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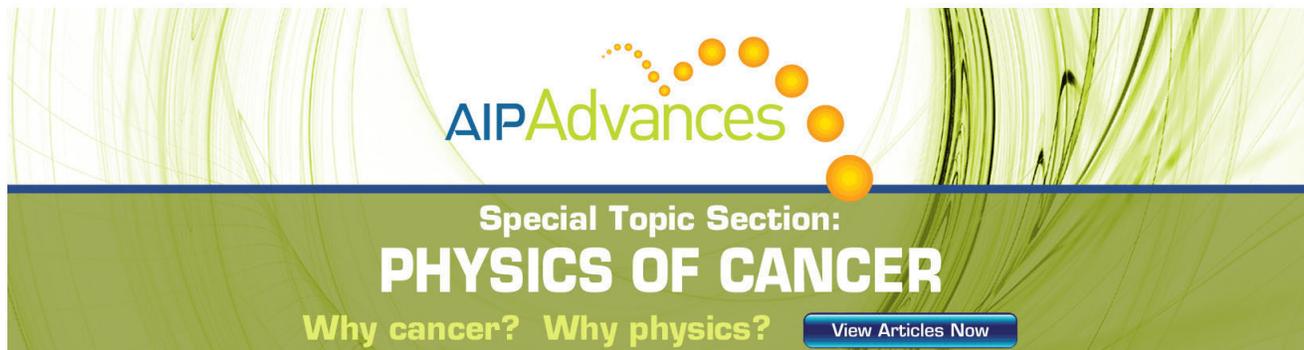
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Formation energy of optically active Er^{3+} centers in Er doped GaN

C. Ugolini,¹ I. W. Feng,¹ A. Sedhain,¹ J. Y. Lin,¹ H. X. Jiang,^{1,a)} and J. M. Zavada²

¹Department of Electrical and Computer Engineering, Texas Tech University, Lubbock, Texas 79409, USA

²Department of Electrical and Computer Engineering, Polytechnic Institute of New York University, Brooklyn, New York 11201, USA

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Erbium doped GaN (GaN:Er) and low In-content $\text{In}_x\text{Ga}_{1-x}\text{N}$ ($x \sim 0.05$) epilayers were synthesized by metal organic chemical deposition. The $1.54 \mu\text{m}$ PL emission intensity was monitored for GaN:Er epilayers grown at different growth temperatures and utilized to establish a value of $1.8 \pm 0.2 \text{ eV}$ for the formation energy (E_F) of the optically active Er^{3+} centers in GaN. The optically active Er^+ centers are presumably Er and nitrogen vacancy (Er-V_N) complexes. The experimentally measured value of the E_F of the optically active Er^{3+} centers is about 0.98 eV larger than the calculated formation energy of Er ions at Ga sites; however, it is $1.1\text{--}2.2 \text{ eV}$ lower than the formation energy of V_N in GaN. Due to the large E_F values, relatively high growth temperatures are required to improve the $1.54 \mu\text{m}$ emission efficiency in GaN:Er. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4742196>]

Due to their outstanding thermal, mechanical, electrical, and optical properties, III-nitride (GaN and AlN) wide bandgap semiconductors have demonstrated excellent performance for high power/temperature electronic devices and UV/blue/green optoelectronic devices.^{1–5} GaN commercial visible photonic devices and high power electronic devices have reached very high performance levels. Due to the intra-4f transition of Er^{3+} at $1.54 \mu\text{m}$ and its overlap with the minimum optical loss region of silica fibers used in optical communications, extensive research has been devoted to the studies of Er incorporation into various semiconductors. The goal is to develop photonic integrated circuits that combine the high functionality and compactness of semiconductor devices with the high information carrying capability of optical fiber networks.^{6–17} Over the last 15 years, several groups have carried out extensive work on materials growth and basic properties studies of Er doped III-nitride semiconductors. These studies have shown that III-nitrides are excellent host materials for Er ions due to their structural properties and the nature of the wide energy band gap.^{10–14} The thermal quenching effect of Er^{3+} emission at $1.54 \mu\text{m}$ in GaN is much smaller than in narrow band gap semiconductor hosts.^{10–17} In addition to the special interest stemming from optical communications, Er doped GaN (GaN:Er) is expected to be an excellent gain medium for solid-state high energy lasers operating in the eye-safe spectral region.

Despite these recent advances, the foremost challenge is still to better understand the formation of optically active centers in GaN:Er and to develop growth procedures to optimize the emission efficiency at $1.54 \mu\text{m}$. In this work, we report on the influence of the growth temperature on the optical and structural properties of GaN:Er and Er doped InGaN (InGaN:Er) epilayers grown by metal organic chemical deposition (MOCVD). From these studies, we have determined the formation energy of optically active centers in Er doped GaN and related the result to optical properties of Er doped InGaN.

The Er doped III-N epilayers were synthesized by MOCVD in a horizontal reactor. Trimethylgallium was used for the Ga source, and blue NH_3 was used as the N source. The metalorganic precursor used for the *in-situ* Er doping was tris(isopropyl)cyclopentadienylerbium (TRIPeEr), which was transported to the reactor by H_2 . All samples were grown on (0001) sapphire substrates. The growth of these epilayers began with a thin GaN buffer layer, followed by a $1.2 \mu\text{m}$ GaN epilayer template grown at 1040°C and a $0.5 \mu\text{m}$ GaN:Er or $0.3 \mu\text{m}$ InGaN:Er epilayer. Due to the weaker bonding between In-N compared to Ga-N, the growth temperatures (T_G) required to produce InGaN epilayers are generally significantly lower than T_G for GaN epilayers.⁴ In this study, Er doped $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$ epilayers (InGaN:Er) were grown at 760°C , while GaN:Er epilayers were grown at varying temperatures from 890 to 1060°C . A photoluminescence (PL) spectroscopy system was employed to study the optical properties of the GaN:Er.¹⁵ The PL system consists of a frequency doubled, tripled, and quadruple 100 fs Ti:sapphire laser operating at an average power of 150 mW at 263 nm and 395 nm , $2\text{--}5 \text{ mW}$ at 196 nm , and a repetition rate of 76 MHz . Infrared detection was accomplished by an InGaAs detector, while visible PL detection was accomplished by a multi-channel plate photomultiplier tube, in conjunction with a 1.3 m monochromator. Secondary-ion mass spectroscopy (SIMS) was performed by *Evans Analytical Group* to probe the Er concentration profile. X-ray diffraction (XRD) rocking curve scans of the (002) peaks were measured to assess the crystalline ordering of GaN:Er for the varying growth environments. Atomic force microscopy was used to characterize the surface morphology.

Figure 1(a) is the Er concentration profiles probed by SIMS for the GaN:Er and InGaN:Er samples. The profiles show that Er concentrations (N_{Er}) can exceed 10^{20} cm^{-3} when III-nitrides are utilized as the host. Figure 1(b) compares the (002) XRD rocking curves of $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$:Er and GaN:Er, which reveals that the crystalline quality of InGaN:Er is nearly identical to that of GaN:Er. The root mean square (RMS) surface roughness of $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$:Er is

^{a)}Electronic mail: hx.jiang@ttu.edu.

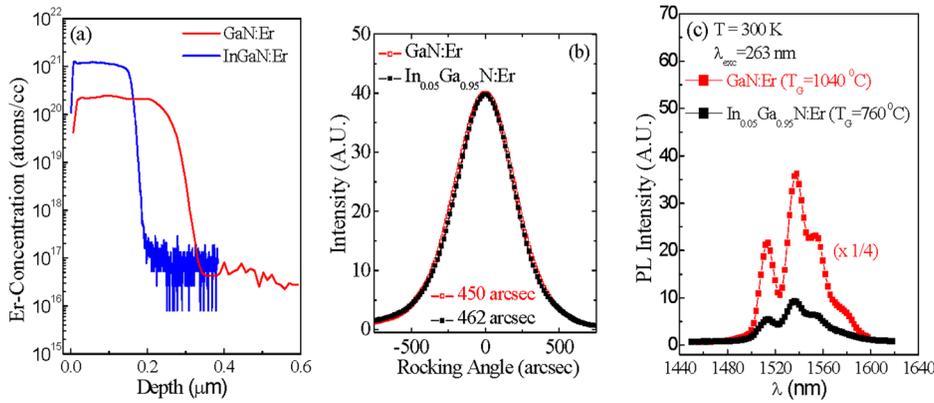


FIG. 1. (a) SIMS profile of a GaN:Er epilayer grown at 1040 °C and an In_{0.05}Ga_{0.95}N:Er epilayer grown at 760 °C by MOCVD. (b) Comparison of the XRD rocking curves of the (002) peak for the epilayers. (c) PL spectra measured at 300 K of In_{0.05}Ga_{0.95}N:Er and GaN:Er epilayers. The excitation wavelength was $\lambda_{\text{exc}} = 263$ nm.

higher (4 nm) than that of GaN:Er (2 nm). Figure 1(c) presents the room temperature (300 K) PL spectra of In_{0.05}Ga_{0.95}N:Er grown at 760 °C and GaN:Er grown at 1040 °C, using excitation wavelength $\lambda_{\text{exc}} = 263$ nm. The most striking observation is that the 1.54 μm emission intensity from In_{0.05}Ga_{0.95}N:Er is about 20 times lower than that from GaN:Er, despite the fact that SIMS data shown in Fig. 1(a) reveals that the Er concentration in In_{0.05}Ga_{0.95}N:Er is nearly $5\times$ higher than in GaN:Er. Based on the fact that both epilayers have a comparable crystalline quality and surface morphology, the results thus suggest that the optically active Er³⁺ concentration in Er doped III-nitrides is not only related to the Er doping concentration, but also to the growth temperature. This appears to be a direct consequence of the existence of a large formation energy of the optically active Er³⁺ centers in both GaN:Er and InGaN:Er.

A theoretical study has shown that the Er impurities bind strongly with nitrogen vacancies in GaN:Er.¹⁸ Based on PL studies of GaN:Er covering from the ultraviolet to the infrared region,¹⁵ it was suggested that the exchange of energy between the electrons bound to the Er_{Ga}-V_N complex (with an energy level at about 190 meV) and the 4f cores states of Er may be the dominant excitation mechanism of the 1.54 μm emission in GaN:Er. Here, Er_{Ga} denotes the substitution of Er atom onto the Ga sublattice and V_N is the nitrogen vacancy. Although the formation energy of V_N in

GaN is large (2.9–4 eV under n-type conditions),¹⁹ the incorporation of rare earth impurities could increase the vacancy concentration by lowering their formation energy (~ 1 eV in the case of Eu–V_N).¹⁸ However, the formation energy of the Er_{Ga}-V_N complex in GaN:Er has not yet been measured.

Knowing the formation energy of the optically active Er³⁺ centers is critical for the further development of GaN:Er materials with improved emission efficiency at 1.54 μm . Figure 2(a) is a plot of the PL spectra at 300 K of GaN:Er epilayers grown at different T_G between 890 and 1060 °C. Growth temperatures above 1060 °C were not employed due to rapid deterioration of the epilayer surface morphology. Figure 2(a) clearly shows that the emission spectral lineshape remains relatively unchanged for GaN:Er epilayers grown at different T_G , yet the 1.54 μm emission intensity increases significantly with increasing T_G . Figure 2(b) compares the (002) XRD rocking curves, which reveals that the crystalline quality of GaN:Er epilayers is nearly identical for different growth temperatures. Furthermore, the targeted Er doping concentrations in these samples are the same. Therefore, the 1.54 μm emission intensity variation is not related to change in the crystalline quality or the Er doping concentration with T_G .

In order to obtain the formation energy of Er³⁺ emission centers, the integrated intensity of the 1.54 μm PL emission vs. T_G was plotted in Fig. 3. The solid curve in Fig. 3 is the

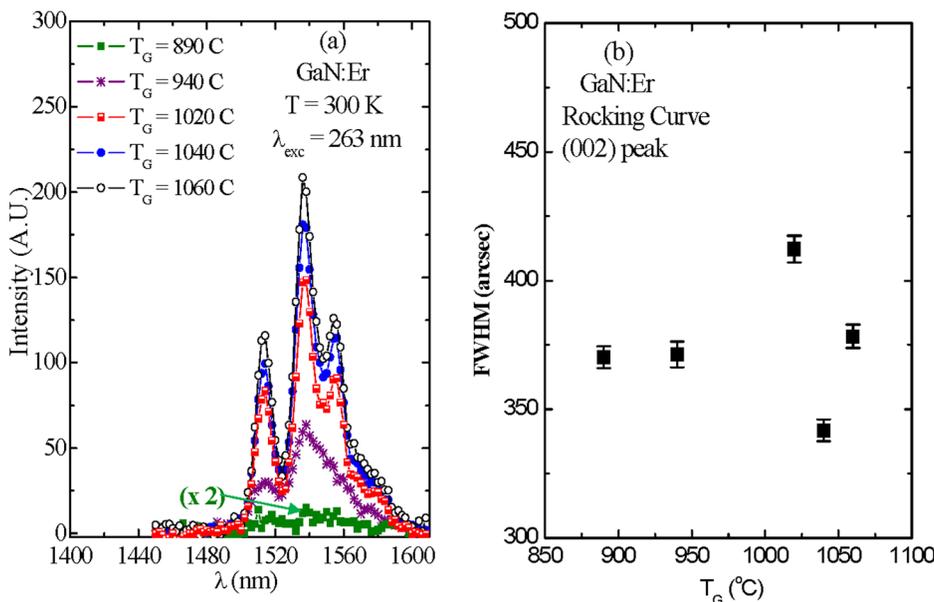


FIG. 2. (a) PL spectra at 300 K of GaN:Er grown at different growth temperatures, $T_G = 890, 940, 1020, 1040,$ and 1060 °C. The excitation wavelength was $\lambda_{\text{exc}} = 263$ nm. (b) Plot of full width at half maxima (FWHM) of the XRD (002) rocking curve of GaN:Er as a function of the growth temperature, T_G .

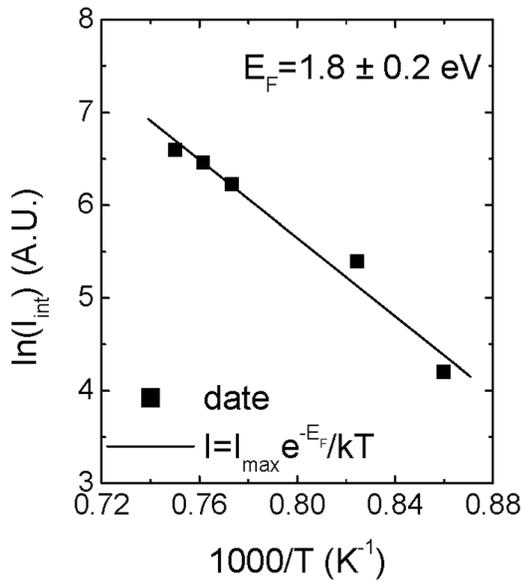


FIG. 3. An Arrhenius plot of the variation of the integrated $1.54 \mu\text{m}$ PL emission intensity with the growth temperature, T_G . The linear line is the least squares fit of the data points according to Eq. (1). The value of E_F determined from the least squares fit is $1.8 \pm 0.2 \text{ eV}$.

least squares fit to the integrated intensity of the $1.54 \mu\text{m}$ PL emission data points using

$$I = I_0 e^{-E_F/kT}, \quad (1)$$

where k is the Boltzmann constant, E_F is the formation energy of the Er^{3+} emission centers, and I_0 is a fitting constant. The least squares fit for the formation energy for the Er emission centers in GaN:Er yields a value of $1.8 \pm 0.2 \text{ eV}$. It is well understood that the formation energy of a defect/impurity is a numerical measure of the probability of that defect/impurity being formed at a fixed growth temperature. Larger formation energies imply that larger T_G must be employed to incorporate a higher concentration of the defect/impurity. In the present case, the associated defect/impurity is believed to be the Er-V_N complex. We noted that the $1.54 \mu\text{m}$ emission increases with a decrease of the V/III ratio used during the GaN:Er epilayer growth, corroborating with our interpretation that the optically active Er^{3+} centers are related to V_N .

The experimentally measured value of the formation energy of the Er-V_N complex is rather large and is about 0.98 eV larger than the formation energy of Er ions at Ga sites in GaN (0.84 eV).¹⁸ However, it is $1.1\text{--}2.2 \text{ eV}$ lower than the calculated formation energy of V_N in GaN.¹⁹ This large value of E_F implies that higher T_G must be utilized in order to obtain concentrations of higher optically active Er^{3+} centers.

The lower $1.54 \mu\text{m}$ emission intensity in $\text{In}_{0.05}\text{Ga}_{0.95}\text{N:Er}$ shown in Fig. 1(c) can therefore be attributed to the lower T_G required for the InGaN:Er epilayers. At higher T_G , In incorporation in the epilayer becomes difficult. On the other hand, the high formation energy of the Er emission centers requires that high T_G be employed. The change in the concentration of Er emission centers between InGaN:Er and GaN:Er can be estimated from the following relationship:

$$\frac{e^{-E_F(\text{GaN})/kT_{\text{GaN}}}}{e^{-E_F(\text{InGaN})/kT_{\text{InGaN}}}}, \quad (2)$$

where T_{GaN} and T_{InGaN} denote the growth temperatures of GaN and InGaN, respectively. Assuming the change in formation energy E_F between GaN:Er and $\text{In}_{0.05}\text{Ga}_{0.95}\text{N:Er}$ is small due to the low fraction of InN, we expect a decrease (by a factor of ~ 28) in the concentration of optically active Er^{3+} centers in InGaN:Er grown at $T_G = 760 \text{ C}$ compared to the GaN:Er epilayers grown at 1040 C . This is in reasonable agreement with the decrease in PL intensity plotted in Fig. 1(c). Furthermore, the value of E_F should be slightly lower in $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$ than in GaN due to the reduced bandgap, which could account for the difference between the experimentally observed emission intensity drop noted in Fig. 1(a) and that estimated using Eq. (2).

In summary, we have investigated the influence of the MOCVD growth temperature on the optical and structural properties of GaN:Er and InGaN:Er. The $1.54 \mu\text{m}$ PL emission intensity was monitored for GaN:Er epilayers grown at different growth temperatures and was utilized to establish a value of $1.8 \pm 0.2 \text{ eV}$ for the formation energy of the optically active Er^{3+} centers in GaN. The optically active Er^{3+} centers in GaN:Er are presumed to be $\text{Er}_{\text{Ga}}\text{-V}_N$ complexes. Our results indicate that the incorporation of Er impurities in GaN can increase the incorporation of the nitrogen vacancy concentration by lowering the formation energy (by around $1.1\text{--}2.2 \text{ eV}$), corroborating a previous theoretical study.¹⁸ Due to the large formation energy of Er-V_N complex in GaN, high growth temperatures are necessary to promote the formation of the optically active Er^{3+} centers and consequently improve the $1.54 \mu\text{m}$ emission efficiency in Er doped III-N epilayers.

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