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A novel hybrid pulsed laser deposition/metalorganic vapour deposition method to form rare-earth activated GaN

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Abstract
A novel low-temperature method based on a combination of pulsed laser deposition and metalorganic chemical vapour deposition was used to fabricate GaN thin films doped with rare-earth (RE) ions. The films were deposited on GaN/Al_2O_3 substrates. The x-ray diffraction analysis of these GaN : RE (RE = Eu, Tb) samples showed that the films have the hexagonal phase of GaN and are polycrystalline with strong texture along the [0 0 1] direction. Cathodoluminescence spectra acquired at room temperature show the near band edge emission of GaN and the corresponding emission lines of the intra-shell transitions of either Eu^{3+} or Tb^{3+} ions.

1. Introduction

The wide band gap semiconductor GaN activated with RE ions (GaN : RE) is being extensively studied because of the widespread applications in novel optoelectronics. A large variety of light emitting devices, such as thick dielectric electroluminescent devices [1], planar electroluminescent devices [2] and a red emitting laser diode [3], are based on RE activated GaN. Also, patterned GaN : Er films have been proven to be a high density optical data storage element [4]. Recent experiments with Eu and Gd activated GaN revealed interesting ferromagnetic properties that could lead to the integration of optical and magnetic microelectronic devices [5]. All these applications are promising solutions to reduce the energy consumption for illumination and the increasing demand for data storage.

The RE ions can be added to GaN in two ways: *ex situ* or *in situ*. High-energy ion implantation is the most employed technique for *ex situ* RE activation of GaN and many studies have been performed by this method [6–11]. On the other hand, *in situ* RE activated GaN has been fabricated by molecular beam epitaxy (MBE) [12–15], metalorganic chemical vapour deposition (MOCVD) [16], metalorganic vapour phase epitaxy (MOVPE) [17], magnetron sputtering [18,19] and, recently, by pulsed laser deposition (PLD) [20].

Due to their characteristic emission colours, Eu^{3+} and Tb^{3+} ions were selected as activators in these experiments of GaN : RE fabrication. Eu^{3+} has been effectively added to GaN, and strong red emission centred at 622 nm ($^5D_0 \rightarrow {}^7F_2$) has been observed from powders and films synthesized by several fabrication methods [10, 11, 13, 15, 16, 20, 21]. In contrast, Tb activated GaN, with an expected green emission
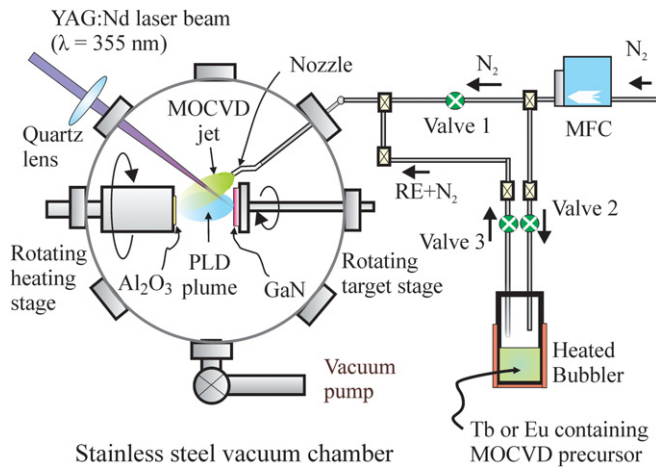
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Figure 1. Schematic diagram of the PLD/MOCVD deposition system.

(This figure is in colour only in the electronic version)

at 546 nm ($^5D_4 \rightarrow {}^7F_5$), has not shown very efficient emission from Tb^{3+} ions [22]. Bang and co-workers reported that the GaN : Tb emission intensity was only 1% of the emission for GaN : Eu for the same RE concentration [14]. According to their analysis, the addition of RE ions to GaN creates a defect level located at $\sim$0.37 eV below the conduction band (CB). This trap level can efficiently transfer energy to the $^5D_3$ excited level of Eu^{3+}, then the ion can relax by a series of non-radiative and radiative processes. The energy transfer is not possible when Tb^{3+} is the activator ion, because it does not have any excited states at such energy levels. Hence, Tb^{3+} emission is dramatically smaller than Eu^{3+} emission and is usually only reported from low-temperature measurements [8, 14, 22, 23].

In this paper we present a new low-temperature technique for *in situ* RE doping of GaN thin films. This procedure consists of a combination of PLD and MOCVD growth techniques. By means of this procedure it is possible to grow GaN : RE at room temperature. In the following sections, results of successful activation of GaN films with Eu^{3+} and Tb^{3+} ions are presented. GaN : Eu and GaN : Tb films fabricated by PLD/MOCVD show cathodoluminescence (CL) emission at room temperature. All samples exhibit near band edge (NBE) emission of the GaN host besides the corresponding characteristic RE emission lines.

2. Experimental

Figure 1 shows the PLD/MOCVD system used for the deposition of GaN : RE thin films on GaN/Al_2O_3 (0 0 0 1) substrates. In this system the source material was pure GaN powder (Alfa Aesar 99.99%) pressed into a ceramic target. For PLD deposition of GaN, the ablation source was the 3rd harmonic of a pulsed YAG : Nd laser, $\lambda = 355$ nm (Spectra-Physics model INDI-40HG). The beam was focused onto the target surface to produce an energy fluence of $\sim$3 J cm^{-2} and the repetition rate could be varied from 1 to 10 Hz. During the deposition, the substrate was rotated counterclockwise at 8 rpm while the GaN ablation target was rotated clockwise at

Table 1. PLD/MOCVD deposition parameters and the resulting RE concentration as determined by EDS for each GaN : RE sample.

Sample name	Substrate temperature (°C)	N_2 flow (sccm)	Laser rep. rate (Hz)	Resulting RE concentration (at%)	Std. Dev. (at%)
GaN : Eu-1	650	100	3	0.47	0.05
GaN : Eu-2	650	150	3	0.55	0.05
GaN : Eu-3	650	190	3	0.85	0.05
GaN : Tb-1	650	100	1	0.10	0.05
GaN : Tb-2	23	100	1	0.15	0.05
GaN : Tb-3	150	150	1	0.30	0.05

20 rpm. The substrate to target distance was fixed at 40 mm. The N_2 pressure in the chamber was maintained at 400 mTorr. In this system, the substrate holder temperature can be set in the range of room temperature to 900 °C.

Simultaneously with the PLD growth process described above, a MOCVD bubbler containing a metalorganic precursor was used to deliver RE ions to the growing GaN film. The MOCVD precursors used in these deposits were tris(2,2,6,6-tetratmetyl-3,5-heptanedionate)europium (III) for Eu or tris(2,2,6,6-tetratmetyl-3,5-heptanedionate) terbium (III) for Tb addition (Strem Chemicals (99.9%)). In both cases, N_2 (99.9999%) was used as the carrier gas. During the deposition the MOCVD bubbler temperature was maintained at 135 °C and the manifold was heated to 145 °C to avoid condensation. The N_2 flow rate could be controlled between 0 and 500 sccm. The mixture of RE ions and N_2 gas was introduced into the vacuum chamber through a 3 mm stainless steel nozzle directed to the substrate. The as-deposited films were dark grey, but after 40 min of annealing at 950 °C in a tube furnace with a 200 sccm NH_3 flow the films became white. The deposition parameters are shown in table 1.

The morphology and thickness of the samples was analysed with a scanning electron microscope (JEOL JSM-5300). The microscope was equipped with an energy dispersive spectroscopy (EDS) probe (INCAEnergy, Oxford Instruments Nanoanalysis) which was used to estimate the RE dopant concentrations. X-ray diffraction (XRD) measurements were performed (with Phillips X'Pert). For the CL measurements the films were introduced into an ultra-high vacuum chamber with a 10 KeV electron gun (Kimball Physics); the CL emission was collected with a spectrometer consisting of a 0.18 m monochromator and a thermoelectrically cooled CCD (Jobin-Yvon). All measurements were performed at room temperature.

3. Results and discussion

For all experiments, three deposition parameters were explored to determine the influence on the resultant RE dopant concentration in the film as shown in table 1. The first parameter is the substrate temperature. Room-temperature grown films have a higher RE concentration than those films grown at 650 °C, as shown for the Tb-doped samples in table 1. This system showed good results for low-temperature deposition. Secondly, the carrier gas flow (N_2) regulates the flux of RE ions impinging the substrate surface and
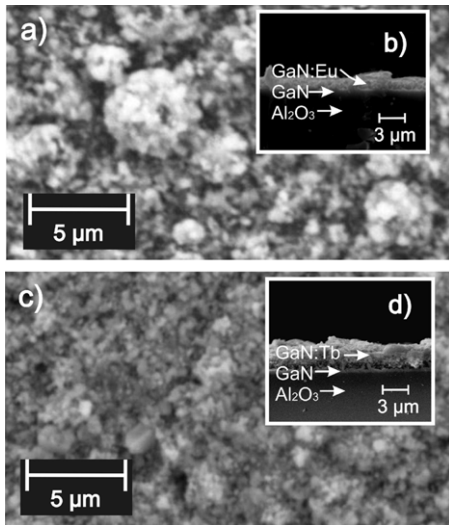
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Figure 2. SEM micrographs of GaN : RE thin films grown by the PLD/MOCVD technique. (*a*) GaN : Eu-2 film surface with inset showing cross-section (*b*) and (*c*) GaN : Tb-1 film surface with inset showing cross-section (*d*).

consequently the RE concentration in the film is nearly directly proportional to the flow rate. Table 1 shows that the Tb concentration increased from 0.47 to 0.85 at% when the carrier gas flow rate increased from 100 to 190 sccm. However, a comparison of these samples with Eu-doped samples is not possible because of the different vapour pressures of the MOCVD precursors used for Tb or Eu addition. Finally, the laser repetition rate, which controls the flux of GaN striking the substrate surface, was varied. It was used to control the film thickness and in combination with the MOCVD carrier gas flow to determine the final RE concentration in the films.

Scanning electron microscopy (SEM) micrographs of cross-sectional views of the films were used to determine the films thicknesses. The surface morphology of the thin film sample GaN : Eu-2 can be observed in the micrograph of figure 2(*a*). Figure 2(*b*) shows the cross-section of the same film in which an average thickness of ~1.7 μm was measured. The Eu concentration in this film was 0.55 at% (by EDS measurement). In figure 2(*c*) the surface morphology of the sample GaN : Tb-1 can be observed. Figure 2(*d*) shows the cross-sectional view of the sample; this film is ~3.2 μm thick. The Tb concentration of the sample GaN : Tb-1 is ~0.1 at%. In general, all these films are formed by conglomerates of submicrometre-sized particles (~0.3 μm); this film morphology is produced by high N_2 pressure deposition. A reduction in the N_2 background pressure will lead to smooth transparent films [24]. This condition can be achieved by increasing the pumping capacity of the vacuum system and is one of our next steps to improve the quality of our films.

The XRD patterns of an Eu activated film (GaNEu-2) and a Tb activated film (GaN : Tb-1) are shown in figure 3. Both samples show a hexagonal GaN phase with high preferential growth orientation along the [0 0 1] direction. Despite the rough surface observed by SEM, these films have high crystalline quality, which was confirmed by the full width half maximum (FWHM) of the (0 0 2) reflection rocking curve. For
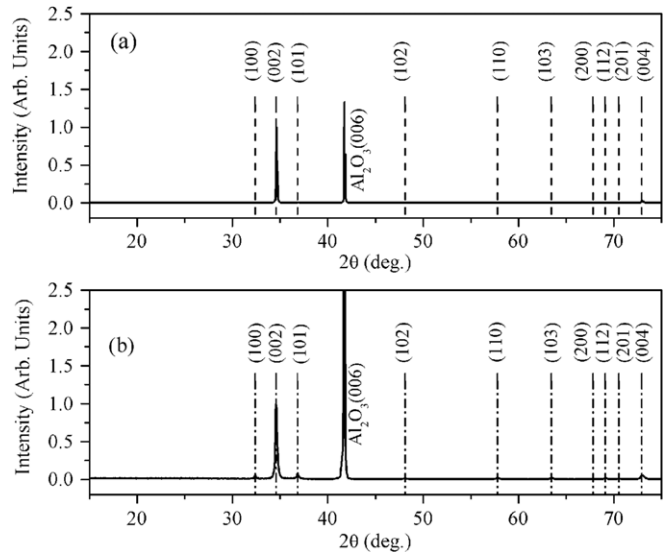

Figure 3. XRD patterns GaN : RE thin films grown by the PLD/MOCVD technique, (*a*) Eu^{3+} doped GaN sample GaN : Eu-2 and (*b*) Tb^{3+} doped GaN sample GaN : Tb-1. Both thin films grew preferentially along the [0 0 2] GaN crystalline direction. GaN indexed from JCPDS # 76-0703.
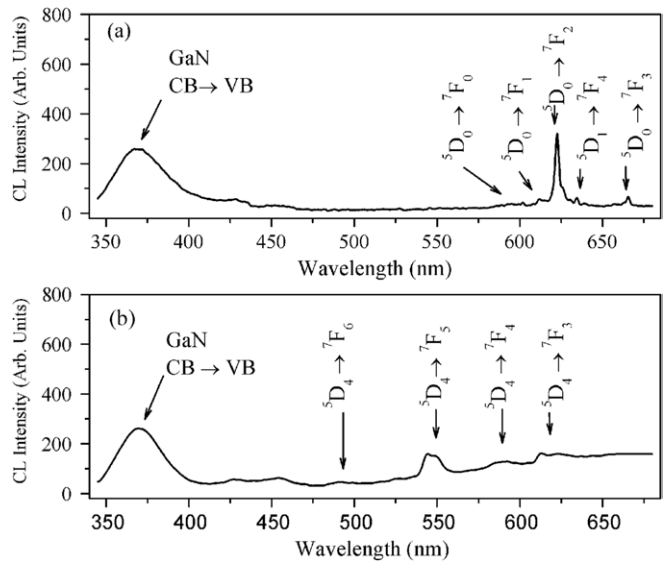

Figure 4. CL emission spectra of GaN : RE acquired at 4 keV electron excitation, (*a*) Eu^{3+} doped GaN thin film sample GaN : Eu-2 and (*b*) Tb^{3+} doped GaN thin film sample GaN : Tb-1. The transitions for the RE are shown on the figures.

GaN : Eu the FWHM is only 0.18° and for GaN : Tb the FWHM is 0.20°: these values are comparable to those reported for GaN : RE grown by MBE [14, 21].

The CL emission spectrum of the GaN : Eu-2 film is shown in figure 4(*a*). The spectrum exhibits emission lines associated with Eu^{3+} transitions from $^5D_1$ and $^5D_0$ levels to the ^7F_J ground state. In the CL spectrum the strongest emission line is located at 620 nm and corresponds to the $^5D_0 \rightarrow {}^7F_2$ transition. Peaks at 591 nm, 633 nm and 663 nm are attributed to the $^5D_0 \rightarrow {}^7F_1$ $^5D_1 \rightarrow {}^7F_4$ and $^5D_0 \rightarrow {}^7F_3$ transitions, respectively [12]. Figure 4(*b*) shows the CL spectrum of sample GaN : Tb-1,

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in which the strongest emission line is assigned to the $^5D_4 \rightarrow$ $^7F_5$ transition of the Tb^{3+} ions and shows weaker peaks at 490 nm, 588 nm and 630 nm, associated with the transitions $^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$, respectively [17]. The broad peak at around 365 nm corresponds to the NBE emission of GaN; the presence of NBE at room temperature indicates the good crystalline quality of the GaN matrix [25].

4. Conclusions

A novel low-temperature method based on a combination of PLD and MOCVD was developed for the synthesis of GaN thin films doped with rare-earth (RE) ions. The luminescent films were deposited on GaN/Al_2O_3 substrates. XRD analysis of these GaN : RE (RE = Eu,Tb) samples showed that the films have the hexagonal phase of GaN and are polycrystalline with strong texture along the [0 0 1] direction. CL spectra acquired at room temperature showed the band edge emission of GaN and the corresponding red or green emissions originated within the intra-shell transitions of either Eu^{3+} or Tb^{3+} ions, respectively. We developed a low-temperature method for the synthesis of RE-doped GaN luminescent films.

Acknowledgments

References

[1] Heikenfeld J and Steckl A J 2002 *IEEE T. Electron. Devices* **49** 557
[2] Kim J H, Holloway P H 2005 *Adv. Mater.* **17** 91
[3] Park J H and Steckl A J 2004 *Appl. Phys. Lett.* **85** 4588
[4] Lee B K, Chi R C-J, Chao D L-C, Cheng J, Chry I Y-N, Beyette F and Steckl A J 2001 *Appl. Opt.* **40** 3552
[5] Hite J, Thaler G T, Khanna T, Bernathy T R, Pearton J, Park J H, Steckl A J and Zavada J M 2006 *Appl. Phys. Lett.* **89** 132119
[6] Kim S, Rhee S J, Li X, Coleman J J and Bishop S G 1998 *Phys. Rev.* B **57** 14588
[7] Lozykowski H J, Jadwisienczak W M and Brown I 1999 *Appl. Phys. Lett.* **74** 1129
[8] Gruber J B, Zandi B, Lozykowski H J and Jadwisienczak W M 2002 *J. Appl. Phys.* **92** 5127
[9] Mamor M, Matias V, Vantomme A, Colder A, Marie P and Ruterana P 2004 *Appl. Phys. Lett.* **85** 2244
[10] Bodiou L, Oussif A, Braud A, Doualan J-L, Moncorgé R, Lorenz K and Alves E 2006 *Opt. Mater.* **28** 780
[11] Monteiro T, Boemare C, Soares M J, Sa Ferreira M R, Carlos L D, Lorenz K, Vianden R and Alves E 2001 *Physica* B **308** 22
[12] Steckl A J and Birkhahn R 1998 *Appl. Phys. Lett.* **73** 1700
[13] Maruyama T, Sasaki H, Miroshima S and Akimoto K 1999 *Japan. J. Appl. Phys.* **38** L1306
[14] Bang H, Morishima S, Li Z, Akimoto K, Nomura M and Yagi E 2001 *J. Phys.: Condens. Matter* **13** 10837
[15] Hömmerich U, Ei Ei Nyein, Lee D S, Heikenfeld J, Steckl A J and Zavada J M 2003 *Mat. Sci. Eng.* B **105** 91
[16] Pan M and Steckl A J 2003 *Appl. Phys. Lett.* **83** 9
[17] Hara K, Ohtake N and Ishii K 1999 *Phys. Status Solidi* b **216** 625
[18] Kim J-H and Holloway P H 2004 *J. Appl. Phys.* **95** 4787
[19] Liu Q L, Bando Y, Xu F F and Tang C C 2004 *Appl. Phys. Lett.* **85** 4890
[20] Perea-Lopez N, Tao J H, McKittrick J, Talbot J B, Raukas M, Laski J, Mishra K C and Hirata G 2008 *Phys. Status Solidi* at press
[21] Bang H, Miroshima S, Li Z, Akimoto K, Nomura M and Yagi E 2001 *Phys. Status Solidi* b **228** 319
[22] Uedono A, Bang H, Horibe K, Miroshima S and Akimoto K 2003 *J. Appl. Phys.* **93** 5181
[23] Dorenbos P and van der Kolk E 2006 *Appl. Phys. Lett.* **89** 061122
[24] Huang T F, Marshall A, Spruytte S and Harris J S Jr 1999 *J. Cryst. Growth* **200** 362
[25] Contreras O, Srinivasan S, Ponce F A, Hirata G A, Ramos F and McKittrick J 2002 *Appl. Phys. Lett.* **81** 1993