Combined Excitation Emission Spectroscopy of Europium ions in GaN and AlGaN films

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ABSTRACT:

Site-selective combined excitation emission spectroscopy studies have been performed on Eu-doped GaN and numerous sites have been identified. Relative numbers and broadening of these peaks has been investigated for different growth conditions and for increasing AL content of the $Al_xGa_{1-x}N$ alloy.

INTRODUCTION

In a wide range of host materials, trivalent rare-earth RE^{3+} ions exhibit inner-shell(intra-4f) transitions resulting in distinct optical absorption and emission with wavelengths ranging from the ultraviolet to the near infrared. Due the shielded nature of 4f electronic states, the transition energies are virtually independent of temperature and vary only slightly under changes of the crystal environment. This makes these ions very attractive as active ions in emitter and laser applications Optically pumped *RE*-based emitters have found many applications as phosphors for displays, solid-state lasers, and fiber-optic amplifiers [1]. However, to achieve electrically pumped *RE* emitters requires a semiconductor host.

One of the most promising semiconductor hosts for RE emitters and lasing is the wide band-gap semiconductor GaN, which has been shown to produce outstanding "intrinsic" light emitting diodes and lasers. The wide band gap and the ability to tailor the band-gap through III-N alloying enable matching this materials system to many RE^{3+} ions.

Electroluminescence from GaN doped with Er, Eu, Pr, Tb, Tm, and other *REs* has been reported [2]. Moreover, laser action in Eu-doped GaN has been reported [3] under optical excitation, rekindling the hope that an electrically-pumped rare doped semiconductor laser can be achieved. In this pursuit, it becomes important that all rare earth ions that are within the laser cavity are exited effectively. To this end, the presence of different incorporation sites complicates this goal and requires the detailed characterization of these sites in terms of their energy states and their capability to be excited electrically. In this contribution we address the first task by applying the site-selective technique of combined excitation emission spectroscopy to the Eu:GaN material system.

EXPERIMENTAL TECHNIQUES

In combined excitation-emission spectroscopy, the Eu-transitions are excited resonantly and the emission spectra are measured for a dense sequence of excitation wavelengths. The use of computer control and CCD-array detection for collection of the emission spectra, allows measurements of a large number of spectra within a short time. In this way a 2D-data set of emission intensities as function of excitation and emission wavelength is obtained. Depicting the data in contour and/or image plots allows relatively easy visual inspection of the data and assignment of the numerous peaks to a given site and transition [6]. In this report, we will concentrate on a single excitation range around 580nm in which the symmetry forbidden, single ${}^{4}F_{0}$ - ${}^{4}D_{0}$ transition is occurring and detect the strong D_{0} - ${}^{4}F_{2}$ emission for which three emission peaks are expected.

SAMPLE PREPARATION

The GaN:Eu samples were grown by the *Interrupted Growth Epitaxy* (IGE) growth technique[4]. In IGE, the material growth is conducted through repetitions of long periods where all beams are incident on the substrate from a few minutes to tens of minutes. Each consecutive cycle is followed by a period where only selected beams are incident on the substrate. In GaN, it is well-known that the incorporation of N into the film is at a much lesser rate than that of Ga. The IGE technique is designed to eliminate this problem, with the GaN film being periodically exposed to the nitrogen beam only while the growth is interrupted. Hence, the IGE film growth is accomplished in a periodic fashion, with the shutters of group III elements (Ga and Eu) being open ("ON") for a part of the cycle and closed ("OFF") throughout the rest of time. The group V was ON throughout the entire IGE cycling time. The ON times were varied from 5 to 60min, as shown in table 1, to maintain a constant growth time of 60min, the IGE cycles were repeated accordingly. The 60min growth sample experienced continuous growth, corresponding to conventional MBE growth [5]. During our initial experiments we determined that material growth occurs only during the ON time. The Eu incorporation in the films was approximately the same at ~ 0.5 at.%, which is below the onset of luminescence concentration quenching.

GaN·Fu	Shutter oper	# of		
Sample No.	Group III ON Group III OFF		Group V open	cycles repeated
C089	60 min	0 min	60 min	1
C095	20 min	5 min	25 min	3
C094	15 min	5 min	20 min	4
C091	10 min	5 min	15 min	6

Table 1. Group III shutter *ON/OFF* cycles and the number of cycle repetitions during growth. The total growth time (total *ON* time) is 60min for all samples.

A set of samples of $Al_xGa_{1-x}N$ with different contents of x of Al has been from the group of Prof. Wakahara. The samples were grown by MBE on sapphire and doped through ion implantation. After implantation the samples were annealed for 2min at 1100°C.

EXPERIMENTAL RESULTS AND INTERPRETATION

In Fig. 1, we present some of the CEES data for four different samples that were grown using the IGE process with different parameters. All of them show clearly three main

excitation peaks (570.9nm, 588.8nm, 585.5nm) in the spectral region of the ${}^{4}F_{o}$ to ${}^{4}D_{o}$ transition (only 2 of them are shown in Fig. 1, indicated by the arrows). As shown in Fig. 2 (a), the emission spectra obtained for these excitation wavelengths are completely identical.



Fig. 1: Image plots for 4 differently prepared GaN:Eu samples (a)CO91, (b) CO89, (c) CO94, (d) CO95



Fig. 2: Emission spectra in sample CO91 (a) at three different excitation wavelengths, that have essentially identical spectra and (b) at four different excitation wavelengths that exhibit clearly different emission spectra.

All these excitation energies have been assigned to the ${}^{4}D_{0}{}^{-4}F_{0}$ transition for different sites in Ref. [7]. However, this transition is expected to be a single one. The presence of three excitation wavelengths that lead to identical emission spectra is inconsistent with this interpretation. The relative intensity of the emission resulting from the excitation at these wavelengths is not changing under variation of the growth conditions. Moreover, under excitation to higher levels, only the emission line at 588.5nm appears. These observations suggest that at least in the emission only one defect site contributes. Possible explanations of this behavior are the following:

- a. Excitation and emission do not take place for the same Eu ion but energy transfer occurs.
- b. The energy differences in the excitation energy are close to Raman transitions [8] (550cm⁻¹, 95cm⁻¹) observed in GaN suggesting that we are dealing with electronphonon coupled transitions which can appear relatively strong due to the forbidden character of the zero-phonon transition. In this interpretation, excitation will lead to the creation of a phonon and the excitation energy will hence be the sum of the electronic transition energy and the phonon energy.
- c. The assignment of the excitation peaks to just the ${}^{4}F_{0} {}^{4}D_{0}$ transition is wrong.

In order to distinguish these possibilities, we performed a variation of Al content in the sample and compared the changes of phonon energies with the shift that we observe in the excitation-emission data. For all compositions, the same types of excitation peaks exist. They are shifting since the transition energy ${}^{4}D_{0}{}^{-4}F_{0}$ depends on the compositions. In Fig. 3, we depict the difference between the lines around 588nm and 570nm. The



Fig. 3: Energy differences for the 588nm and 570nm excitation peaks as a function of $Al_xGa_{1,x}N$ composition.

observed increase resembles quite closely the one observed for the GaN-like E_2 mode [9]. This strongly hints towards option (b). The values for the energy differences are about

5% lower as for the phonon mode suggesting that this mode might be locally perturbed by the presence of the Eu-defect.

The interpretation (b) is further supported by the observation that the excitation peaks at 585nm and 570nm are much wider compared to the one at 588nm. This is typical for electron-phonon type transitions.

Under closer inspection of the image plots in Fig. 1, we find also excitation energies that lead to emission spectra, which are different from each other and from the main emission discussed above. These are unambiguously related to different sites. The spectra of four of these sites are depicted in Fig. 2(b). Their excitation energies are indicated by white dotted lines in Fig. 1. For these sites, selective excitation is possible allowing the fingerprinting of the energy level ${}^{4}F_{j}$ levels, which ultimately will allow identifying the sites under different excitation conditions and clarifying their role in the electrical excitation schemes. In table 1, we list the characteristic excitation and emission energies for four sites that could be distinguished most clearly. It should be noted that similar to the excitation transitions the number of observed emission lines is inconsistent with the multiplicity of the ${}^{4}D_{o}{}^{-4}F_{2}$ zero-phonon transitions. This question is currently under investigations.

The emission strength ratios for the four sites are shown in Fig. 4, for the four samples shown in Fig. 1. The relative strength of the associated emission lines is changing significantly under variation of the sample growth conditions. In regards to the nature of the observed sites, we assume that the main site (2) corresponds to the Eu on a Ga sites with a regular N environment. The additional sites that change drastically in their relative numbers under variation of the growth condition we assign to different perturbations in the N sublattice around the Eu defect.



Fig. 4: Emission strength for the different defect sites indicated in Fig. 1. The height of the bars represents emission intensities at spectral positions at which the sites are most distinct and do therefore not represent relative numbers of defects sites. Only comparison of relative changes between the samples is meaningful.

Site	Excitation wavelength [nm]	Emission Wavelength [nm]			
1	584.6	617.09	623.69		629.00
2	585.5, 588.8, 570.9	620.90	621.66	622.6	634.02
3	587.9	620.96		623.32	632.05
4	589.3			624.12	

Table 1: Excitation and emission wavelength of different sites

SUMMARY

Using the highly site-selective method of combined excitation emission spectroscopy, we identified several different incorporation sites for Eu in GaN. Number and relative strength of these sites depend on details of the sample preparation but are quite similar to the ones observed for Er ions [6]. Correlating the site distribution with the efficiency of electroluminescence (EL), can give hints of the nature of the defect sites that are involved in excitation mechanism that result in EL.

For the main defect site, we have found several excitation peaks for the single ${}^{4}F_{o}{}^{-4}D_{o}$ excitation transition. The observed energy differences and the behavior under variation of the Al content suggest that rather efficient electron-phonon coupled excitation is present for the symmetry forbidden electronic transition. Further investigations are necessary to further confirm this interpretation and to study the electron-phonon coupling strength as a function of composition and defect site.

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