1999 *J. Crystal Growth* **197** 155–162

[3]   Kamiyama S, Iwaya M, Takeuchi T, Akasaki I, Syväjärvi M and Yakimova R 2011 *J. Semicond.* **32(1)** 013004

[4]   Kaiser M, Hupfer T, Jokubavicus V, Schimmel S, Syväjärvi M, Ou Y, Ou H, Linnarsson M K and Wellmann P 2013 *Mater. Sci. Forum* **740 – 742** 39-42

[5]   Sun J W, Kamiyama S, Jokubavicius V, Peyre H, Yakimova R, Juillaguet S and Syväjärvi M 2012 *J. Phys. D: Appl. Phys.* **45** 235107

[6]   Sasaki S, Kawahara K, Feng G, Alfieri G and Kimoto T 2011 *J. Appl. Phys.* **109** 013705

[7]   Danielsson O, Forsberg U and Janzén E 2003 *J. Cryst. Growth* **250** 471-478

[8]   Schmitt E, Straubinger T, Rasp M, Vogel M and Wohlfart A 2008 *J. Cryst. Growth* **310** 966-970

[9]   Ashman C R and Pennington G 2008 *Surf. Science* **602** 3617-3622