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Eu³⁺ activated GaN thin films grown on sapphire by pulsed laser deposition

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By means of pulsed laser deposition, polycrystlline thin films of GaN doped with Eu^{3+} were grown on sapphire. The PLD target was formed in three steps. First, stoichiometric amounts of Ga₂O₃ and Eu₂O₃ were dissolved in nitric acid, which produces Ga_(1-x)Eu_x(NO₃)₃. Next, the nitrates were oxidized in a tubular furnace with O₂ flow forming Ga_{2(1-x)}Eu_{2x}O₃. Finally, the oxide powder was flushed with anhydrous ammonia to produce the desired nitride product: Ga_(1-x)Eu_xN. Film growth was done in a stainless steel vacuum chamber partially filled with N₂ (400 mTorr). For the deposit, the 3rd harmonic of a Nd:YAG laser ($\lambda = 355$ nm) was focused on the surface of the target. After deposition, annealing in NH₃ was required to produce films with pure GaN hexagonal phase. The luminescence of the film was characterized by photo- and cathodoluminescence. In addition, the chemical and structural properties were analyzed by X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy.

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1 Introduction Gallium nitride is the compound of choice among the direct band gap semiconductors in solid-state lighting applications [1], mainly because of its wide band gap, which can be modulated from 0.7 to 6.1 eV by alloying it with AIN and/or InN. However, attempts to make InGaN alloys with high In content, capable of emit-ting in the green to red region of the visible spectrum have not been very successful [2]. Research has been focused on finding alternative approaches to generate visible radiation from GaN-based alloys. One such approach has been rare earth (RE) doping of GaN. Red and NIR emitting thin film electroluminescent devices has been fabricated using Eu³⁺ activators respectively [3, 4].

RE ions have been used before solid-state lighting devices were invented, they were used in past to activate many luminescent materials. A very common use of RE is in luminescent phosphors for fluorescent lighting. Light emission from RE ions originates from intra-shell electronic transitions within the 4f-shell. Since the se 4f elec-



To date, RE activation of GaN is performed *in situ* by the molecular beam epitaxia (MBE) [3, 4, 6] or the metalorganic chemical vapour deposition (MOCVD) [7] film growth techniques. Also, it can be done *ex situ* by high energy ion implantation [8]. In this work we present a process to produce GaN films activated with Eu^{3+} ions by the pulsed laser deposition (PLD) technique.

PLD has been used to produce pure GaN films with excellent quality [9]. Some of the advantages of PLD compared to other growth techniques like MBE or MOCVD are lower substrate temperature and the stoichiometry conservation, *i.e.* the film's stoichiometry is the same as that of target. In the case of nitride growth, this avoids the use of highly reactive gases like NH₃ or nitrogen plasma to supply atomic nitrogen during the growth process [10].



2 Experimental PLD thin films of GaN activated with Eu³⁺ ions were fabricated using a two-step process approach, in which, post deposition annealing of the film in an adequate atmosphere is required, in this case NH₃.

2.1 Target fabrication The GaN:Eu powder required to press the PLD target was synthesized as described by Kudrawiec *et al.* [11]. This synthesis method started with the dissolution of stoichiometric amounts of Ga₂O₃ and Eu₂O₃ in nitric acid, producing Ga_(1-x)Eu_x(NO₃)₃. The nitrates were then oxidized for 3 hours at 500 °C in a tubular furnace with 100 sccm O₂ flow to form Ga_{2(1-x)}Eu_{2x}O₃. Finally, the oxide powders were flushed with NH₃ to produce Ga_(1-x)Eu_xN. The activator concentration was 1at% (x = 0.01). The resulting nitride powder was ground in an agate mortar and then pressed at ~200 MPa in a 2.54 cm diameter mold. The resultant pellet was sintered in NH₃ atmosphere at 1100 °C for 1 hr.

2.2 Film fabrication GaN:Eu thin films were deposited directly on Al₂O₃ substrates oriented along the (0001) direction. The deposition process was done in a stainless steel vacuum chamber evacuated by a turbomolecular pump, with base vacuum reaching 1.3 x 10⁻⁷ Torr. The 3rd harmonic of a YAG:Nd laser ($\lambda = 355$ nm) was used as the ablation source. The laser beam was focused on the target surface by a quartz lens producing an energy fluency of ~0.55 Jcm⁻² and repetition rate of 10 Hz. During deposition, substrate temperature was kept at 600 °C and N₂ (99.999%) was introduced to the chamber as background gas at 400 mTorr. Target to substrate distance was 40 mm.

After deposition the films were removed from the deposition chamber and annealed in a tube furnace at 950 °C in flowing NH₃ (200 sccm) for 45 minutes.

Luminescence, chemical and structural properties were measured at room temperature (RT). X-Ray diffraction (XRD) was measured in a Phillips X'pert diffractometer with $Cu_{K\alpha 1}$ ($\lambda = 0.154056$ nm). Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and cathodoluminescence (CL) measurements were performed in a scanning electron microscope (JEOL JSM5300) with the appropriate sensors for each measurement. Photoluminescence (PL) measurements were performed using the 325 nm line of a He-Cd laser (Omnichrome Series 56) as excitation source. The emitted light was coupled to a 1/4 m monochromator (Oriel ms257i) with a 1200 lines/mm diffraction grating and measured by a thermoelectrically cooled CCD (Instaspec IV). In order to eliminate the excitation peak from the emission spectra, a 350 nm high pass optical filter was placed at the monochromator entrance.

3 Results and discussion Figure 1 shows the XRD pattern of a GaN:Eu thin film grown on sapphire by PLD. In addition to the very intense (006) peak of the sapphire substrate ($2\theta = 41.67^{\circ}$) the (100), (002) and (102) reflections from hexagonal (*wurtzite*) GaN have been identified, which indicates that the film is polycrystalline. Given the



Figure 1 X-ray diffraction pattern of the GaN:Eu thin film grown on sapphire by PLD. The intensity of the (002) peak indicates that the film is textured along this crystalline direction.

higher intensity of the (002) peak compared with the other GaN peaks, it can be concluded that the film is textured along the <002> crystalline growth direction.

SEM images in Fig. 2 show the surface morphology. Figure 2(b) shows a higher magnification of a surface particle where the film is formed from submicron size crystals with hexagonal shape. The surface of this sample is rougher than other PLD films due to the high growth rate ($\sim 0.8 \text{ nm/sec}$) and the high nitrogen pressure used for deposition (400 mTorr). It has been observed that the increase of the background gas pressure causes a decrease in the velocity of the species in the plasma plume [12]; hence, the films grown at high pressure conditions are likely to exhibit more defects than those deposited at lower pressures [13]. Additionally, the film was grown directly on sapphire (no buffer layer) so that consequently the film is strained. All the above mentioned conditions could be the cause of the observed surface morphology of this film.



Figure 2 SEM images of the GaN:Eu thin film grown on sapphire by PLD, a) low magnification view of the surface, b) higher magnification of an aggregate of submicron hexagonal GaN crystals.



EDS measurements indicate that Eu concentration is around 0.45 at%, which is less than half of the intended concentration for the powder precursor. The decrease of Eu content in the film, compared to that of the powder might be caused by the multiple annealing processes.

Figure 3 shows the PL emission spectrum of a GaN:Eu film grown by PLD. The spectrum contains a very strong contribution of UV emission from the near band edge (NBE) of GaN host with maximum intensity at 364 nm (~3.4 eV). Eu^{3+} intra-shell transition lines appear at longer wavelengths, and are labelled according to those previously observed for substitutional Eu³⁺ ions in GaN [6-8]. The most intense peak is centred at 620 nm and is ascribed to the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition. Lower intensity peaks due to other transitions are also indexed. It is noted that the ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$ transition observed at 580 nm in PLD GaN:Eu films is not observed in samples fabricated with lower growth rate techniques like MBE or MOCVD. That transition is forbidden and its presence indicates that Eu³⁺ is located in sites with lower symmetry than the C_{3v} sites of Ga [8]. This may be due to the dynamics inherent to the growth technique and the high pressure growth, which probably introduced numerous defects resulting in a loss of symmetry.



Figure 3 PL spectrum of GaN:Eu produced by PLD measured at room temperature, ($\lambda_{exc} = 325$ nm).

CL spectra of PLD grown GaN:Eu is shown in Fig. 4 shows that GaN near band edge emission (370 nm) is almost 4 times stronger than the strongest line of Eu^{3+} (620 nm), whereas under PL the peaks were almost equal. One explanation for this intensity difference might be the saturation of Eu^{3+} luminescent centers in CL, which is very probable since Eu content is only ~0.45 at%.

4 Conclusions GaN thin films doped with Eu^{3+} were directly grown on (0001) oriented Al_2O_3 substrates by the PLD growth technique. In these samples PL and CL emission from both the GaN host and the substitutional Eu^{3+} ions can be observed at RT. XRD analysis confirmed that PLD grown GaN:Eu on sapphire has hexagonal crystalline structure. In future work, efforts will be made to improve

the film quality, which will include the use of a buffer layer and the optimization of the background gas pressure and growth rate parameters.



Figure 4 CL spectra of GaN:Eu produced by PLD and measured at RT, UV-visible scan where NBE from GaN and Eu^{3+} emissions.

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