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Photoexcited carrier trapping and recombination at Fe centers in GaN

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Fe doped GaN was studied by time-resolved photoluminescence (PL) spectroscopy. The shape of PL transients at different temperatures and excitation powers allowed discrimination between electron and hole capture to Fe³⁺ and Fe²⁺ centers, respectively. Analysis of the internal structure of Fe ions and intra-ion relaxation rates suggests that for high repetition rates of photoexciting laser pulses the electron and hole trapping takes place in the excited state rather than the ground state of Fe ions. Hence, the estimated electron and hole capture coefficients of $5.5 \times 10^{-8} \text{ cm}^3/\text{s}$ and $1.8 \times 10^{-8} \text{ cm}^3/\text{s}$ should be attributed to excited Fe³⁺ and Fe²⁺ states. The difference in electron capture rates determined for high (MHz) and low (Hz) (Fang *et al.*, Appl. Phys. Lett. **107**, 051901 (2015)) pulse repetition rates may be assigned to the different Fe states participating in the carrier capture. A weak temperature dependence of the electron trapping rate shows that the potential barrier for the multiphonon electron capture is small. A spectral feature observed at $\sim 420 \text{ nm}$ is assigned to the radiative recombination of an electron in the ground Fe²⁺ state and a bound hole.

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I. INTRODUCTION

Fe ions in III-V and II-VI compound semiconductors act as deep acceptors and are used during the growth of semi-insulating layers for electronic and photonic devices.¹ In that regard, Fe is especially important for GaN because the material experiences an unintentional n-type doping. Besides, Fe ions in GaN efficiently trap photoexcited carriers, producing carrier lifetimes in the ps range.² The ultrashort carrier lifetimes, the semi-insulating properties, and the large breakdown field enable applications in the ultrafast high power optoelectronics. In addition, GaN:Fe may be interesting for spintronics because of the predicted room temperature ferromagnetism.³

In order to reveal the full potential of GaN:Fe, properties of Fe centers, such as the electronic structure and the carrier trapping dynamics, must be determined and understood. The electronic structure of Fe ions in GaN has been studied by photoluminescence (PL), PL excitation, absorption, and electronic paramagnetic resonance and is well established.^{4,5} On the other hand, the reported cross-section values for the electron capture to Fe³⁺ vary over three orders of magnitude, between $1 \times 10^{-13} \text{ cm}^2$ and $4.6 \times 10^{-16} \text{ cm}^2$.^{2,6,7} Estimation of the cross section for the hole capture to Fe²⁺ is limited to a single study performed by time-resolved PL.² The rich level structure of Fe ions in GaN formed by Stark effect, spin-orbit coupling, and Jahn-Teller effect^{4,5} has never been considered while discussing the carrier capture.

In this work, we study carrier trapping to Fe centers in GaN with the help of time-resolved PL spectroscopy.

Excitation power dependence of PL decay and unusual transient shapes at high excitation powers allowed an unambiguous separation between the electron and hole trapping processes. Most importantly, comparison of the experimental data with previous reports and analysis of the internal structure of the Fe ions suggest that at high photoexciting pulse repetition rates excited rather than ground states of Fe ions are most relevant for the carrier trapping.

II. EXPERIMENTAL DETAILS

The studied samples were grown in a custom designed hydride vapor phase epitaxy (HVPE) reactor on sapphire substrates. The GaN layers were grown to a thickness of $\sim 1.5 \text{ mm}$, removed from the substrates, and polished to a thickness of $\sim 0.5 \text{ mm}$. Fe and impurity atom concentrations were evaluated by secondary ion mass spectrometry (SIMS) and are presented in Table I.

Time-resolved PL measurements were performed using frequency-tripled Ti:sapphire laser pulses at 269 nm (4.61 eV) central wavelength, a 200 fs pulse duration, and a 76 MHz pulse repetition frequency. A spectrometer and a

TABLE I. Dopant and impurity concentrations in the studied samples.

Sample name	[Fe] (cm ⁻³)	[O] (cm ⁻³)	[Si] (cm ⁻³)	[C] (cm ⁻³)
1.7×10^{18}	1.7×10^{18}	$\leq 2.0 \times 10^{16}$	1.2×10^{16}	1.3×10^{17}
2.4×10^{18}	2.4×10^{18}	$\leq 2.0 \times 10^{16}$	6.8×10^{16}	1.1×10^{17}
5.6×10^{18}	5.6×10^{18}	$\leq 2.0 \times 10^{16}$	1.5×10^{16}	2.8×10^{17}
3.0×10^{19}	3.0×10^{19}	$\leq 1.0 \times 10^{16}$	2.4×10^{16}	$< 1.3 \times 10^{17}$
Undoped	$< 1 \times 10^{15}$	2.0×10^{16}	1.5×10^{16}	$< 5 \times 10^{15}$

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streak camera system with a time resolution of 4 ps were used for signal detection. To estimate the PL decay times below the resolution limit, a deconvolution procedure with the Gaussian system response function was applied. The sample temperature was varied between 4 and 290 K with the help of a closed cycle He cryostat. Average excitation powers were between 3 and 20 mW. For a laser spot diameter of $30\ \mu\text{m}$ (full width at half maximum of a Gaussian profile), an absorption coefficient of $1.8 \times 10^5\text{ cm}^{-1}$, and a reflection coefficient of 0.15, this corresponds to photoexcited carrier densities (averaged over the laser spot diameter and the absorption length) immediately after the pulse between 8.7×10^{17} and $5.8 \times 10^{18}\text{ cm}^{-3}$. An undoped GaN sample grown under the same conditions was used as a reference.

III. RESULTS

A. Time-integrated spectra

PL spectra of the Fe doped samples were dominated by the band gap peak around 360 nm. The spectra also have a much weaker broad PL peak around 420 nm (2.95 eV). A typical room temperature time-integrated PL spectrum, measured for sample 1.7×10^{18} , is presented in Fig. 1. The ratio between the integrated PL intensities of the 420 nm peak and band gap emission was around 2%–3%. For sample 3.0×10^{19} , due to the weak overall PL intensity, the 420 nm peak could not be detected.

While the origin of the band gap PL peak is clear, transitions causing the 420 nm peak are not well established, even though PL at energies between 2.8 and 3.0 eV is often observed for high-resistivity HVPE grown GaN.^{8–10} Previously, the peak was assigned to transitions between a deep donor (probably a nitrogen vacancy) and the valence band,⁹ the conduction band and a deep acceptor (probably a carbon impurity),¹¹ and the conduction band and a H and C complex.¹² We did not observe the 420 nm peak in the control sample. Thus, the origin of the 420 nm peak in our samples is most likely related to Fe doping. Following the Fe ion energy scheme, the transition energy

FIG. 1. Time integrated PL spectra for sample 1.7×10^{18} at 290 K.

(2.95 eV) is similar to that of the absorption band in Fe^{2+} .⁵ A possible recombination mechanism for this PL peak will be discussed in Section IV.

B. Photoluminescence transients at room temperature

Spectrally integrated band gap PL transients for 13 mW average excitation power are shown in Fig. 2. For samples 1.7×10^{18} to 5.6×10^{18} , the PL decay is single exponential. PL decay times, determined after deconvolution of the system response from the signal, are between 8 and 2 ps. For sample 3.0×10^{19} , the transients have a shape of the system response. Therefore, for this sample the decay times were evaluated by comparing its time-integrated PL intensities to that of other samples, for which the decay times could be measured directly. In this evaluation, the same value of the transition matrix element for all the samples was assumed. The PL decay in GaN:Fe is much faster than that in the undoped GaN sample (inset to Fig. 2). In the latter case, the PL decay is nonexponential. The initial faster decay occurs due to the carrier diffusion away from the surface and deeper into the sample,¹³ while the slower decay at longer times may be ascribed to the nonradiative recombination through native defects.¹⁴ A similar ultrafast PL decay as in GaN:Fe was previously observed for Fe doped InP and InGaP.^{15,16} Short carrier lifetimes in GaN:Fe were also detected in pump-probe experiments.⁶ These studies have shown that Fe ions act as efficient nonradiative recombination centers.

PL transients for the 420 nm peak (Fig. 3) in the initial part of the decay can be described by a single exponential as well. The decay times are 69, 57, and 24 ps for samples 1.7×10^{18} , 2.4×10^{18} , and 5.6×10^{18} , respectively. These times are too short to be assigned to the radiative recombination; on the other hand, they are an order of magnitude longer than the ultrafast carrier trapping times measured at the band gap (Fig. 2). For the 420 nm peak, no significant PL

FIG. 2. 290 K normalized band gap PL transients for samples with different Fe concentrations at 13 mW average excitation power; sample 1.7×10^{18} (a), 2.4×10^{18} (b), 5.6×10^{18} (c), and 3.0×10^{19} (d). The inset (log scale) shows PL dynamics for the undoped sample.

FIG. 3. Normalized 420 nm peak PL transients for samples 1.7×10^{18} (a), 2.4×10^{18} (b), and 5.6×10^{18} (c) measured at 10 mW average excitation power at 290 K.

decay time dependence on the excitation power in 1–10 mW range was observed.

C. Carrier trapping dynamics

After a laser pulse, photoexcited carriers are captured by Fe traps and charge transfer processes, in a simplified form described as $\text{Fe}^{3+} + \text{electron} \rightarrow \text{Fe}^{2+}$ and $\text{Fe}^{2+} + \text{hole} \rightarrow \text{Fe}^{3+}$, take place. Carrier trapping and recombination through Fe ions affect the PL decay time τ_{PL}

$$\frac{1}{\tau_{PL}} = \frac{1}{\tau_e} + \frac{1}{\tau_h} = c_e[Fe^{3+}] + c_h[Fe^{2+}] = \bar{v}_e \sigma_e [Fe^{3+}] + \bar{v}_h \sigma_h [Fe^{2+}]. \quad (1)$$

Here, τ_e and τ_h are electron and hole capture times, c_e and c_h are corresponding capture coefficients, $\bar{v}_e$ and $\bar{v}_h$ are average thermal velocities, and σ_e and σ_h are capture cross-sections. As pointed out in Ref. 17, the capture coefficients are more fundamental quantities because in dynamical experiments the thermal velocities are not constant. Further on, $[Fe^{3+}]$ and $[Fe^{2+}]$ are neutral and ionized Fe trap concentrations, related to the total Fe dopant concentration via $[Fe] = [Fe^{3+}] + [Fe^{2+}]$. However, the cross-sections have a more intuitive interpretation and are provided in most of the relevant publications. In Eq. (1), only carrier trapping to Fe-related centers is considered, which is justified by the slow PL decay for the reference undoped sample. Here, we assume that recombination through other impurities, defects, and surface states do not change significantly with the iron doping.

Since the concentration of unintentional donors, such as Si and O, is lower than the concentration of C acceptors with the energy level closer to the valence band than Fe^{3+} ,^{5,12} prior to the photoexcitation majority of Fe ions are in the Fe^{3+} state, i.e., $[Fe^{3+}] \gg [Fe^{2+}]$. To get a qualitative picture on the photoexcited carrier capture processes, let us examine two extreme cases:

For low excitation ($\Delta n < [Fe]$, where Δn is the photoexcited electron concentration), the PL dynamics are primarily determined by the electron trapping to Fe^{3+} , the first term of Eq. (1). Under such conditions, the electron capture rate is proportional to the total Fe concentration, and the capture coefficient can be evaluated in a straightforward way. Fig. 4 shows electron capture rates (inverse PL decay times) estimated from the single exponential decay at low and high temperatures for low excitation power as a function of Fe concentration. The capture rate increases proportionally with the Fe dopant concentration, which allows evaluating the electron capture coefficient $c_e = 7.5 \pm 2.0 \times 10^{-8} \text{ cm}^3/\text{s}$. Surprisingly, there is little difference between the capture rates for different temperatures. This observation is discussed in Section III E.

Under high excitation conditions ($\Delta n > [Fe]$), and if the hole capture coefficient to Fe^{2+} is not much larger than the coefficient of electron capture to Fe^{3+} , majority of Fe^{3+} traps get filled with electrons during or shortly after the excitation leading to $[Fe^{2+}] > [Fe^{3+}]$. In this case, the initial decay would be dominated by the second term of Eq. (1). After some time, Fe^{2+} concentration would decrease due to the hole capture, and eventually the system would reach a dynamical equilibrium.

To illustrate these two situations, we provide examples of excitation power dependent PL transients for sample 5.6×10^{18} at 4 K (Fig. 5(a)) and sample 1.7×10^{18} at 290 K (Fig. 5(b)). When $\Delta n < [Fe]$, the PL decay is single exponential. With an increased power (intermediate conditions), the decay time increases, as the hole capture becomes non-negligible. For high excitation powers, an unusual double exponential decay shape develops with the initial decay 2 to 3 times slower compared to the subsequent faster component. Qualitatively, one can understand the high-excitation situation as follows. Due to the fast electron trapping to Fe^{3+} , electrons excited at high densities quickly transform most of Fe^{3+} ions into Fe^{2+} . Thus, the slower PL decay should be mainly determined by the hole trapping. The following faster decay is comparable to the decay at intermediate powers and is slower than that for the low excitation. In this time range, $[Fe^{3+}]$ and $[Fe^{2+}]$ are comparable, and PL transients are

FIG. 4. Capture rate dependence on the Fe concentration for 3 mW average excitation power at 4 K and 290 K.

FIG. 5. Excitation dependent PL transients: sample 5.6×10^{18} at 4 K (a) and sample 1.7×10^{18} at 290 K (b).

determined by both terms of Eq. (1). In Fig. 5, this regime is defined as combined carrier trapping.

At 4 K, Fe^{3+} saturation was observed in all the samples but the one with the highest doping (3×10^{19}). At room temperature, this effect was observed only for the sample with the lowest Fe concentration (1.7×10^{18}). This difference may be assigned to the thermal activation of other nonradiative recombination channels, not considered in Eq. (1). These could be native defects, such as Ga vacancies (dominant in undoped GaN),^{14,18} C impurities,¹² and N vacancies (the concentration of which is expected to increase with the Fe doping).¹⁰ More details on the interplay between Fe^{3+} and Fe^{2+} centers will be provided below. However, already from this simple qualitative evaluation one can conclude that the hole trapping rate is slower than the electron trapping rate, otherwise the double exponential shape with the initial slow component could not be observed.

D. Numerical modeling

To support these qualitative considerations and retrieve the hole trapping coefficient, simple numerical simulations were performed. In general, at low to moderate photoexcited

carrier concentrations, carrier dynamics and PL transients are affected by radiative recombination, carrier trapping, recombination at deep centers and surface states, PL reabsorption, and carrier diffusion. However, the ultrafast carrier trapping to Fe centers resulting in ultrashort carrier lifetimes allows discarding the majority of these effects, which considerably simplifies the description of the PL transients. As mentioned (Fig. 2), comparison with the undoped sample suggests that radiative recombination and carrier trapping to impurities, native defects and surface states are much slower than their trapping to Fe centers. This assumption is supported by the following arguments. First, the SIMS data show that Fe doping does not introduce impurities, such as O, C, and Si (Table I). Then, Fe doping has been found to decrease the concentration of Ga vacancies.¹⁰ Finally, we do not anticipate that Fe doping considerably modifies the surface state concentration. At least in GaAs:Fe, where Fe is not the dominant carrier trap, doping with iron has no major influence on the carrier trapping rates.¹⁹ Concerning the lateral carrier diffusion in the sample plane, its length is negligible in comparison to the excitation spot size. The PL reabsorption in samples with short carrier lifetimes can also be neglected.¹³ Thus, besides the Fe-related trapping, the only effect that might influence the PL transients by changing the carrier concentration is the carrier diffusion toward the bulk of the sample. However, this effect is only important when the photoexcited carrier concentration is similar to that of Fe dopants. For high Fe doping and low photoexcited carrier concentration, $\Delta n \ll [\text{Fe}]$, decrease of the carrier concentration due to diffusion does not affect the trapping rate. For high excitation, diffusion can still be neglected at early times, during which it does not affect the carrier concentration substantially and the relation $\Delta n > [\text{Fe}]$ is maintained for most of the carriers. For example, during the first 10 ps after the excitation, the average carrier concentration within the first absorption length decreases by only $\sim 20\%$ (in the estimation, the ambipolar diffusion coefficient of $1.6 \text{ cm}^2/\text{s}$ (Ref. 20) was used).

Neglecting the influence of carrier diffusion on the PL transients, the latter can be described by

$$I(t) \propto \Delta n(t) \Delta p(t). \quad (2)$$

The non-equilibrium carrier concentrations Δn and Δp can be found by describing the system with the rate equations that take into account the dynamic relation between $[\text{Fe}^{3+}]$ and $[\text{Fe}^{2+}]$

$$d\Delta n/dt = -c_e[\text{Fe}^{3+}](t)\Delta n(t), \quad (3a)$$

$$d\Delta p/dt = -c_h[\text{Fe}^{2+}](t)\Delta p(t), \quad (3b)$$

$$d[\text{Fe}^{3+}]/dt = -c_e[\text{Fe}^{3+}](t)\Delta n(t) + c_h[\text{Fe}^{2+}](t)\Delta p(t), \quad (3c)$$

$$d[\text{Fe}^{2+}]/dt = c_e[\text{Fe}^{3+}](t)\Delta n(t) - c_h[\text{Fe}^{2+}](t)\Delta p(t). \quad (3d)$$

The initial conditions are: $\Delta n = \Delta p$, $[\text{Fe}^{3+}] = [\text{Fe}]$, and $[\text{Fe}^{2+}] = 0$.

Let us first consider the situation $\Delta n < [\text{Fe}]$. Using the electron capture coefficient determined from the linear dependence of the PL decay rate, PL transients were calculated

neglecting the variation of the hole concentration and the process of the trap state transfer from Fe^{2+} to Fe^{3+} . To match the experimental conditions, the calculated transients were convoluted with the Gaussian system response function. The simulation results for sample 5.6×10^{18} are shown in Fig. 6(a). The calculated transients match the experimental results up to 8 mW excitation, after which photoexcited electron concentration exceeds that of Fe dopants. For high excitation powers and at longer times after the excitation, the condition $[\text{Fe}^{2+}] > [\text{Fe}^{3+}]$ holds, and Fe^{3+} can no longer be considered the dominant trap (Fig. 6(b)). Neglecting the transition $\text{Fe}^{2+} + \text{hole} \rightarrow \text{Fe}^{3+}$ affects the transients and induces a discrepancy between the experimental and the calculated PL intensity values (Fig. 6(a)).

To investigate the hole trapping, simulations of PL transients for high excitation powers were made. Results for samples 1.7×10^{18} and 2.4×10^{18} at 20 mW average power are shown in Fig. 7(a). The simulations have allowed refining the value of the electron capture coefficient that was estimated from Fig. 4. The coefficient obtained from the simulations is $5.5 \times 10^{-8} \text{ cm}^3/\text{s}$, which is within the error margin of the roughly estimated value. The room temperature electron capture cross section, adjusted for the hot carrier effect (see below), is $2.4 \times 10^{-15} \text{ cm}^2$.

FIG. 6. Experimental (points) and calculated (curves) PL transients for sample 5.6×10^{18} at different average excitation powers (a). Part (b) shows calculated Fe^{3+} and Fe^{2+} concentrations (solid and dashed lines, respectively) neglecting the transition $\text{Fe}^{2+} + \text{hole} \rightarrow \text{Fe}^{3+}$. Average excitation powers in (b): 3 mW (curve 1), 5 mW (2), 8 mW (3 and 5), and 13 mW (4 and 6).

FIG. 7. Experimental (points) and calculated (lines) 290 K PL transients for samples 1.7×10^{18} and 2.4×10^{18} at 20 mW average power (a). Part (b) shows temporal dependence of $[\text{Fe}^{3+}]$ (solid lines 1 and 2) and $[\text{Fe}^{2+}]$ (dashed lines 3 and 4) for samples 1.7×10^{18} (lines 1 and 3) and 2.4×10^{18} (lines 2 and 4).

The hole capture coefficients were evaluated from simulations of PL transients at early times after the excitation. The best agreement between the experimental and the calculated results was obtained for the hole capture coefficient of $1.8 \times 10^{-8} \text{ cm}^3/\text{s}$. Estimation of the hole capture cross-section is complicated by the uncertainty in the hole effective mass.²¹ Using the average value of $1.58m_0$ (Ref. 21) and the carrier temperature of 330 K, the calculated hole capture cross-section is $2.0 \times 10^{-15} \text{ cm}^2$, which can be compared with the previously² determined upper limit of $2.1 \times 10^{-15} \text{ cm}^2$ (recalculated for the hole mass of $1.58m_0$).

Figure 7(b) shows time dependence of Fe^{3+} and Fe^{2+} trap concentrations. For both samples, Fe^{2+} becomes the dominant trap of nonequilibrium carriers within a few ps. For sample 1.7×10^{18} , the condition $[\text{Fe}^{2+}] > [\text{Fe}^{3+}]$ holds until about 85 ps after the excitation. This supports the assumption made in Section III C that the more oblique slope of the PL transients reflects the hole capture. For sample 2.4×10^{18} , the time interval over which $[\text{Fe}^{2+}] > [\text{Fe}^{3+}]$ is shorter because of the higher Fe concentration leading to a faster recovery of the Fe^{3+} traps.

Despite the crude simplification of the model by ignoring the spatial nonuniformity of the carrier concentration and its change due to diffusion, the calculated and experimental curves of PL dynamics match well. Primarily, this occurs because of the relatively similar electron and hole capture coefficients, which assure that there is not much difference between electron capture to Fe^{3+} or hole capture to Fe^{2+} .

E. Temperature dependence

Optical measurements of carrier trapping to deep centers are almost exclusively performed at room temperature. However, measurements at low temperatures and the temperature dependence of the carrier capture are interesting for several reasons. At low temperatures, the phonon occupation number is low; hence, processes with the phonon absorption, like the thermionic emission, are eliminated. Besides, the relevance of the slow nonradiative recombination channels, mentioned above, is reduced.

PL transients, determined by the carrier capture to the Fe centers, show little temperature dependence (Fig. 8(a)). PL decay times, with the increase of the lattice temperature T_L from 4 K to 290 K, decrease by a factor of 2 for 1.7×10^{17} sample, show an even smaller decrease for 2.4×10^{18} sample and remain temperature independent for 5.6×10^{18} sample. When dealing with the ultrafast carrier trapping, one should bear in mind that carriers may be trapped prior to their relaxation in the bands, i.e., being hot. Hot carriers more easily overcome potential barriers; thus, the carrier temperature should also be taken into account when estimating the capture cross-sections. The cross-sections, estimated using Eq. (1), are affected by the carrier temperature T_C via the average thermal velocity $\bar{v} = \sqrt{8kT_C/(\pi m^*)}$, where m^* is an effective mass.

For carriers with a Boltzmann distribution, the carrier temperature T_C can be estimated from the high-energy slope of a PL spectrum. For photon energies $h\nu$ exceeding the band gap E_g , $I(h\nu) \propto \exp(-(h\nu - E_g)/(kT_C))$.²² In this work, because of the very short carrier lifetimes, temporal evolution of the carrier temperature was not considered and average carrier temperatures were estimated from time-integrated

spectra. The carrier temperatures at low excitation power are shown in Fig. 8(b). The average T_C is larger than T_L for all samples and all lattice temperatures. From the three samples shown in Fig. 8, the smallest variation of the carrier temperature with T_L is for sample 5.6×10^{18} with the shortest carrier lifetime. The larger T_C variation for other samples occurs because of the longer time the carriers spend in the bands, during which they cool down. T_C for sample 3.0×10^{19} (not shown) was almost 100 K higher than T_L because of the sub-band trapping.

Carrier capture to deep centers, such as Fe in GaN, takes place via multiphonon absorption.²³ Recent calculations of carrier capture coefficients for different defects in GaN and ZnO showed that the temperature dependence of the trapping coefficient is strongly affected by the configuration diagram of the particular defect.¹⁷ For instance, hole capture coefficients of Li_{Zn} impurity in ZnO or of $(\text{Zn}_{\text{Ga}}\text{-V}_{\text{N}})$ complex in GaN have a weak temperature dependence because of very small energy barriers for the hole capture. Our nearly temperature independent electron capture rates to Fe^{3+} suggests that this process also has a small barrier, which can be easily overcome by hot electrons.

IV. DISCUSSION

The room temperature electron capture coefficient determined in our experiments and simulations is $5.5 \times 10^{-8} \text{ cm}^3/\text{s}$. This is close to the value of $4.6 \times 10^{-8} \text{ cm}^3/\text{s}$ obtained in similar experiments on the films grown by low-pressure metal-organic vapor phase epitaxy.² Possible Fe clustering in the latter case might account for the difference. However, compared to recent time-resolved transmission and photo-Hall data, the difference in electron capture coefficients is much larger. The value estimated from differential transmission decay times in low pulse repetition rate (10 Hz) pump-probe measurements on HVPE grown bulk crystals is about $1 \times 10^{-8} \text{ cm}^3/\text{s}$.⁶ The coefficient evaluated from continuous wave (cw) photo-Hall experiments at very low carrier densities ($\sim 10^8 \text{ cm}^{-3}$) on samples similar to ours is even smaller, $2.2 \times 10^{-9} \text{ cm}^3/\text{s}$.²⁴ To understand why different experiments produce different results, one should consider the internal 3d level structure of the Fe centers.

In equilibrium conditions, the ratio between Fe^{3+} and Fe^{2+} concentrations is determined by unintentional donors and acceptors. Besides, Fe^{3+} and Fe^{2+} centers are in their ground states, since the intra-center excitation energies⁵ are much larger than the thermal energy at room temperature. After electron-hole pairs are excited by a laser pulse into the bands, carrier capture by Fe traps and charge transfer processes take place. In a simplified form, the latter can be described as $\text{Fe}^{3+} + \text{electron} \rightarrow \text{Fe}^{2+}$ and $\text{Fe}^{2+} + \text{hole} \rightarrow \text{Fe}^{3+}$. However, because of the *d* level structure and the inter-center relaxation, these processes are subtler.

It has been reported that Fe^{3+} in GaN has four states in the band gap, and Fe^{2+} has two.⁵ The ground state of Fe^{3+} is ${}^6\text{A}_1$ with the spin $S=5/2$, and the first excited state is ${}^4\text{T}_1$ with $S=3/2$ (Fig. 9). Since the relaxation ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$ involves a spin-flip, it is slow, in the ms range.⁵ The relaxation times from higher excited states ${}^4\text{T}_2$ and ${}^4\text{E}$ states to the

FIG. 8. PL decay times (a) and carrier temperatures (b) at 3 mW average excitation power for samples 1.7×10^{18} , 2.4×10^{18} and 5.6×10^{18} .

FIG. 9. Recombination model for the high pulse repetition rate time-resolved PL experiment. An electron, excited over the GaN band gap, is captured to the excited state of Fe^{3+} (process 1) transforming it into the excited state of Fe^{2+} (green dotted line), from where it recombines with a hole in the valence band (process 2) returning the ion to the excited state of Fe^{3+} . The radiative recombination from ground state of Fe^{2+} is indicated as process 3. Higher Fe^{3+} excited states are not shown. Level positions with respect to the bands and interlevel energies are not in scale.

ground state ${}^6\text{A}_1$ are not known; however, considering that these states are also characterized by $S = 3/2$,²⁵ one could expect that the electron relaxation from the higher to the first excited state is considerably faster than the transition ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$. Due to the lack of more detailed information about the intra-ion transitions involving the higher excited states, we will simplify our discussion to the ground state and the first excited state, the latter representing all the excited states of the ion. For Fe^{2+} , the ground and the excited states are ${}^5\text{E}$ and ${}^5\text{T}_2$ with $S = 2$.²⁶ The relaxation rate for the transition ${}^5\text{T}_2 \rightarrow {}^5\text{E}$ in GaN has not been reported, however, for other III-V materials, such as InP, GaAs, and GaP, this time is in the μs range.^{1,27}

After the excitation of an electron-hole pair over the GaN band gap, the electron is captured in the ground state of Fe^{3+} transforming it into Fe^{2+} . In the case of InP:Fe, it has been shown that such a charge transfer transition creates Fe^{2+} in its excited state ${}^5\text{T}_2$.²⁶ Considering that properties of Fe ions in different host materials are similar,¹ we would expect the same transition to take place in GaN too. After capturing a hole, Fe^{2+} transforms back into Fe^{3+} , but not in its ground, but in the excited state.^{4,5} Such transition pattern is characteristic for other III-V:Fe semiconductors as well.²⁸ Now, in high pulse repetition rate experiments, the time interval between the pulses is six orders of magnitude smaller than Fe^{3+} relaxation time; besides, the photoexcited carrier concentration in our experiments is comparable to $[\text{Fe}]$. Consequently, Fe^{3+} does not have sufficient time to relax to its ground state, making the excited state the prevailing one for the Fe^{3+} ions. This is the key difference between our experiment and the low carrier density cw photo-Hall or the low pulse repetition rate experiment, in which Fe^{3+} ions have time to relax to their ground state before arrival of the next optical pulse. It is well known that excited states exhibit higher carrier capture-cross sections.²⁹ Thus, this difference of the dominating Fe^{3+} state is the likely reason for the

much larger electron capture coefficient determined from the high pulse repetition rate experiments compared to other studies. The cw photo-Hall and the low pulse frequency measurements of carrier dynamics provide parameters for the electron capture to the ground Fe^{3+} state. Capture parameters determined in the high pulse repetition rate experiments correspond to electron capture to the excited state of Fe^{3+} . This has important implications for modeling of GaN:Fe based optoelectronic devices. For devices aimed at low repetition rate applications, capture cross-sections to the ground Fe^{3+} state should be used. For the high frequency devices, parameters corresponding to the excited state should be applied.

Now, let us discuss the hole capture to Fe^{2+} . The μs long excited state relaxation time is about 2–3 orders of magnitude longer than the time interval between the exciting pulses. Thus, the dominant state of the Fe^{2+} ions should be the excited state ${}^5\text{T}_2$. Here again, as in the case of Fe^{3+} , we generalize the first excited state as representative for eventual higher excited states that were observed, for instance, in ZnSe:Fe.³⁰ In the hole energy scale, relevant for the nonradiative hole capture,³¹ the excited state is closer to the valence band than the ground state (Fig. 9) and is a more efficient hole trap than the ground state.³¹ This, along with the Coulomb attraction between a negatively charged Fe^{2+} ion and a hole in the valence band, could explain the relatively large value of the hole capture coefficient derived from our experiments.

Concerning the 420 nm PL peak, several experimental observations are noteworthy. First, its energy is similar to the energy interval between the Fe^{2+} ground state and the valence band.^{5,24} Second, its decay time is close to the hole capture rate evaluated from the band gap time-resolved PL. For example, consider the hole trapping for sample 1.7×10^{18} . Shortly after the pulse, the Fe^{2+} concentration is $\sim 1 \times 10^{18} \text{ cm}^{-3}$ (Fig. 7). For the hole capture coefficient of $1.8 \times 10^{-8} \text{ cm}^3/\text{s}$, the hole capture time is 56 ps, close to the 420 nm peak PL decay time of 69 ps. Third, the 420 nm peak decay time does not depend on photoexcited hole concentration. This feature is characteristic for transitions between a negatively charged center and a hole bound to it, as discussed for GaP:Fe in Ref. 32. Thus, our experimental results suggest that the 420 nm peak is caused by the radiative transition between the Fe^{2+} ground state and a bound hole. Its low intensity can be explained by the weak population of the Fe^{2+} ground state because of the long Fe^{2+} relaxation time with respect to the time interval between the exciting pulses.

V. CONCLUSIONS

In conclusion, time-resolved PL measurements were performed on heavily Fe doped GaN at different temperatures and excitation powers. The peculiar shape of the PL transients clearly demonstrates that the electron capture to Fe^{3+} centers is faster than the hole capture to Fe^{2+} . Measurements and simulations have allowed determining electron and hole capture coefficients of $5.5 \times 10^{-8} \text{ cm}^3/\text{s}$ and $1.8 \times 10^{-8} \text{ cm}^3/\text{s}$ at room temperature. Discrepancy between our electron capture coefficient and the literature

values is assigned to the difference in the Fe^{3+} states relevant for a particular experimental configuration. In the low carrier density cw and the low repetition rate pulsed experiments, the electron capture to the ground Fe^{3+} state plays the main role. For high pulse repetition rates, the excited Fe^{3+} state is dominant. The temperature dependence of the electron trapping has been found to be weak, showing that potential barrier for the multiphonon electron capture is small. The 420 nm PL peak is assigned to the radiative transitions between the Fe^{2+} ground state and a bound hole.

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