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Optical Excitation of Er Centers in GaN Epilayers grown by MOCVD

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ABSTRACT

In this paper we present results of photoluminescence (PL), photoluminescence excitation (PLE), and time resolved PL spectroscopy of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition in Er optical centers in GaN epilayers grown by metal-organic chemical vapor deposition. Under resonance excitation via the higher-lying inner 4*f* shell transitions and band-to-band excitation of the semiconductor host, the PL and PLE spectra reveal an existence of two types of Er optical centers from isolated and the defect-related Er centers in GaN epilayers. These centers have different PL spectra, local defect environments, decay dynamics, and excitation cross-sections. The isolated Er optical center, which can be excited by either excitation mechanism, has the same decay dynamics, but possesses a much higher cross-section under band-to-band excitation. In contrast, the defect-related Er center can only be observed through band-to-band excitation but has the largest cross-section. Our results indicate pathways for efficient optical excitation of Er-doped GaN semiconductors.

Keywords: GaN, Erbium, Photoluminescence spectra, Excitation mechanisms

1. INTRODUCTION

Rare earth (RE) doped semiconductors have received considerable attention in optoelectronics.[1-9] RE elements have a partially filled inner ($4f^n$) shell shielded from the influence of the local crystal field by completely filled outer 5*s* and 5*p* shells of electrons. This results in optical emission of very sharp lines at wavelengths from the UV to the IR, which are relatively independent of the host material and are determined by the energy of the transition between 4*f* states of the RE. The host semiconductor materials have a weak influence on the emission wavelength, but it has a very strong effect on the radiative transition probability. Among the various rare earth elements, Er has attracted particular attention because the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition involving nonbonding 4*f* shell electrons of the Er^{3+} ion occurs at the technologically important wavelength of 1.54 μm, matching the absorption minimum of silica-based optical fibers.[1-3, 6] GaN is expected to be an ideal host material for RE doping because it is a wide and direct bandgap semiconductor, which exhibits less thermal quenching and stronger RE emission at room temperature than RE-doped Si.[10-13] As a result of a continuing research effort, GaN:Er-based light emitting diodes have now been developed.[14, 15] In spite of impressive developments in this area, the GaN:Er system remains poorly understood and even controversial in regard to the excitation mechanisms underlying the luminescent of Er^{3+} ions which constitutes a barrier to further increase the device emission efficiency and thermal stability.

The excitation of Er^{3+} ions can take several steps before reaching the luminescence of the ions.[16, 17] A common way of exciting Er^{3+} which has been done in most RE-based lasers is to employ an optical pumping source with a photon energy that matches a higher-lying inner 4*f* shell transition. This type of excitation scheme is therefore called direct or resonant excitation. The method needs a high optical pumping power due to a low excitation cross-section for RE ions in insulators with a typical value of 10^{-20} cm^2.[6] Other types of excitation mechanisms involve host excitation first and then Er^{3+} ions using a band-to-band excitation. The common feature to these excitation processes involves the recombination of electrons and holes with a non-radiative energy transfer to nearby Er^{3+} ions. These processes are called indirect or non-resonant band-to-band excitation with an efficiency about three to five orders of magnitudes higher than the resonant process. Both electron and hole carriers can be bound to each other forming either a free exciton or a bound exciton (BE)

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trapped by RE ions or an impurity/local defect nearby RE ions. In this paper, we report direct evidence of two different mechanisms for two Er optical centers in GaN:Er epilayers prepared by metal-organic chemical vapor deposition (MOCVD) using direct and indirect excitation processes.

2. EXPERIMENTAL DETAILS

The Er doped GaN epilayers in this study were prepared by MOCVD in a horizontal reactor on (0001) *c*-plane sapphire substrates.[18] A GaN:Er epilayer of 0.5 µm thickness on a thin un-doped GaN layer of 1.2 µm on a top of an AlN layer of 0.5 µm thickness. With the *c*-plane sapphire substrate, the GaN epilayers have the wurtzite crystal structure as confirmed by X-ray diffraction (XRD) measurement. The Er concentration (n_{Er}) was 2×10^{20} cm^{-3} as determined using secondary ion mass spectrometry (SIMS) conducted by Evans Analytical Group. Following MOCVD growth, the samples were characterized by XRD and photoluminescence (PL) measurements. The XRD spectra indicated high crystallinity and no second phase formation. The bandgap energy at room temperature of GaN:Er epilayers is ~3.3 eV.[19]

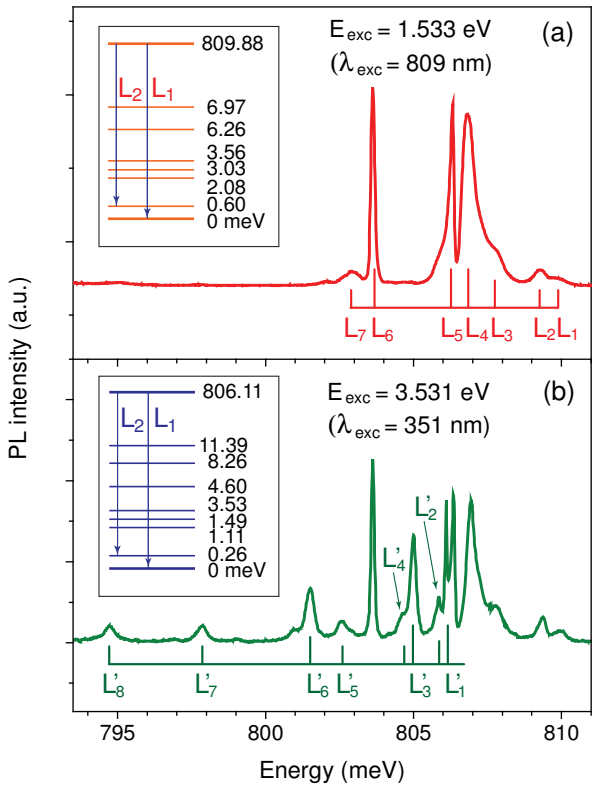

Figure 1. PL spectra of the GaN:Er epilayer of 0.5 µm thickness at 1.54 µm within the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition as measured at 15 K under (**a**) $^4I_{15/2} \rightarrow {}^4I_{9/2}$ resonant (1.533 eV or 809 nm), (inset) energy level diagram of the isolated Er optical center, and (**b**) non-resonant or band-to-band (3.531 eV or 351.1 nm) excitation, (inset) energy level diagram of the defect-related Er optical center.

The PL spectra were obtained with a high resolution spectroscopy (Horiba iHR550) equipped with a 900 grooves/mm grating blazed at 1.5 µm and detected by a high sensitivity liquid nitrogen InGaAs detector (DSS-IGA). In this specific case the PL spectrum resolution is 0.1 nm. Optical measurements were performed using a closed-cycle optical cryostat (Janis) accessing the 10 – 300 K range. The time-resolved measurements were carried out using a Tektronix TDS 3000 digital oscilloscope in combination with the InGaAs detector. The time resolution was measured as 50 µs. We have employed a tunable wavelength Ti:Sapphire laser around 809 nm (1.533 eV) with a repetition rate of 80 MHz for the resonant excitation from $^4I_{15/2} \rightarrow {}^4I_{9/2}$ of Er^{3+} in GaN and an Argon laser operating at 351.1 nm (3.531 eV) for the over

band gap excitation of GaN:Er material. The excitation modulation was achieved by using a pinhole and chopping the laser beam mechanically at 20 Hz. Both GaN:Er structures led to identical PL spectrum shown in Figure 1.

3. RESULTS AND DISCUSSIONS

Our experimental data show direct evidence of two mechanisms responsible for the excitation of optically active Er^{3+} ions in GaN epilayers grown by MOCVD. We have employed the high resolution PL spectroscopy under resonant (λ_{exc} = 809 nm[5, 20, 21] from a tunable wavelength Ti:Sapphire laser for the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transition) and non-resonant band-to-band excitation (λ_{exc} = 351.1 nm from an Ar laser) of Er in GaN to understand the optical properties of epilayers (Figure 1). The difference between resonant and non-resonant band-to-band spectra allows us to identify two types of optical centers with different local defect environments: (1) Er ions in an isolated local environment can be excited via both the resonant excitation $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transition and also the non-resonant excitation due to the recombination of electrons and holes with a non-radiative energy transfer. This optical center is referred to an isolated Er optical center labeled L with PL lines L_1 to L_7. (2) Er ions strongly associated with nearby defects or impurities can only be observed through band-to-band excitation via the host involving a trapped (bound) exciton. This center is referred to a defect-related Er optical center labeled L' with PL lines L'_1 to L'_8. The difference of PL spectra indicates a difference of the local defect environment for two Er optical centers under different excitation processes. [Note: a few PL lines with very low intensity (about 1% of the total PL intensity) appear in the PL spectrum. These PL lines probably come from other optical centers.][22]

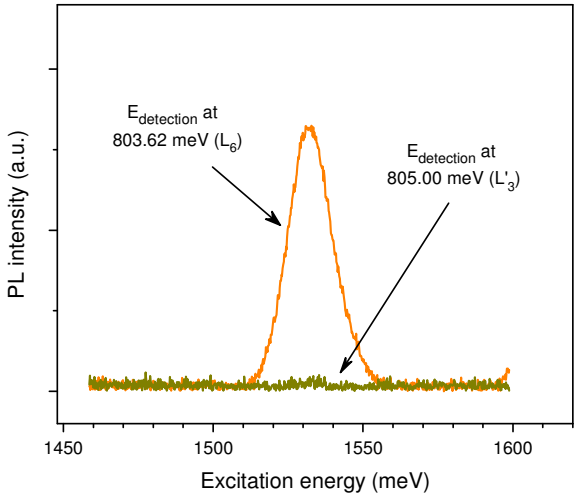

Figure 2. A comparison of PL excitation spectra around 1.533 eV (809 nm) detected at $E_{detection}$ = 803.62 meV (1542.83 nm) for line L_6 and $E_{detection}$ = 805.00 meV (1540.19 nm) for line L'_3 reveals a low number of optical centers for the L' center.

We also have performed PL excitation measurements for the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transition of these Er optical centers to verify the above assumption (Figure 2). The PL signals were detected at line L_6 (803.62 meV) and line L'_3 (805.00 meV). As can be seen from the PL excitation measurements while the PL from the L center shows a strong signal at the excitation wavelength of 1.533 eV, the PL signal from L' center under the resonant excitation is very weak, below our detection level. The results suggest that the L' center has a low number of optical centers with low efficiency for the resonant excitation at 809 nm.

Isolated Er optical center: Our magneto-optical measurements have shown that the isolated Er centers (L center) occupy Ga substitutional sites. RE ions in the substitutional sites were considered as an isoelectronic impurity center.[23] The center has no net charge in the local bonding region. A hole or an electron can be localized at such a center by a local core potential; subsequently, the secondary particle can be captured by Coulomb field of the first particle. The recombination of the two particles will transfer their energy to the Er ion. The isolated Er optical center can be excited by two mechanisms of resonant excitation via the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transition and the non-resonant band-to-band excitation through the recombination of electron and hole pairs.

Defected-related Er optical center: The excitation mechanism for the defect-related Er centers (L' center) is believed to be related to defects, impurities or defect–impurity complexes, rather than to RE ions acting as traps. The excitation of the Er center is commonly described as involving (trapped) BEs with subsequent non-radiative transfer of the BE energy to nearby Er ions. The efficiency of this process is high, but the requirement of BEs for excitation will open non-radiative recombination channels for the luminescence process. A typical non-radiative recombination channel is the Auger de-excitation process which shows a fast lifetime on the decay dynamics.[24-26] With non-recombination channels, the PL intensity is quenched strongly with the increasing of temperature. Thus we cannot obtain the optical amplification in these optical centers at room temperature.[25]

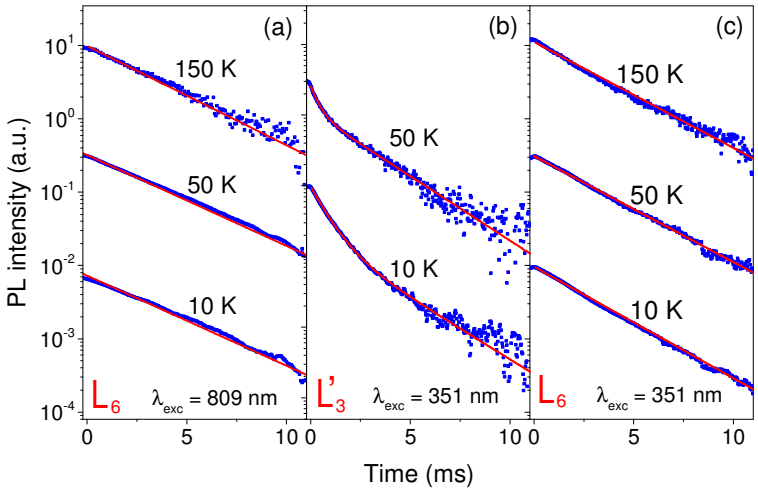

Figure 3: Decay dynamics of PL lines at different temperatures and excitation energies. (a) Under resonant excitation (λ_{exc} = 809 nm), the decay dynamics of L_6 are temperature independent with a time of 3.3 ms at 10 to 150 K. (b) Under band-to-band excitation (λ_{exc} = 351.1 nm), the dynamics for the line L'_3 belonging to the defect-related center shows a double-exponential function with 0.8 and 2.1 ms decay times at 10 and 50 K. (c) The dynamics of the line L_6 is independence with temperature of 3.1 ms, shown at 10 to 150 K.

Decay kinetic: Decay dynamics of optical centers allows us to understand the energy transfer and recombination processes in the solid materials. Under resonant excitation, the dynamics of all PL lines of the isolated Er optical centers appear as a single experiential decay dynamics of 3.3 ± 0.3 ms at all temperature (Figure 3a). The value is similar with previous reports on the Er in GaN.[21, 27, 28] It indicates that the isolated Er optical center has no quenching channels. Under band-to-band excitation, while again the isolated Er optical center reveals a similar decay time of 3.1 ± 0.3 ms and an independence with temperature as for the resonant excitation method (Figure 3c), whereas the defect-related Er optical center shows a double-exponential decay dynamics with decay time constants of 0.8 and 2.1 ms, which strongly depend on the temperature (Figure 3b). Above 150 K, we cannot detect any PL lines for this optical center. The double-exponential decay process of the optical center indicates that there are non-radiative recombination processes taking place in the PL signal.

Excitation cross-section: The behavior of the excitation flux dependence of the PL intensity under cw laser for band-to-band excitation at 10 K is different for the two optical centers (Figure 4). Specifically, while the Er PL intensity from defect-related optical centers appears to saturate at lower photon flux, the Er PL intensity from the isolated optical centers obviously increases with photon flux. Under steady state conditions, the excitation photon flux (Φ) dependence of Er PL intensity is well described with the formula:[25, 26]

$$I_{\mathrm{PL}} \propto N_{Er}^{*} = \frac{N_{\mathrm{Er}}\sigma\tau\Phi}{1+\sigma\tau\Phi} \qquad (1)$$

where N_{Er}^{*}, N_{Er} are the concentration of optically active and the total erbium ions, σ is an effective excitation cross-section of Er^{3+} ion, τ is the effective lifetime of Er^{3+} in the excited state, $^4I_{13/2}$. From the fitting (solid curves), we get

$\sigma'_{\lambda_{exc}=351.1nm} = (3.8 \pm 2) \times 10^{-16}$ cm^2 for PL lines of the defect-related Er optical center and $\sigma_{\lambda_{exc}=351.1nm} = (9.5 \pm 2) \times 10^{-17}$ for PL lines of the isolated Er optical center. The isolated optical centers do not require a related-defect or an impurities center, thus the capture as well as recombination processes of electrons and holes are less efficient than the defect-related center, and as a result $\sigma' > \sigma$. The high excitation cross-section combined with the temperature independence of decay dynamics and high percentage of optically active center of the isolated Er optical centers makes the GaN:Er materials synthesized by MOCVD interesting for GaN photonics. In particular, the material appears promising for realization of population inversion and, consequently, optical amplification at room temperature.

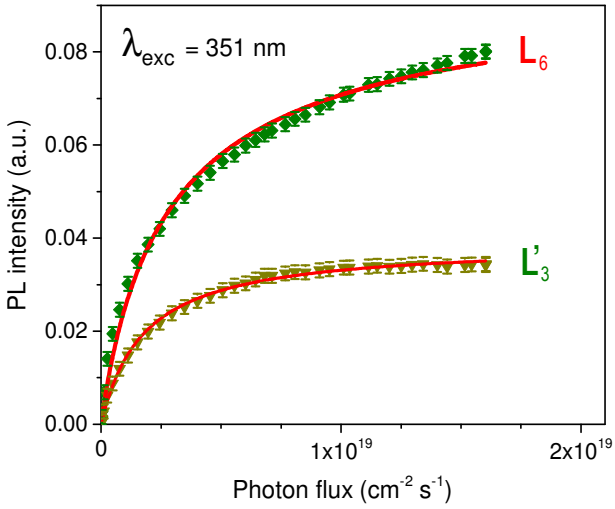

Figure 4: PL intensities measured at 10 K as a function of excitation flux for line L_6 from the isolated Er optical centers and L'_3 from the defect-related Er optical centers, under band-to-band excitation (λ_{exc} = 351.1 nm).

We note that although the GaN:Er system exhibits a long excited state lifetime, due to the forbidden character of the intra-4*f*-electron shell transitions, population inversion and laser action have not been achieved in crystalline GaN:Er (while optical amplifiers based on Er-doped insulators are routinely manufactured). Realization of lasing action would provide a major boost for optoelectronic applications of GaN. In order to achieve gain, the absorption by Er^{3+} ions should be maximized and losses minimized. The latter include absorption of the 1.5 μm radiation in the host and non-radiative recombinations of excited Er^{3+} ions. The temperature independence of the long decay time of 3.0 ms and a similar dynamics with the resonant excitation process indicate that there is no non-radiative recombination process in the isolate Er optical center prepared by the MOCVD. In addition, by integrating all PL intensities from the isolated Er optical center in the PL spectrum under band-to-band excitation and taking into account the decay dynamics for both optical centers, we find that there is more than 70% contribution of the isolated Er optical centers to the PL spectrum.

4. SUMMARY AND CONCLUSIONS

Using PL and PLE we have investigated the optical excitation of Er centers in GaN epilayers prepared by MOCVD. The data, under resonant and non-resonant band-to-band excitation, reveal the existence of two types of optical centers; the defect-related and the isolated Er optical centers. The defect-related optical centers display a strong temperature dependence in PL intensity with a double-exponential decay dynamics and the highest excitation cross-section. This Er optical center can only be observed by the band-to-band excitation. The isolated Er optical centers which can be excited by both resonant and non-resonant processes show a temperature independence of decay dynamics with a decay time constant of ~3.0 ms. The excitation cross-section of this optical center under band-to-band excitation is much larger than that using the resonant excitation process via the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ transition. The high excitation cross-section combined with the temperature independence of decay dynamics and high percentage of optically active center of the isolated Er optical centers make the GaN:Er epilayers promising materials for realization of population inversion and optical amplification at room temperature for optical communication applications.

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