Temperature Dependencies of Free-Carrier-Absorption Lifetime in Fluorescent 6H-SiC Layers

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Abstract. The nonradiative decay of majority electrons has been studied over a wide temperature range from 80 K to 600 K using the time-resolved free-carrier-absorption (FCA) technique. At high injection level of the highly-luminescent N-B codoped 6H-SiC epilayer, we revealed three main relaxation components of injected free electrons over ps-to-ms time ranges. By means of temperature dependency, two components can be ascribed to thermal activation of holes from a shallow (200 meV) and a deep (500 meV) acceptor. The third one, which has a hundred µs-time scale, we attribute to minority hole recombination from the valance band into the electron trap (53 meV). This recombination channel seems to compete with the deep-acceptor (Boron) to-donor (Nitrogen) pair visible emission at and below 300 K.

1. Introduction
The need for artificial daylight illumination has driven research to the concept for white light-emitting diodes (LEDs). The spread LED models are based on III-V nitrides with a yellow phosphor coating acting as a light converter. These phosphors require rare-earth metals which are becoming scarce. The problem becomes pronounced because of a high color temperature and too low color-rendering index [1]. The 6H-SiC can be a substrate for growth of GaN LED structures to growth. On the other hand, if properly doped, such SiC can be composed of two different co-doped layers (B-N and Al-N) acting as light converters that emit into two visible broad spectral light ranges by an efficient donor-to-acceptor pair (DAP) recombination. Such 6H-SiC B-N epilayer have already have been demonstrated and thus show a new potential especially when the material quality is improved significantly [2]. Therefore, among remaining scientific issues, there is a fundamental question if the competing nonradiative process in heavily co-doped SiC material can be minimized so that it will not interplay greatly with the DAP recombination channel.

In this work epitaxial co-doped B-N 6H-SiC layers have been grown by the fast sublimation growth process and studied by time-resolved FCA technique under high injection in order to reveal the relation of non-radiative recombination processes with existing trap levels and their relation to the main dopants of the material.
2. Samples and experimental techniques

The fast sublimation growth process was used to grow homoepitaxial layers on low-off axis 6H-SiC substrates. Nitrogen (N) and boron (B) were introduced into epilayer via controlled co-doping from the polycrystalline SiC source and the N concentration was also enhanced by the gas ambient during the growth. The epilayer thickness was $d \approx 45 \mu m$ and the concentration of N and B dopants was established by secondary ion mass spectrometry in the sample (ELS118) to be $9.2 \times 10^{18}$ and $5.2 \times 10^{18} \text{cm}^{-3}$, respectively [1].

The FCA measurements have been performed from 80 K to 600 K in an open cycle liquid nitrogen cryostat with a heater. The sample was excited from the epi-surface side with 8 ps duration pulses of the third harmonic from a Nd$^{3+}$:YLF laser (351 nm) operating at 10 Hz. The pump light creates a dense electron-hole plasma with exponential in-depth distribution amid a penetration depth $1/e = 11 \mu m$ which is nearly independent of temperature. The carrier density in the substrate can be virtually neglected. The FCA probing was performed in a collinear geometry with delayed pulses at either 1053 nm or 1064 nm wavelength in the transparency region of 6H-SiC. The delay of the probe was implemented in two ways: optically, by changing the optical path of the ps-probe (to 4 ns), or electrically, when another YAG laser with 4 ns pulse was electrically synchronized with the pump laser (delay range $\approx 200 \mu s$).

3. Experimental results and analysis

To show the complete time range, in Fig 1a we plot the FCA signals $[\ln(T_0/T) = \Delta \alpha d]$ on a log delay-scale. The FCA maxima are artificially set at 10 ps. These data are measured at indicated temperatures for a constant 40 mJ/cm$^2$ pump flux that results in a $7 \times 10^{19}$ cm$^{-3}$ concentration of the excess electron-hole (e-h) pairs over the absorption depth, e.g. above the doping levels for about the half of the epilayer thickness. The “fast” decay (for $t < 0.04$ ns) is observed at this excitation level but does not appear for excitation below the doping level (not shown). Its amplitude and relaxation time is T-independent. The appearance of the “fast” part is not well understood; therefore we tentatively attribute it to the impurity-assisted Auger processes. In this study, we will focus on the extended “slow” decay parts that, in n-type 6H-SiC, most probably are related to the recombination processes of remaining majority excess electrons in the conduction band. From Fig. 1a it can be depicted that components in the “slow” decay are strongly T-dependent. Multiple three decay processes might be presented after analysis of decays curves. This is demonstrated by exponential fits (dashed lines) in Fig. 1b at 200 K and similarly at other temperatures. The fitting is satisfactory taking into account that the trap occupation is not complete by excitation at the deep depth of the epilayer.

The fitting parameters, namely the relaxation time and the component amplitude are presented in Fig. 2a,b into an Arrhenius diagram. It should be stated that all relaxation times are separated by an order of magnitude in value, or more. This allows the assumption that the obtained components do not
affect each other and, thus, it is reasonable to apply a simple exponential fitting, as in Fig. 1b. From results in Fig. 2 we see that two faster components denoted as “1” and “2” have a strong T-deactivated relaxation time but weakly T-dependent amplitudes. Whereas the component “3” shows clearly an opposite case; T-independent relaxation time and strongly thermally deactivated amplitude.

Since the negatively charged acceptor is a minority carrier trap with much smaller capture cross section for majority electrons, consequently, the hole trap occupation in the forbidden energy band gap is of the major importance between 400-600 K. It is known that B atoms are acceptors in SiCs and can have positions with different ionization levels [3]. When we depict a linear fit by solid lines to the obtain results in Fig. 2a, these extracting values give thermal deactivation energies $E_{a1} \approx 200\pm30$ meV and $E_{a2} \approx 500\pm120$ meV. The large scatter for $E_{a2}$ is caused by the “fast” component at high temperatures which actually was subtracted artificially from the plot of Fig. 2a. The line fitting in this T range, however, is of sensitive to the subtracted amount.

Since B is the dominant acceptor impurity in the investigated epilayer [1], both the activation energies should be compared to B acceptors, one for a shallow level (sB) and one for a deep level (dB). The obtained experimentally values are lower than the actual energies reported for sB (220-350 meV) and for dB (550-750 meV) [4]. It should be noted that the dB level is related to a complex center on carbon sublattice but distributed over a smaller volume than in the case of the sB acceptor. It can also possibly be located either at an h-site or on a k-sites [3]. The discrepancy between our findings and reported values can arise due to three reasons. The first one is the B (as well as N) concentration probably induces a band-gap shrinkage and, partly, the particle level spread into an impurity energy band. The second reason may arise from the fact that close distance dB-N pairs can transform the dB complex structure. The third one is that we have omitted the re-capture process for holes in our consideration. As the temperature increases, the capture results in an apparent activation energy that is lower than the trap level [5]. However, the above determined energy values for minority carriers can be a proof that B impurity atoms are perhaps responsible for those decay components. Moreover, as in Fig. 2b the signal amplitudes from each independent mechanism, that correspond to B levels, reveals that the concentration of shallow centers is slightly exceeding that of deep ones as it is reported for epitaxially grown layers [4].

The third relaxation mechanism, denoted as “3” in Fig 2, has shown a potential effect at 300 K and below. Observed carrier trapping that features the amplitude reduction without changing relaxation time has been analysed by Ichimura [5]. According to provided his analysis, the situation can be attributed to minority carrier recombination through the majority carrier trap in the upper part of the forbidden band gap. Once electrons are emitted from the trap, the trap cannot capture minority holes.

**Figure 2a.** Arrhenius plot for the three independent relaxation processes of the “slow” decay. Extracted thermal activation energy of component “1” and “2” is indicated by a solid line fit at high T.

**Figure 2b.** Signal amplitudes of three independent processes. While component “1” and “2” amplitudes are weakly T-dependent, the component “3” amplitude is strongly T-dependent.
Then the occupation probability $f = 1/[1 + g \exp(E_a - E_F)]$ is given for thermal equilibrium, where $g$ is the degeneracy of unpaired electrons. Noting $n = N_C \exp\{(E_F - E_C)/kT\}$ is a constant, one can arrive to $(1 - f)/f = (N_C g/n) \exp\{(E_a - E_C)/kT\}$. A plot in Fig. 3a shows the amount of the “3” component amplitude normalized by that at the low temperature limit denoted as $R$ (where the factor $T^{3/2}$ corrects for the temperature dependence of $N_C$). This plot reveals that thermal activation energy of this mechanism is $E_{a3} \approx 53 \pm 5$ meV. This value is true for N atoms close to conduction band in heavily doped 6H-SiC but lower than the atomic level at $h$-site for low doping (80 meV [4]). We note that a carrier recombination process on N site is indirect, and hence, for a detailed analysis one has to take under account phonons contributions which we have omitted in the present study. In Fig. 3b the three relaxation processes which have been discussed at previous paragraphs are presented schematically.

**Figure 3a.** Arrhenius plot for the amplitude of the “3” component (Fig. 2b) where $R$ is the amount of amplitude normalized by that at the low temperature limit.

**Figure 3b.** Schematic of DAP radiation with carrier’s relaxation processes “1”, “2” and “3” denoted to thermally emitted holes from shallow and deep Boron and to recombination through N sites. Competing recombination channel through $Z_{1/2}$ center is also indicated.

### 4. Conclusions

By applying time-resolved FCA technique we have shown that long living decay processes in B-N co-doped 6H-SiC are composed of three main components, which are well separated on a time-scale and obey quite different T-dependences. The “1” and “2” component can be ascribed to accelerated nonradiative recombination rate due to hole thermal emission from shallow and deep levels of B with thermal activation energies determined $E_{a1} \approx 200$ meV and $E_{a2} \approx 500$ meV. The third component, which is responsible for the far longer decay times, can be ascribed to free holes recombination with electrons at the indirect trap related to N with a thermal energy of $E_a \approx 53$ meV. This lifetime is competing with a radiative DAP emission rate. Thus, all observed recombination channels are related to the main dopants that are introduced. We assume that there also exists a competing recombination through the known $Z_{1/2}$ centers with $\mu$s-time scale (Fig. 3b), therefore, it is suppressed due to strongly restricted diffusivity of the free carriers in a heavily co-doped 6H-SiC [see Gulbinas, this issue].

### References

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