SYMPOSIUM G: GaN and Related Alloys – G11.1

LUMINESCENCE FROM ERBIUM-DOPED GALLIUM NITRIDE THIN FILMS


‡U.S. Army European Research Office, London, UK NW1 5TH; *Hampton University, Department of Physics, Research Center for Optical Physics, Hampton, VA 23668; **University of Florida, Department of Materials Science and Engineering, Gainesville, FL 32611; ***U.S. Army Research Laboratory, Adelphi, MD, 20783; Kansas State University, Department of Physics, Manhattan, KN; †Consultant, Stevens Ranch, CA 91381

E-mail: jzavada@army.ehis.navy.mil

ABSTRACT

The III-V nitride semiconductors appear to be excellent host materials for optical device applications involving thin films doped with rare earth atoms. In particular, GaN epilayers doped with Er ions have shown a highly reduced thermal quenching of the Er luminescence intensity from cryogenic to elevated temperatures. The remarkable thermal stability of the light emission may be due to the large energy bandgap of the material, as well as to the optical inactivity of material defects in the GaN film. In this paper we present recent developments concerning the luminescence characteristics of Er-doped GaN films. We have used two methods for doping GaN films with Er ions, ion implantation and in-situ incorporation during gas source metal-organic molecular beam epitaxy (MOMBE). Bandedge (at ~ 0.34 µm) and infrared (at ~ 1.54 µm) photoluminescence (PL) spectra have been measured for both types of Er-doped GaN films. Considerably different emission spectra have been observed depending upon the incorporation method and the heat treatment procedure. In situ Er-doped GaN layers have been processed into hybrid light emitting devices and emission spectra at 1.54 µm have been measured.

Erbium in Semiconductors and Thermal Quenching

The optical properties of rare earth ions in insulating materials have been extensively studied for applications in solid state lasers and optical fiber amplifiers [1]. Solid state lasers, such as Nd³⁺:YAG, are based on the 4f intra-subshell transitions of the rare earth trivalent ions (RE³⁺) which exhibit a very stable lasing wavelength and minimum temperature dependence. Because of these characteristics, such lasers have found widespread applications in laboratory and military systems. Er-doped silica fibers are being used for amplification of optical signals in wavelength division multiplexing (WDM) communication systems operating at 1.54 µm and Pr-doped fibers are being developed for use at 1.3 µm [2].

Investigations of the optical properties of rare earth-doped III-V semiconductors have begun relatively recently. Beginning with the work of Ennen et al. in 1983 [3], the luminescence of rare earth ions in III-V compound semiconductors has received considerable attention. The main goal of this work has been to develop electrically pumped optical sources and amplifiers for use in optical communication systems. Studies of rare earth ions in a variety of different semiconductors have been conducted [4,5,6]. Due to the importance of the 1.54 µm region for optical communications, Er has been the main rare earth element to be investigated.
Favennec et al. studied the dependence of the emission intensity of the $\text{Er}^{3+}$ ions on the bandgap of the host semiconductor and on the sample temperature [7]. Several different semiconductors were implanted with $\text{Er}^{+}$ ions and the emission intensity was measured at different temperatures. It was found that the intensity decreased at higher temperatures. This thermal quenching of the emission intensity was more severe for the smaller bandgap materials, such as Si and GaAs. The wide bandgap II-VI compounds, such as ZnTe and CdTe, exhibited the least temperature dependence.

Since the wider bandgap semiconductors lead to less thermal quenching of the $\text{Er}^{3+}$ emission, the III-V nitride alloys appear to be especially promising host materials for rare earth doping. These alloys have a bandgap ranging from 1.9 eV for InN to 3.4 eV for GaN and 6.2 eV for AlN. However, due to a lack of a lattice matched substrate, present III-V nitride epilayers contain a high density of dislocation defects and various impurity elements. Nevertheless, very encouraging results have been obtained with Er-doped III-V nitride materials.

**Erbium Doping Methods**

Several different methods have been used for incorporating Er atoms into III-V semiconductor materials, mainly ion implantation and epitaxial growth. Each method presents certain advantages as well as difficulties. Apparently, there are no reports of Er incorporation into these semiconductor materials during bulk growth or by diffusion. Ion implantation has been widely used in processing integrated electronic circuits and optoelectronic devices. Because this method is a non-equilibrium process, it is not limited by solubility constraints or by surface chemistry. Wilson et al. [8] were the first to introduce Er into GaN and AlN materials using ion implantation. They observed strong infrared luminescence centered at 1.54 µm. However, co-implantation with O and subsequent furnace annealing was needed to achieve this luminescence. Subsequently, several other research groups used ion implantation to dope III-N semiconductors with Er atoms [9, 10, 11].

Three different methods of epitaxial growth have been used successfully for doping III-N semiconductors with Er atoms: gas source Gen II metal-organic molecular beam epitaxy (MOMBE) [12]; hydride vapor phase epitaxy (HVPE) [11], and solid source molecular beam epitaxy (MBE) [13]. However, with each of these techniques, there have been difficulties incorporating Er atoms into the epilayers and obtaining optically active centers. The maximum concentration of Er in these epilayers has been on the order of $10^{19}$ cm$^{-3}$. Nevertheless, high quality epilayers, doped with Er ions, have been achieved and good luminescence characteristics have been observed.

**Optical Excitation Spectroscopy**

Photoluminescence (PL) spectroscopy has been the main optical technique used to characterize the emission of Er-doped III-N semiconductor materials. This technique involves optical excitation of the $\text{Er}^{3+}$ ions and measurement of the spectrum of the light emission as a function of intensity and energy. In a simplified view, optical excitation, at above-bandgap energy, leads to creation of electron-hole pairs. Some of the electron-hole pairs may transfer energy to the $\text{Er}^{3+}$ ions, exciting the 4f-electrons to higher energy states and resulting in optical emission. Most of the PL measurements of Er-doped semiconductors have involved use of a laser operating at an energy above that of the bandgap of the host semiconductor. This corresponds to an indirect excitation of the $\text{Er}^{3+}$ ions by electron-hole pairs. A few experiments have been
carried out in which the Er$^{3+}$ ions have been excited directly by the optical pump radiation [14]. In this case, the Er$^{3+}$ ions are excited directly by the optical pump, with the energy of the laser radiation equal to that of one of the higher energy states of the Er$^{3+}$ ion. Defects and impurities in the material serve as non-radiative recombination centers which can reduce the light emission. Recent studies [15,16] have shown that defects can also serve as absorption centers transferring below-bandgap optical energy to the Er$^{3+}$ ions, resulting in emission at 1.54 µm. The exact mechanism for transferring optical energy to the Er$^{3+}$ ions, either through electron-hole pairs or by defects is not well understood at present.

We performed a series of experiments to determine the thermal quenching of luminescence in an Er-doped GaN films [15]. The GaN films, which were grown on sapphire substrates, were co-implanted at room temperature with Er and O ions. The Er$^{3+}$ emission in the region of 1.54 µm was measured over a range of temperatures from 13 - 550 K. For temperature-dependent measurements between 15 and 300 K, the Er-implanted GaN sample was placed onto a cold finger of a closed-cycle helium refrigerator. For measurements above 300 K, a home-made heating element was used. The sample was excited with above-bandgap radiation, using a HeCd laser operating at 325 nm, and with below-bandgap radiation from an Ar laser operating at 488 nm. In Fig. 1 (a) are shown the high-resolution PL spectra at 300 and 550 K of the sample pumped with above-bandgap excitation. There were only minor changes in the PL spectra between 300 and 550 K. The full width half maximum (FWHM) of the PL spectrum at 300 K was ~ 80 nm, suggesting inhomogeneous broadening of the emission. This broadening indicated that the Er$^{3+}$ ions occupy a range of sites, with slightly different atomic configurations, in the GaN host. The integrated PL intensity of the luminescence was found to be nearly constant over the entire range of measurement temperatures, see Fig. 1 (b). Relative to its value at 15 K, the integrated PL intensity at 550 K decreased by only about 10 %. This remarkable temperature stability of the Er$^{3+}$ luminescence is the best reported data from any Er-doped semiconductor.

**Figure 1:** (a) High-resolution Er$^{3+}$ PL spectra, taken at 300 and 550 K, of an Er-implanted GaN sample using above-bandgap excitation. (b) The integrated PL intensity measured between 15 and 550 K.
including Er-doped SiC [17]. In a cathodoluminescence study of Er+O co-implanted GaN films, Qiu et al. found that the integrated intensity decreased by less than 5% as the temperature was raised from 6K to 300 K [18]. These results demonstrate that Er-doped GaN is an attractive material for high temperature optoelectronic applications.

In Fig. 2 (a) are shown the high-resolution PL spectra at 300 and 550 K of the sample with below-bandgap excitation. This excitation method corresponds to pumping the Er$^{3+}$ ions through the broad, defect-related, absorption band. There were significant changes in the PL spectrum between 300 and 550 K. In addition, above-bandgap and below-bandgap excitation resulted in considerably different PL spectra as shown in Figs. 1 (a) and 2 (a). Depending upon the excitation method, different subsets of Er$^{3+}$ ions are excited leading to distinct PL spectra. The full width half maximum (FWHM) of the PL spectrum at 300 K was ~ 50 nm, which was narrower than that in Fig. 1 (a). There was also a large change in the integrated PL intensity over the range of measurement temperatures, as indicated in Fig. 2 (b). Relative to its value at 15 K, the integrated PL intensity at 550 K decreased by about 50%. While this behavior is not as good as the data shown in Fig. 1 (b), this reduced thermal quenching is still better than that reported from any other Er-doped III-V semiconductor.

![Figure 2](https://doi.org/10.1557/S1092578300003616)

**Figure 2:** (a) High-resolution Er$^{3+}$ PL spectra, taken at 300 and 550 K, of an Er-implanted GaN sample using below-bandgap excitation. (b) The integrated PL intensity measured between 15 and 550 K.

We have measured bandedge PL spectra for both the GaN films implanted with Er and for the GaN films doped with Er during MOMBE growth. In general, there is little or no PL signal after implantation. With annealing, under a N ambient, there is a slight recovery of the bandedge PL signal. However, even after annealing at 950 C, the Er-implanted films contain highly defective surface regions with only weak PL signals. Hansen et al. reported similar results with Er-implanted GaN films [10]. These data are consistent with studies by Zolper et al. on Si-
implanted GaN films [19]. Higher annealing temperatures are required before a significant recovery of the bandedge PL signal occurs. In contrast, there was a strong bandedge PL signal from the GaN films doped with Er during MOMBE growth. The PL spectra had a peak at 3.28 eV which is quite different from the PL spectra from undoped GaN films.

**Light Emitting Device**

Recently, we have demonstrated a hybrid light emitting device in which an Er-doped III-V nitride film is optically pumped by a green InGaN LED to produce emission at 1.54 µm. In these experiments, a Nichia InGaN LED, with a peak emission at 520 nm was used to excite the Er\(^{3+}\) ions in a GaN film, grown on sapphire by MOMBE. The epoxy bubble of the InGaN LED was cut and polished to provide a flat surface near the LED top contact. The GaN film/sapphire sample was place in close proximity to the LED, as shown in the inset in Fig. 3. The spectrum of the Er-related luminescence is also shown in this figure. While the emission at 1.54 µm is weak, the spectrum is similar to that in Fig. 2 (a). A green InGaN LED was used in this hybrid device, since

**Figure 3:** Temperature dependence of the integrated PL intensity from in-situ Er doped GaN for above and below gap excitation.

a absorption spectrum for the film indicated a strong absorption in this region, both with the sharp line transition at 525 nm and with the broad defect-related absorption. The luminescence at
1.54 µm was collected through the sapphire substrate. While the resulting emission at 1.54 µm was weak, in comparison with the PL studies, it does demonstrate that the electroluminescence of an InGaN LED can be used to excite the Er centers in a GaN film. Furthermore, a monolithic semiconductor device, in which an Er-doped GaN film is grown directly on top of an InGaN LED structure, appears feasible. Questions concerning overall efficiency and light collection schemes need to be further addressed.

Summary

Considerable progress has been made in the past ten years in understanding the optical properties of Er-doped III-V semiconductors. Luminescence of Er$^{3+}$ ions in many III-V semiconductors has been observed. A number of experiments have shown that the use of wide gap semiconductors, such as the III-V nitrides, reduces the thermal quenching of the Er$^{3+}$ luminescence. However, difficulties remain concerning the incorporation of Er atoms in the III-V nitride materials and the proper processing conditions necessary for optical activation. Experimental evidence indicates that the Er atoms occupy a variety of sites within the III-N crystal. Furthermore, different Er centers yield different emission spectra and different thermal quenching characteristics. Due to the intense current research in III-V nitride semiconductors for blue light emission, major improvements in the crystal quality and in the processing technology of these materials are very likely to occur. Such advances will assist efforts to develop devices based on III-V nitride semiconductors doped with Er ions, making possible a new class of optoelectronic components for optical communication and display systems.

REFERENCES