Excitation dynamics of the 1.54 μ m emission in Er doped GaN synthesized by metal organic chemical vapor deposition

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The authors report on the excitation dynamics of the photoluminescence (PL) emission of Er doped GaN thin films synthesized by metal organic chemical vapor deposition. Using the frequency tripled output from a Ti:sapphire laser, the authors obtained PL spectra covering the ultraviolet (UV) to the infrared regions. In the UV, a dominant band edge emission at 3.23 eV was observed at room temperature; this is redshifted by 0.19 eV from the band edge emission of undoped GaN. An activation energy of 191 meV was obtained from the thermal quenching of the integrated intensity of the 1.54 μ m emission line. This value coincides with the redshift of the band edge emission and is assigned to the Er_{Ga}-V_N complex level. © 2007 American Institute of Physics. [DOI: 10.1063/1.2450641]

Much research has been devoted to the incorporation of Er into semiconductors for application in telecommunication devices due to the stability of the energy levels of the 4fshell of Er inside a solid host and the intra-4f transition that corresponds to a wavelength of minimum loss in silica based fibers $(1.54 \ \mu m)$.¹ Although the wavelength of emission is not affected by the solid host, the transition probability (i.e., emission intensity) is affected by the neighboring environment. It has been empirically determined that Er emission from semiconductors of smaller band gaps has low efficiency at room temperature due to a strong thermal quenching effect.² Although an exact understanding of this thermal quenching mechanism is not completely understood, the empirical work by Favennec *et al.*² has directed researchers to use wide band gap semiconductors (WBGS) as hosts for Er. Of these WBGS, GaN has proven to be an accomplished host, with reports of fabrication of light-emitting diodes operating in the visible and infrared region.^{3–5} However, since these devices suffer from a low quantum efficiency at the IR wavelength, a better understanding of the excitation and emission dynamics of the Er doped GaN system must be attained in order to create materials suitable for telecommunication applications.

There are many proposed mechanisms of this thermal quenching, with some reports having it associated with an Er related trap energy level located within the energy band gap.^{6–9} Through this Er trap, the 4f core states are excited by an Auger energy transfer via bound carriers or excitons. The radiative transitions of electrons in these 4f core states result in the desired photon emission. Once the thermal energy of the surrounding environment becomes large enough, the carriers or excitons are dissociated from the Er center. Due to this dissociation, the energy transfer efficiency drops dramatically, thus resulting in the apparent thermal quenching of transition efficiency.

In this work, we report on the temperature dependence of the 1.54 μ m photoluminescence (PL) emission of Er

doped GaN thin films grown by metal organic chemical vapor deposition (MOCVD), and propose a model for the thermal quenching of this emission. A detailed description of the growth process and epilayer structure used here has been reported previously.¹⁰ The Er doped GaN epilayer has a thickness of 0.5 μ m with an estimated Er concentration of 2×10^{21} cm⁻³. The optical properties of the Er doped GaN were probed by time-resolved ultraviolet (UV) PL emission spectroscopy. The excitation laser system consists of a frequency tripled, 100 fs Ti:sapphire laser operating at an average power of 70 mW at 263 nm, and a repetition rate of 76 MHz. IR PL detection was accomplished by an InGaAs detector, while visible PL detection was accomplished by a multichannel plate photomultiplier tube, in conjunction with a 1.3 m monochromator. Temperature dependent PL measurements were performed using a closed cycle refrigerator with a temperature controller.

Figure 1 depicts the PL emission of Er doped GaN cov-



FIG. 1. PL spectra of Er doped GaN covering a broad spectral range from UV to IR for λ_{exc} =263 nm at (a) 300 K and (b) 10 K.

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FIG. 2. Comparison of the PL spectra of the IR emission in Er doped GaN for λ_{exc} =263 nm between 10 and 450 K.

ering a broad spectral range from the UV to near IR at 10 and 300 K for an excitation wavelength (λ_{exc}) of 263 nm. Emission lines at 1.0 and 1.54 μ m are clearly seen at both temperatures, corresponding to the intra-4f Er³⁺ transitions of the ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$ levels to the ground state (${}^{4}I_{15/2}$), respectively. The dominant band edge emission at 300 K in the UV region is at 3.23 eV, which is redshifted by 0.19 eV from the 3.42 eV band edge emission of undoped GaN at 300 K.¹¹ The spectral redshift of the band edge emission in Er doped GaN is related to the presence of Er and the 3.23 eV emission line in Er doped GaN is believed to be due to the recombination between electrons bound to the $\mathrm{Er}_{\mathrm{Ga}}$ - V_{N} complex and free holes in the valence band, as will be discussed below. Here, ErGa represents the substitution of Er onto the Ga sublattice and V_N is the nitrogen vacancy.

Figure 2 compares the PL spectra of the IR emission near 1.5 μ m of Er doped GaN for λ_{exc} =263 nm between 10 and 450 K. It is evident that the 1.54 μ m emission is dominant at low temperatures. As the temperature is increased, the spectral nature of the Er emission changes as evident from the two additional emission peaks at 1.51 and 1.56 μ m. The presence of multiple peaks at room temperature for the Er doped GaN system may allow for broadband optical amplification around the main c-band telecommunication wavelength (1.54 μ m).

Figure 3 is a plot of the integrated PL emission intensity (I_{int}) of the 1.54 μ m emission line from Er doped GaN between 10 and 450 K for λ_{exc} =263 nm. The Er emission has a 20% decrease in Iint between 10 and 300 K, which represents the lowest reported degree of thermal quenching for rare earth doped GaN.¹² In order to improve upon the thermal stability of this Er emission, a better understanding of the quenching mechanism must be determined.

The data from Fig. 3 were fitted by the equation

$$I_{\rm int} = \frac{I_0}{1 + ce^{-E_0/kT}},$$
(1)

where I_0 is the integrated intensity at low temperature, c is a fitting constant, E_0 is the activation energy of the thermal quenching, and k is Boltzmann's constant. The inset in Fig. 3 is an Arrhenius plot of the integrated PL emission intensity at



FIG. 3. Integrated PL emission intensity of the 1.54 μ m emission of Er doped GaN between 10 and 450 K for λ_{exc} =263 nm. The inset is an Arrhenius plot of the integrated PL intensity of the 1.54 μ m emission.

1.54 µm between 10 and 450 K. From this plot, an activation energy of 191±8 meV was determined.

The density functional study of the Er doped GaN system by Fihol *et al.*⁹ showed that Er_{Ga} - V_{N} complexes in the Er doped GaN system have a half-filled energy level at approximately 0.2 eV below the conduction band. This theoretical calculation is in good agreement with our experimental results obtained both from the activation energy of the 1.54 μ m emission quenching and from the band edge PL emission spectra. Thus, an Er trap-related donor level with an energy of 191 meV was identified and assigned to this Er_{Ga}-V_N complex. Our experimental results also match reasonably well with the work by Song *et al.*,¹³ who used deep level transient spectroscopy measurements on Er implanted GaN and measured an $Er_{Ga}-V_N$ complex level of 188 meV below the conduction band. Thus, we conclude that the exchange of energy between the electrons bound to the $Er_{Ga}-V_N$ complex (with an energy level at 191 meV) and the 4f core states of Er is the dominant excitation mechanism of the 1.54 μ m emission in MOCVD grown Er doped GaN using the above band gap excitation.

Our results also provide a better understanding of the low degree of thermal quenching in WBGS. It is well established that for semiconductors, effective donor levels increase with increasing energy band gap. The low degree of thermal quenching for Er doped WBGS may be a result of this behavior. For smaller band gap semiconductors, the majority of electrons bound to the Er traps are thermally excited into the conduction band even at low temperatures since the binding energy is small. Thus, the electrons cannot efficiently transfer energy to the 4f electrons via an Auger-like process, resulting in a reduction of intra-4f excitation. However, for WBGS, the electrons remain bound to the Er related donor levels at higher temperatures since the energy levels are deeper. The Auger energy transfer between bound electrons and 4f electrons can still occur, and the subsequent thermal quenching is dramatically reduced.

In Figure 4, we compare in more detail the dominant band edge emission of undoped and Er doped GaN at 10 and 300 K for λ_{exc} =263 nm. In contrast to the dominant band edge transition of undoped GaN at a room temperature of Downloaded 12 Jul 2010 to 129 118.86.45. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp



FIG. 4. Comparison of the band edge emission of undoped and Er doped GaN at (a) 300 K and (b) 10 K for λ_{exc} =263 nm. The inset is the temporal response of the 3.23 eV emission intensity in Er doped GaN at 10 K.

3.42 eV,¹¹ the dominant band edge emission of Er doped GaN is 3.23 eV. The difference in the transition energies of the band edge emissions for undoped and Er doped GaN at room temperature (3.42-3.23=0.19 eV) coincides with that of the extrapolated thermal activation energy (0.191 eV). In order to further identify the nature of this transition, the dynamical behavior of the emission has been studied through time-resolved PL. The inset of Fig. 4 is the temporal response of the 3.23 eV PL emission peak in Er doped GaN measured at 10 K. The lifetime of the 3.23 eV transition was determined to be 200 ps, which suggests that this is an impurity-to-band related transition.¹⁴ Thus, the dominant 3.23 eV band edge PL emission in Er doped GaN is believed to be due to the recombination between electrons bound to the $\text{Er}_{Ga}-V_N$ complex and free holes in the valence band.

In summary, we have studied the thermal quenching of the 1.54 μ m PL emission of Er doped GaN and its relation to an Er related energy level. An Er related energy level of 191 meV was obtained from the temperature dependence of the integrated PL emission intensity of the 1.54 μ m peak and was assigned to the Er_{Ga} - V_{N} complex. Our results indicate the fact that the thermal quenching of the 1.54 μ m emission in Er doped GaN is controlled by the thermal activation of electrons captured by Er_{Ga} - V_{N} complexes. The low degree of thermal quenching in Er doped WBGS may result from a reduced thermal activation of electrons bound to Er related donor levels that increase in energy as a result of increasing band gap. It is also observed that the dominant band edge emission in Er doped GaN is redshifted by 0.19 eV. The deep nature of the Er related impurity energy levels leads to a low degree of thermal quenching in conjunction with the broad nature of the Er emission at room temperature. These features make MOCVD grown Er doped GaN promising materials for telecommunication device applications.

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