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Temperature dependence studies of Er optical centers in GaN epilayers grown by MOCVD

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ABSTRACT

We report the temperature dependence of Er optical centers in GaN epilayers prepared by metal-organic chemical vapor deposition under the resonant excitation ($^4I_{15/2} \rightarrow {}^4I_{9/2}$) excitation using a Ti:Sapphire laser (λ_{exc} = 809 nm). High resolution infrared spectroscopy and temperature dependence measurements of photoluminescence intensity from Er ions in GaN have been performed to identify the crystal filed splitting of the first excited state, $^4I_{13/2}$. Here, we have employed a simple approach to determine activation energies which are related to the thermal population of electrons from the lowest level to the higher level of the crystal field splitting of the first excited state.

INTRODUCTION

Rare earth doped wide-bandgap semiconductor is of significant interest for optoelectronic device applications, because of their temperature independent, atomic-like and stable emission together with the possibility of optical or electrical excitation [1-3]. Much of the research has focused on the element Er with the emission from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) at 1.54 μm that is the minimum loss window of silica fibers for optical communications and in the eye-safe wavelength region [4-10]. GaN with the direct bandgap semiconductor appears to be excellent host materials for Er ions, not only due to their structural and thermal stability [11, 12] but also to the recent advancements in growth techniques of high-quality crystals of both n- and p-type [2]. While light emitting diodes based on GaN:Er have been demonstrated [13], the realization of GaN:Er materials for optical amplification is still under investigation. For this reason, it is necessary to determine important factors which influence the optical performance of Er embedded in GaN. The information would provide us with the direction to optimize the optical properties of GaN:Er material.

Previous work has revealed that a number of Er optical centers as well as a variety of energy transfer routes take place in GaN [14, 15]. The existence of various Er optical centers depends on preparation methods, such as ion implantation [16, 17], metal-organic chemical vapor deposition (MOCVD) [18] and molecular beam epitaxy (MBE) [19], as well as growth and annealing conditions [16]. The absorption and emission studies together with the crystal field calculation provided an understanding of energy transfer mechanism to Er ions and the Er related luminescence process [20]. Non-radiative recombination channels were also investigated to understand photoluminescence (PL) quenching [21]. The Er-related trap centers with energy levels in the GaN bandgap act not only as active centers for bound excitons transferring their energy to 4*f* electrons of Er^{3+} ions, but also as PL quenching centers [12, 22]. These previous studies provided important insights for the improvement of Er emission in material engineering towards optimizing the energy transfer between the GaN host and Er ions.

In our previous report, isolated Er and defect-related Er optical centers have been identified through high-resolution infrared PL spectroscopy [23]. Understanding the optical excitation mechanisms, optical activity of Er^{3+} infrared luminescence and quenching channels is essential to enhance the emission

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efficiency of GaN:Er. A low thermal quenching of 20% from 10 K to room temperature from the isolated Er optical centers in GaN epilayer at the 1.54 μm emission has been demonstrated.

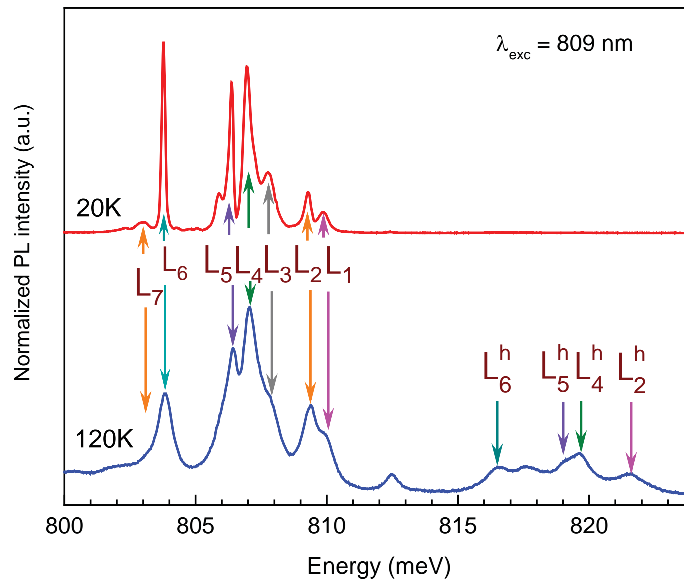

Figure 1. The PL spectra at 20 K and 120 K of the GaN:Er epilayer at 1.54 μm within the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition under the resonant excitation ($^4I_{15/2} \rightarrow {}^4I_{9/2}$) excitation using a Ti:Sapphire laser (λ_{exc} = 809 nm). At low temperature, the spectrum of the isolated Er optical center consists of a set of narrow and intense PL lines (L_1 to L_7). At higher temperatures, hotlines, $L^h_{1,2}$, L^h_4, L^h_5, L^h_6, appear and are displaced by about 12.6 meV. The intensities of hotlines rapidly increase with increasing temperature while the intensities of the main PL lines decrease.

SAMPLES AND EXPERIMENTAL METHODS

The Er doped GaN epilayer samples were prepared by MOCVD method in a horizontal reactor [12, 18, 24]. A GaN:Er epilayer, with 0.5 μm thickness and Er concentration (n_{Er}) of ~ 10^{21} cm^{-3} were grown on a thin un-doped GaN template of 1.2 μm on top of (1000) *c*-plane sapphire substrate. The growth temperature of Er-doped GaN layer was 1040 ^{0}C. The X-ray diffraction spectra indicated that GaN:Er epilayers have high crystallinity and no second phase formation. The band gap energy of GaN:Er epilayers is about 3.4 eV at room temperature. A detail description of the growth process and epilayer structure has been reported previously [12, 13, 18, 23, 24].

The high resolution PL spectra were conducted using a Horiba iHR550 spectrometer equipped with a 900 grooves/mm grating blazed at 1500 nm and detected by a high sensitivity liquid nitrogen InGaAs DSS-IGA detector. The resolution of PL spectrum is 0.05 nm. The PL experiments were carried out in a variable temperature closed-cycle optical cryostat (Janis) providing a temperature range from 10 K to 300 K. Both resonant excitation and the non-resonant excitation were employed to investigate the optical properties of Er in GaN epilayers [23]. The resonant excitation PL spectra from $^4I_{15/2} \rightarrow {}^4I_{9/2}$ of Er^{3+} in GaN were obtained using a tunable wavelength Ti:Sapphire laser around 809 nm (1.533 eV) with a repetition rate of 80 MHz [23].

The influence of Er^{3+} site on the PL emission can be determined from optical excitation mechanisms. We have reported direct evidence of two mechanisms responsible for the excitation of optically active Er^{3+} ions in GaN epilayers grown by MOCVD in our previous work [23]. Under

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resonance excitation via the higher-lying inner 4*f* shell transitions and non-resonant (band-to-band) excitation of the GaN host, the high resolution PL spectra at 10 K reveal an existence of two types of Er optical centers including the isolated and the defect-related Er optical centers in GaN epilayers [23]. For the first case, the isolated Er optical centers occupying Ga substitutional sites were observed under both the resonant ($^4I_{15/2} \rightarrow {}^4I_{9/2}$) excitation and the band-to-band excitation. Er ions in substitutional sites are considered as an isoelectronic impurity center [25]. The center, with no net charge in the local bonding region, can be excited by resonant and band-to-band excitation. Under the band-to-band excitation, a hole or an electron can be localized at the isolated 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. For the second case, the defect-related Er optical center can only be observed through the band-to-band excitation of the host involving a trapped (bound) exciton. The observation has been confirmed with a photoluminescence excitation measurement [23]. The excitation mechanism for the defect-related Er centers is believed to be related to intrinsic defects, impurities or defect-impurity complexes near the Er optical center. These defects capture excitons and subsequently transfer non-radiatively their energy to nearby Er ions. The efficiency of this process is high, but the requirement of bound excitons for excitation opens up non-radiative recombination channels for the luminescence process. At room temperature, we do not observe PL emission from the defect-related Er optical centers. For optoelectronic applications of the GaN:Er epilayers, this work focuses on the optical characterization of the isolated Er optical centers under the resonant excitation.

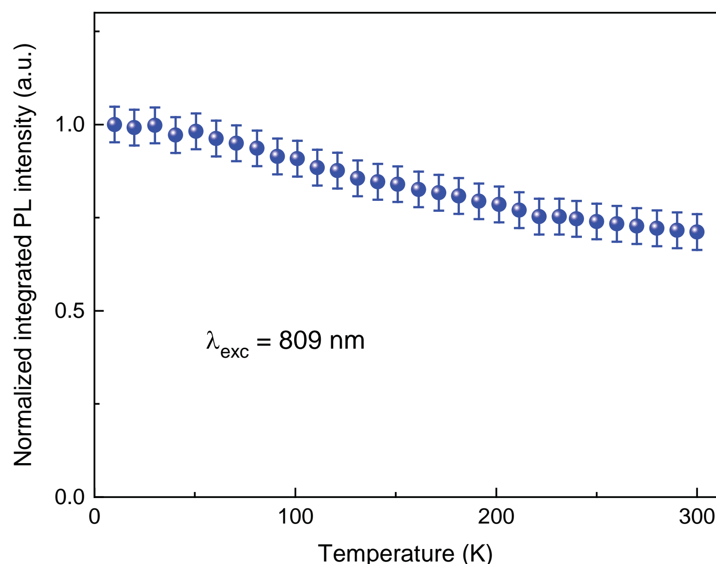

Figure 2. The temperature dependence of PL intensity measured under the resonant excitation (λ_{exc} = 809 nm) indicates a low thermal quenching from Er^{3+} ions in our GaN:Er epilayer. The integrated PL intensity measurements at 1.54 μm band show a thermal quenching of 20% from 10 K to room temperature from isolated Er optical centers.

DISCUSSION

To determine the crystal field splitting of the first excited state ($^4I_{13/2}$) of the isolated Er optical centers, the high resolution spectra as well as the temperature dependence of PL spectra, have been investigated under resonant excitation (Fig. 1). At low temperatures, the spectrum of the isolated Er optical center consists of a set of narrow and intense PL lines (L center): L_1, L_2, L_3, L_4, L_5, L_6 and L_7 at energies of 809.88, 809.28, 807.80, 806.85, 806.32, 803.62, 802.91 meV, respectively [23]. At higher

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temperatures, other PL lines, labeled hotlines $L^h_{1,2}$, L^h_4, L^h_5, L^h_6, appear at ~ 821.5, 819.6, 819.2 and 816.5 meV, respectively (Fig. 1). The PL intensity of PL lines L_1, L_3, L_7, are weak at low temperature and we cannot resolve the PL of hotlines L^h_1, L^h_3, L^h_7 at higher temperature. These hotlines are displaced by about 12.6 meV. At high temperature, the intensities of the hotlines rapidly increase with increasing temperature while the intensities of the main PL lines decrease. We note that due to the temperature broadening at high temperature the PL from L_1, L_2 lines merge into one PL line, thus we cannot resolve the PL hotlines L^h_1, L^h_2. The integrated PL intensity measurements for the whole 1.54 µm band under the resonant excitation (λ = 809 nm) indicate a low thermal quenching of 20% from 10 K to room temperature from Er^{3+} ions in our GaN:Er epilayer (Fig. 2).

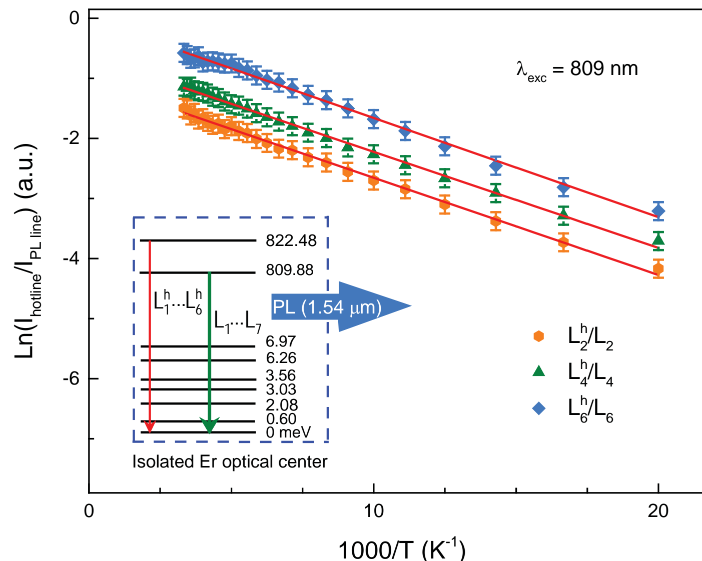

Figure 3. Arrhenius plots of the temperature variation of the intensity ratios of the hot lines L^h_2, L^h_4, L^h_6 to that of PL lines L_2, L_4, L_6, respectively. Activation energies are found to be ΔE = 13.1 ± 0.5 meV, equal to the spectroscopic splitting. Inset shows the Stark sub-energy level diagram of the first excited and ground states of the isolated Er optical center in GaN.

The temperate dependence of luminescence has been investigated in detail in order to determine the electronic level scheme of the optical center. We have measured the PL intensity ratios of the hotlines L^h_2, L^h_4, L^h_6 to that of PL lines L_2, L_4, L_6, respectively, as a function of temperature (Fig. 3). These measurements determine the thermal population of electrons to higher lying excited states, which show the thermal quenching of PL emission from isolated Er optical centers. In this model, the observed PL intensity for main PL lines of isolated centers should follow the Arrhenius equation:

$$I\ (\mathrm{T}) = \frac{I_0}{C\ \exp\left(-\frac{\Delta E_\mathrm{A}}{k_B \mathrm{T}}\right)} \qquad (1)$$

where I(T) is the integrated PL intensity at the temperature of T, I_0 is the integrated PL intensity at 10 K, E_A is the activation energy of the thermal population processes, C is a fitting constant, and k_B is Boltzmann's constant. As shown in the Fig. 3, the solid lines present the best fit to the PL intensity ratios using Eq.1. The activation energy values derived from the fitting are ΔE_A = 13.1 ± 0.5 meV.

Obviously, the replications of PL lines at higher temperature originate from the transition of the second-lying crystal field split level of the first ($^4I_{13/2}$) excited state to the sublevels of ($^4I_{15/2}$) ground state. When temperature increases, electrons from the lowest level of the first excited state gain energy and populate at the second-lying crystal field split level. Thus, the intensity of the main PL lines decreases and

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the intensity of hotlines increases with temperature. These hot lines are displaced by 12.6 meV, which is nearly equal to the activation energy of 13.1 ± 0.5 meV. An energy level diagram for the luminescence of isolated Er optical centers is illustrated in the inset of Fig. 3.

CONCLUSIONS

In summary, we have investigated the temperature dependence studies of Er optical centers in GaN epilayers grown by MOCVD. The PL intensity measurements under the resonant excitation (λ = 809 nm) indicate a low thermal quenching of 20% from 10 K to room temperature from Er^{3+} ions in our GaN:Er epilayer. Employing the temperature dependence measurements of the PL intensity, we have determined the crystal field splitting of the first excited state ($^4I_{13/2}$) of the optical center in GaN.

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