Properties of Erbium and Ytterbium Doped Gallium Nitride Layers Fabricated by Magnetron Sputtering

V. Prajzler, Z. Burian, I. Hüttel, J. Špirková, J. Hamáček, J. Oswald, J. Zavadil, V. Peřina

We report about some properties of erbium and erbium/ytterbium doped gallium nitride (GaN) layers fabricated by magnetron sputtering on silicon, quartz and Corning glass substrates. For fabricating GaN layers two types of targets were used - gallium in a stainless steel cup and a Ga_2O_3 target. Deposition was carried out in the Ar + N_2 gas mixture. For erbium and ytterbium doping into GaN layers, erbium metallic powder and ytterbium powder or Er_2O_3 and Yb_2O_3 pellets were laid on the top of the target. The samples were characterized by X-ray diffraction (XRD), photoluminescence spectra and nuclear analytical methods. While the use of a metallic gallium target ensured the deposition of well-developed polycrystalline layers, the use of gallium oxide target provided GaN films with poorly developed crystals. Both approaches enabled doping with erbium and ytterbium ions during deposition, and typical emission at 1 530 nm due to the Er^{3+} intra-4f $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition was observed.

Keywords: Gallium nitride, Erbium, Ytterbium, magnetron sputtering, photoluminescence.

1 Introduction

Gallium nitride (GaN) has become one of the most promising wide band gap (3.4 eV) direct semiconductor materials for utilization in high power and high frequency transistors, solid state photo detectors and high brightness blue light emitting diodes (LEDs), laser diodes (LDs) and full colour flat panel displays [1], [2]. Er^{3+}-doped optical materials are candidates for fabrication of optical amplifiers and lasers operating at 1 550 nm [3] due to the Er^{3+} intra-4f emission, which corresponds to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition. This wavelength is commonly used in telecommunication systems due to the fact that it corresponds to a low loss window of silica based optical fibers.

Erbium doped amplifiers are usually optically pumped by a source operating at 1 480 nm or 980 nm. When only Er^{3+} ions are present in short waveguides, optical pumping at 980 nm is not sufficiently efficient, because the Er^{3+} absorption cross-section at this wavelength is not very good. This problem can be overcome by adding Yb^{3+}, as its $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition is approximately ten times stronger than that of $^4I_{13/2} \rightarrow {}^4I_{15/2}$ [4], [5]. The Basic schematic energy levels and laser transitions of Er^{3+} and Yb^{3+} are shown in Fig. 1.

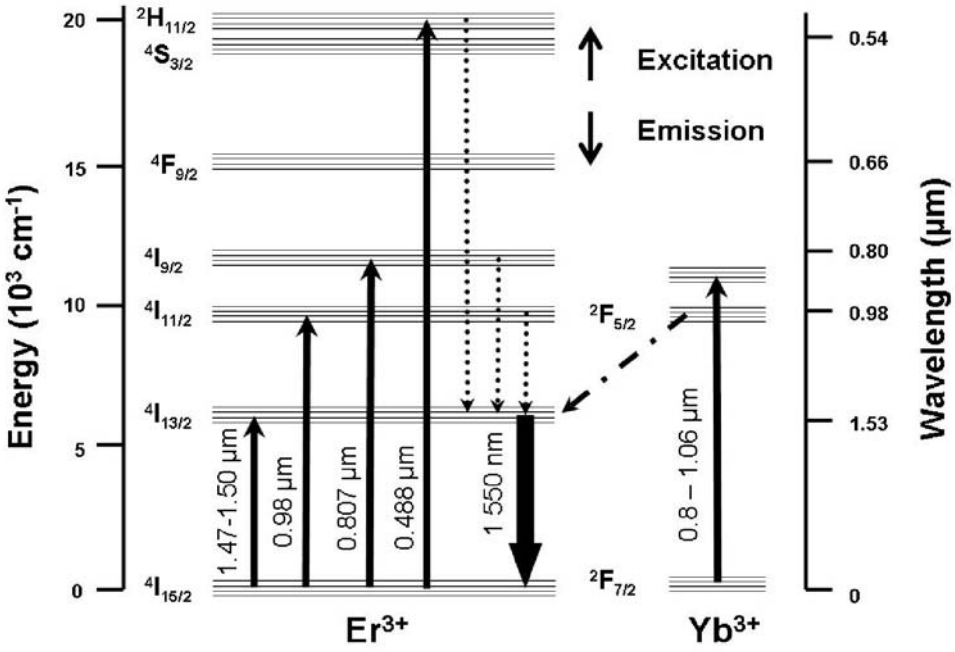

Fig. 1: Schematic energy levels and laser transitions of Er^{3+} and Yb^{3+} ions

It was previously shown in [6] that thermal quenching in Er^{3+}-doped semiconductors decreases with increasing band gap. Therefore, wide-band gap semiconductors such as GaN are attractive hosts for Er^{3+} and Yb^{3+} ions (RE ions).

GaN layers are usually grown by epitaxy methods such as Metal Organic Chemical Vapor Deposition (MOCVD) and Molecular Beam Epitaxy (MBE) [7], [8]. Epitaxy methods such as Hydride Vapor Phase Epitaxy (HVPE) and Liquid Phase Epitaxy (LPE) [9], [10] are used for fabricating of free standing GaN substrates. To obtain GaN layers doped with erbium and ytterbium ions, two procedures are basically available. The first procedure involves fabricating GaN layers and then doping them by ion implantation [11], [12]. The second way involves doping the GaN layers by erbium and ytterbium ions during the deposition process [13], [14]. RE-doped GaN layers fabricated by the epitaxy method are of high quality; however, the deposition process is rather complicated (for GaN fabricated by MOCVD a toxic precursor is needed, and for GaN fabricated by MBE an ultrahigh-vacuum chamber must be applied).

Instead of these rather complicated methods an easier approach to GaN fabrication is now being investigated. Yang et al. in 2003 already managed to fabricate high quality GaN layers [15] by using magnetron sputtering. Their GaN samples exhibited luminescence at 354 nm wavelength at room temperature. Erbium and ytterbium can easily be doped into the deposited GaN layers in the course of the sputtering process [16]. Moreover, sputter deposition is relatively inexpensive and it is ideal for covering a large area.

2 Experiment

2.1 Fabrication of the samples

The GaN samples were fabricated by radio frequency (RF) magnetron sputtering (*Balzers Pfeiffer PLS 160*) on silicon, quartz or Corning glass. Before deposition, the substrates were cleaned by a standard cleaning procedure. The sputtering experimental set-up is shown in Fig. 2. We used two types of target: Ga target and Ga_2O_3 target. Because of its very low melting point (29.78 °C), gallium cannot be used directly as a target, so we had to pour it into a stainless steel crucible. Another way is to use Ga_2O_3 target, as already reported in [17]. This would satisfactorily solve the problem arising from the low melting point of gallium, as Ga_2O_3 melts at about 1600 °C. In our experiments we sintered Ga_2O_3 powder (Sigma-Aldrich) to form a target 5 cm diameter.

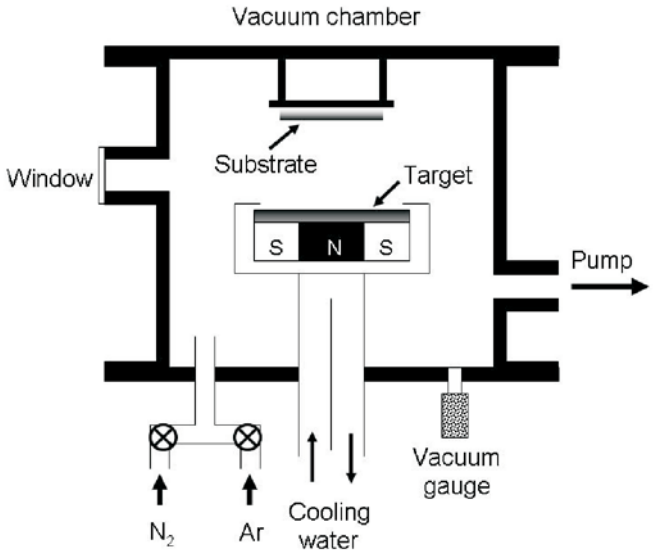

Fig. 2: Schema of the planar magnetron-sputtering set-up used for deposition of GaN layers

Typical deposition parameters were: temperature 300 K, time 60 min, nitrogen-argon ratio 3:7, power 50 W. The apparatus was evacuated before each experiment below 0.01 Pa, and deposition was done at total gas pressure 3.4 Pa. The further details of the fabrication process are given in Table 1. Typical thickness of the deposited layers was 0.5 to 3.2 μm, depending on the time of deposition.

For erbium doping into gallium nitride layers, the Er metallic powder and Yb powder were laid on the top of gallium targets, or, Er metallic powder and Yb powder or Er_2O_3 and Yb_2O_3 pellets 5 or 10 mm in diameter were put on top of the Ga_2O_3 targets. The Er_2O_3 and Yb_2O_3 pellets were fabricated by pressing Er_2O_3 and Yb_2O_3 powder (Sigma-Aldrich).

Table 1: Deposition parameters for Er/Yb:GaN fabrication

Target		Ga, Ga_2O_3
Power (13.56 MHz)		50 W
Gas precursor (purity 99.999%)		mixture N_2/Ar (3:7)
Total gas pressure		3.4 Pa
Target substrate distance		3.7 cm
Deposition time		1–4 hr
Deposition temperature		300 K
RE doping	using pellets	Er_2O_3, Yb_2O_3
	using powder	Er metallic powder, Yb powder

2.2 Measurement

The structure of the deposited GaN layers was studied by XRD (X-ray diffraction). The compositions of the samples were determined with the use of nuclear chemical analysis (Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection Analysis (ERDA)). The GaN stoichiometry and the O admixture amount was checked by RBS using 2.4 MeV protons. For this energy the non-Rutherford cross-section for N and O is sufficiently enhanced to obtain satisfactory sensitivity. The amounts of the erbium and ytterbium dopants were checked by RBS with both 2.4 MeV protons and 2.2 MeV alpha particles. The areas in the spectra above the surface of the Ga energy edge enabled us to determine the RE concentrations up to a depth of 600 and 240 nm from the GaN surface for 2.4 MeV protons and 2.2 MeV alpha particles, respectively. The H impurity was checked by ERDA with the 2.7 MeV alpha particles. The evaluations of the RBS and ERDA spectra were done by GISA3 [18] and SIMNRA [19] code, respectively.

The transmission spectra of the samples in the spectral region from 400 nm to 1 000 nm at room temperature were also taken. For this purpose, a tungsten lamp and MDR 23

monochromator were used as light sources, and the light transmitted through the samples was detected by a pyrodetector. The photoluminescence measurement was carried out at three excitation wavelengths:

- Ar laser ILA-120 operating at $\lambda_{ex} = 488$ nm, $E_{ex} = 100$ mW,
- Ar lasers operating at $\lambda_{ex} = 514.5$ nm, $E_{ex} = 300$ mW,
- Semiconductor laser P4300 operating at $\lambda_{ex} = 980$ nm, $E_{ex} = 500$ mW.

An FEU62 photocell was used to detect the wavelength from 500 to 1 000 nm, while a Ge detector was used for the wavelengths from 1 000 nm to 1 600 nm. The reference chopper frequency was 75 Hz. All the luminescence measurements were performed at room temperature.

3 Result and Discussion

The structure of the deposited GaN thin films was studied by XRD (X-ray diffraction), and the results have already been given in [20]. It was shown that the GaN structures depended on the type of the target and temperature used for the deposition. GaN films grown using the Ga_2O_3 target at room temperature had an amorphous structure, while GaN films fabricated using the Ga target at room temperature had polycrystalline structure (According to the literature, GaN layers fabricated at an elevated temperature (above 800 °C) can have a single crystalline structure [21]).

The exact composition of the deposited GaN layers was determined by nuclear analytical methods (RBS, ERDA). The typical RBS spectrum of an erbium doped GaN layer is shown in Fig. 3.

The analyses proved that the samples contained gallium, nitrogen, oxygen, argon, hydrogen and erbium and/or ytterbium ions (see Table 2). The amount of incorporated Er^{3+} and Yb^{3+} ions differed depending on the area of the target covered by the erbium and ytterbium co-dopant, and also on the erosion area represented by the part of the surface target

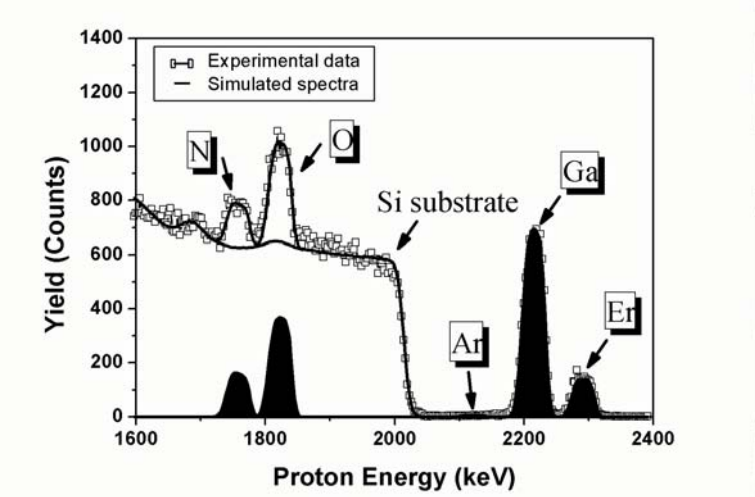

Fig. 3: RBS spectrum of Er-doped GaN containing 1.3 at % Er

Table 2: Composition of RE-doped GaN samples as determined by Rutherford Backscattering Analysis and Elastic Recoil Detection Analysis

Samples		Composition (at %)				
		Ga	N	O	H	Er+Yb
#160	Reference sample *	39.2	14.1	41.5	5.2	0
#110	Er 1 × Er_2O_3 **	33	26.9	32	8	0.1
#111	Er 3 × Er_2O_3 **	35.3	25.4	30.5	8.6	0.2
#112	Er 5 × Er_2O_3 **	32.6	16.1	42.3	8.5	0.5
#161	Er $m_{Er} = 0.05$ g ***	36.8	21.4	34.6	6	1.2
#162	Er/Yb $m_{Er} = 0.05$ g *** $m_{Yb} = 0.0997$ g	33.8	15.5	41.9	6	2.8
#165	Er/Yb $m_{Er} = 0.05$ g *** $m_{Yb} = 0.4996$ g	37.7	11.3	35.6	8.9	6.5
#163	Er/Yb $m_{Er} = 0.05$ g *** $m_{Yb} = 1.0008$ g	19.4	12.6	48.3	4.7	15

* Sample without Er +Yb doping, ** number of Er_2O_3 pellets (5mm diameter) put on top of the Ga_2O_3 target, *** weight of Er or Yb powder put on top of the Ga_2O_3 target

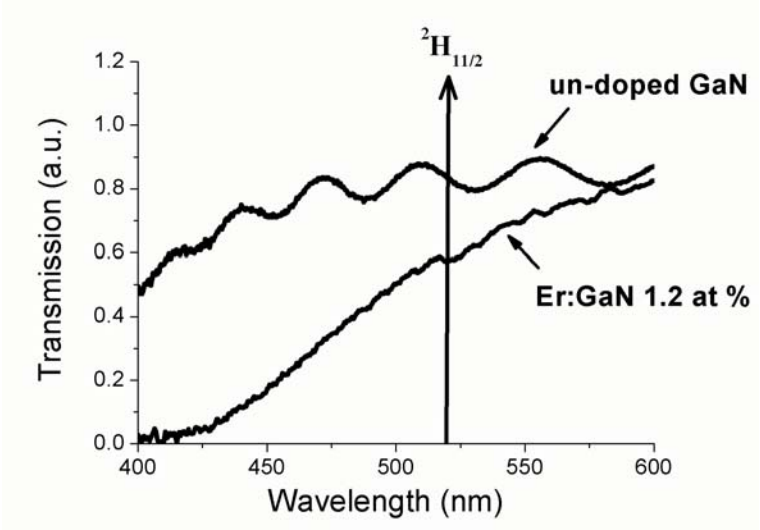

Fig. 4: Transmission spectra of the Er:GaN sample

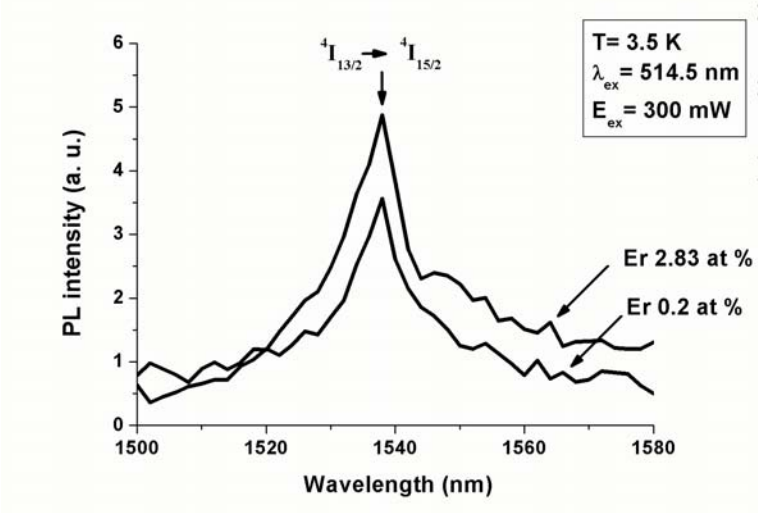

Fig. 5: PL spectra of the Er-doped GaN layers fabricated by magnetron sputtering using a Ga target and erbium metallic powder laid on top of the target

covered by erbium and ytterbium. As Er and Yb have very close, atomic weight values these two elements cannot be distinguished in the RBS spectra, so that only the sum of the two elements can be obtained. According to Table 2, a significant amount of hydrogen is found in GaN films, with the relative concentrations ranging between 4 and 9 at %. This unintended presence of hydrogen in the samples is probably a consequence of the residual contamination of the Ar and/or

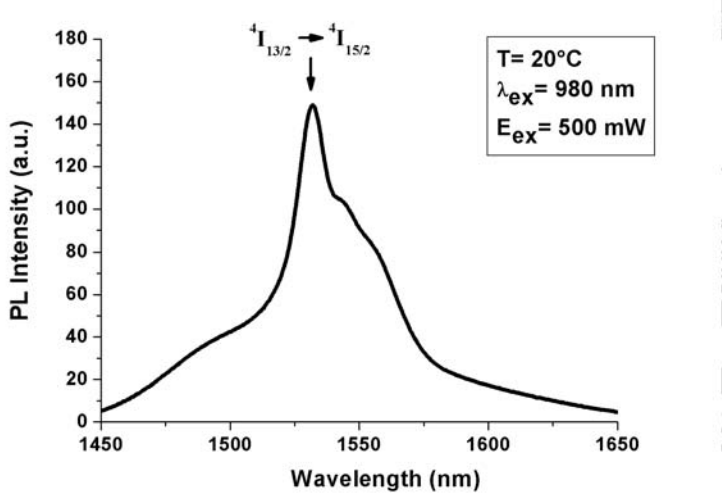

Fig. 6: PL spectra of an Er-doped GaN layer fabricated by magnetron sputtering using the gallium oxide target and two pellets (5 mm diameter) of erbium oxide laid on the top of the target

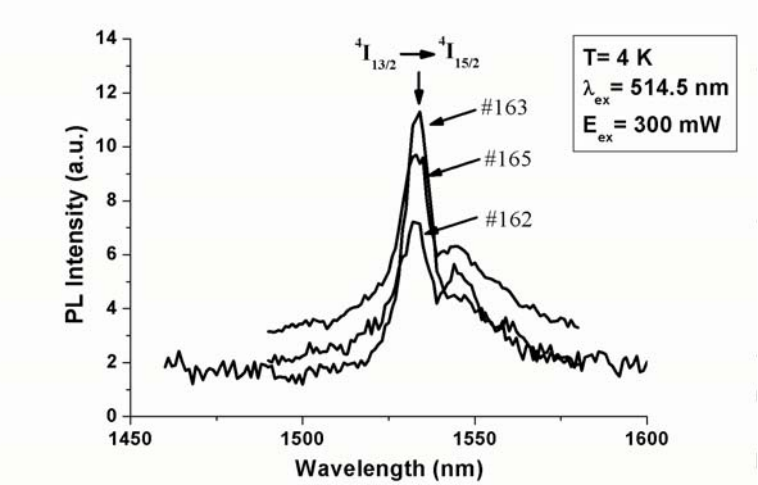

Fig. 7: PL spectra of Er/Yb-doped GaN layers fabricated by magnetron sputtering using erbium and ytterbium powder laid onto a Ga_2O_3 target

N_2 gases that are employed. They contained approximately 5 ppm of hydrogen [22]. The GaN samples also contained a small amount of argon (around the detection limit 1 at %), due to the argon atmosphere used during deposition.

Fig. 4 compares the transmission spectra of the sputtered GaN doped with 1.2 at. % of erbium with the un-doped GaN sample. The arrows in the figure mark the strongest transitions of the Er^{3+} ions ($^2H_{11/2}$). However, we observed only a weak peak attributed to the Er^{3+} transition. We did not observe any transition of the Yb^{3+} ions at 980 nm ($^2F_{5/2}$) with the erbium doped GaN layers co-doped by Yb^{3+} ions, probably because the absorption coefficients for ytterbium ions are very low and/or the deposited layers are rather thin.

The photoluminescence spectrum of the Er^{3+} doped GaN layers fabricated using a Ga target excited at $\lambda_{ex} = 514.5$ nm at a temperature of 4 K is given in Fig. 5. The figure shows typical photoluminescence bands attributed to the erbium transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$. We obtained the best result for the GaN sample containing about 2.83 at % of erbium.

Fig. 6 shows the photoluminescence spectra of a GaN layer doped by Er^{3+} fabricated using the Ga_2O_3 target and Er_2O_3 pellets laid on top of the target, obtained by using optical pumping at 980 nm at room temperature.

Fig.7 shows the 1530 nm region of the photoluminescence spectra of the Er^{3+}/Yb^{3+} containing GaN samples fabricated by doping from erbium-ytterbium powder put onto a Ga_2O_3 target, excited by an Ar laser ($\lambda_{ex} = 514.5$ nm, temperature 4 K). The typical photoluminescence bands attributed to erbium 4I13/2 → 4I15/2 increased in intensity with increasing ytterbium content (for details, see Table 2). The best results were obtained when we laid 0.05 g of erbium metallic powder and 1 g ytterbium powder onto the target.

Fig. 8 shows the same photoluminescence spectra as Fig. 7, but now obtained by optical pumping at 980 nm at room temperature, which indicates better quality of the samples.

4 Conclusion

Two basic approaches for RF magnetron sputtering of GaN thin films have been presented. The first one, utilizing a metallic gallium target, provides deposition of well-developed

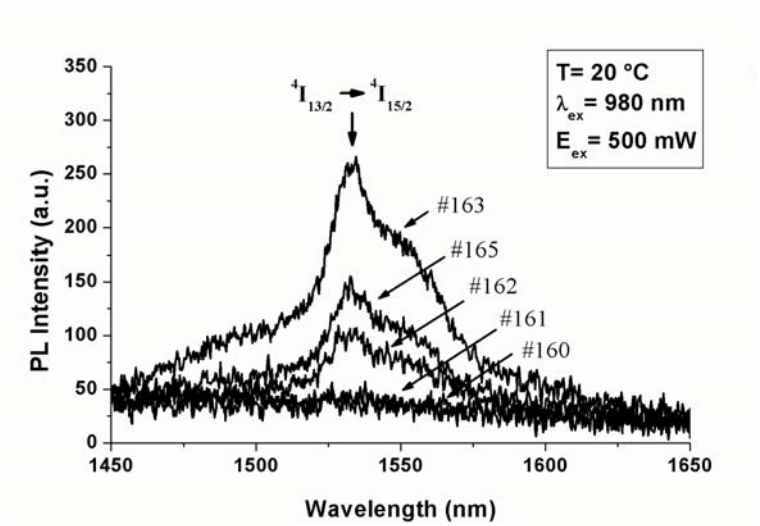

Fig. 8: PL spectra of Er/Yb-doped GaN layers fabricated by magnetron sputtering using erbium and ytterbium powder laid onto a Ga_2O_3 target

polycrystalline layers. The second, using a gallium oxide target, resulted in almost amorphous GaN films with poorly developed crystals. The Er/Yb doped GaN samples exhibited the typical emission at 1 530 nm due to the Er^{3+} intra-4f $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition even pumped at 980 nm at room temperature. The layers co-doped with Yb ions revealed increased intensity of luminescence.

Thus the possibility of fabrication of erbium and ytterbium ions containing GaN films by magnetron sputtering was demonstrated.

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Ing. Václav Prajzler
e-mail: xPrajzlv@feld.cvut.cz

Doc. Ing. Zdeněk Burian, CSc.
e-mail: Burian@fel.cvut.cz

Department of Microelectronics

Czech Technical University
Faculty of Electrical Engineering
Technická 2
166 27 Prague, Czech Republic

Doc. Ing. Ivan Hüttel
e-mail: Ivan.Huttel@vscht.cz

RNDr. Jarmila Špirková, CSc.
e-mail: Jarmila.Spirkova@vscht.cz

Ing. Jiří Hamáček
e-mail: Jiri.Hamacek@vscht.cz

Institute of Chemical Technology
Technická 5
166 27 Prague, Czech Republic

Ing. Jiří Oswald, CSc.
e-mail: Oswald@fzu.cz

Institute of Physics, Czech Academy of Sciences
Cukrovarnická 10
162 53 Prague, Czech Republic

RNDr. Jiří Zavadil, CSc.
e-mail: Zavadil@ure.cas.cz

Institute of Radio Engineering and Electronics
Czech Academy of Sciences
Chaberská 57
182 51 Prague, Czech Republic

RNDr. Vratislav Peřina, CSc.
e-mail: Perina@ujf.cas.cz

Institute of Nuclear Physics
Czech Academy of Sciences
250 68 Řež near Prague, Czech Republic

