Photoluminescence Study of Eu-doped Ga_2O_3 and GaN Nanowires and Nanoparticles Produced by Hydrothermal Growth

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***Abstract* — We present results on preparation of Eu doped GaN nanoparticles and nanowires on the basis of Ga_2O_3 nanomaterial produced by hydrothermal growth. The monoclinic Ga_2O_3 nanoparticles and nanowires have been prepared with gallium nitrate and sodium hydroxide as precursors. The geometrical form on the nanomaterial is determined by the duration of the hydrothermal process. The Ga_2O_3 nanomaterial is transformed unto GaN nanoparticles and nanowires by nitridation in a flow of NH_3 and H_2. The photoluminescence properties Eu doped Ga_2O_3 and GaN nanomaterial are investigated under pulsed and continuum wave excitation. The produced material is also investigated by means of XRD analysis, Raman scattering and Fourier transform infrared (FTIR) spectroscopy.**

***Key words* — nanoparticles, nanowires, hydrothermal growth, nitridation, luminescence**

I. Introduction

Due to advantageous properties such as wide bandgap, pronounced chemical and thermal stability, gallium nitride is currently considered as one of the most important semiconductor materials for practical applications. III-nitride compounds are nowadays widely used in fabrication of short-wavelength light-emitting devices [1,2] and heterostructure field-effect transistors (HFETs) for high-frequency/high-power applications [2-4]. Another emergent field of applications for III-nitride group of materials is related to fabrication and implementation of microelectromechanical (MEMS), microoptoelectromechanical (MOEMS), and nano-electromechanical (NEMS) systems. Over the last years, various microelectromechanical (MEMS) structures based on AlGaN/GaN heterostructures have been explored for novel sensor applications. In particular, AlGaN/GaN-based MEMS confining a two dimensional electron gas (2DEG) have been realized by means of the developed dry etching technology [5].

Apart from bulk and layer material, there is actually a considerable interest in the preparation of nanoparticles and nano- microwire on the basis of semiconductor and oxide materials due to the influence of its dimensionality upon their optical, radiative, and magnetic properties. Particularly, radiative properties of GaN doped Eu nanowires are interesting for applications in solid-state lightening [6,7].

GaN materials can be synthesized by means of different methods, for instance by combustion in a NH_3 flow to convert the Ga_2O_3 nanoparticles to GaN ones [8]. GaN nanoparticles with sizes between 10 and 20 nm are obtained by this method. Monoclinic β-Ga_2O_3 nanoparticles have been obtained from $Ga(NO_3)_3$ dissolved in nitric acid by adjusting the pH of the solution through the addition of ammonium hydroxide with a subsequent thermal treatment of the produced GaO(OH) at the temperature of 400°C during 4 hours [9], and a further thermal treatment of the Ga_2O_3 powder in a NH_3 flow at the temperature of 900°C during 10 to 120 minutes to produce GaN nanoparticles. A direct method of GaN nanoparticles synthesis from Li_3N and $GaCl_3$ was also applied [10,11]. Good quality GaN nanocrystals have also been prepared by a simple and cost-effective sol-gel method with Ga_2O_3 powder, a mixture of concentrated HCl and HNO_3, citric acid, acetone, ammonium hydroxide, ethylenediamine, and free ammonia crude materials [12].

We report on hydrothermal growth of monoclinic Ga_2O_3 nanoparticles and nanowires doped with Eu and conversion of the obtained Ga_2O_3 nanoparticles and nanowires into GaN nanocrystals by nitridation [8].

II. Technological Details

High purity $Ga(NO_3)_3$ $9H_2O$ and 1M NaOH chemicals from Sigma-Aldrich have been used for synthesis of Ga_2O_3 nanoparticles in the hydrothermal growth. The experimental

procedure consists in dissolution of 2.5M of gallium nitrate in 50 ml of distilled water and adjustment of the solution pH to the value of 9 by means of the 1M NaOH solution under vigorous stirring. The suspension is introduced in a teflon autoclave with a steel shell to ensure a good sealing.

The hydrothermal process lasts for 5 to 24 hours at the temperature of 220°C. The particle separation after autoclaving was performed by settling and filtering with a subsequent drying in an oven during 2 hours at 80°C. As a result, Ga_2O_3 nanoparticles or nanowires are produced with hydrothermal growth of 5 and 24 hours, respectively, as illustrated in SEM images of Fig. 1.

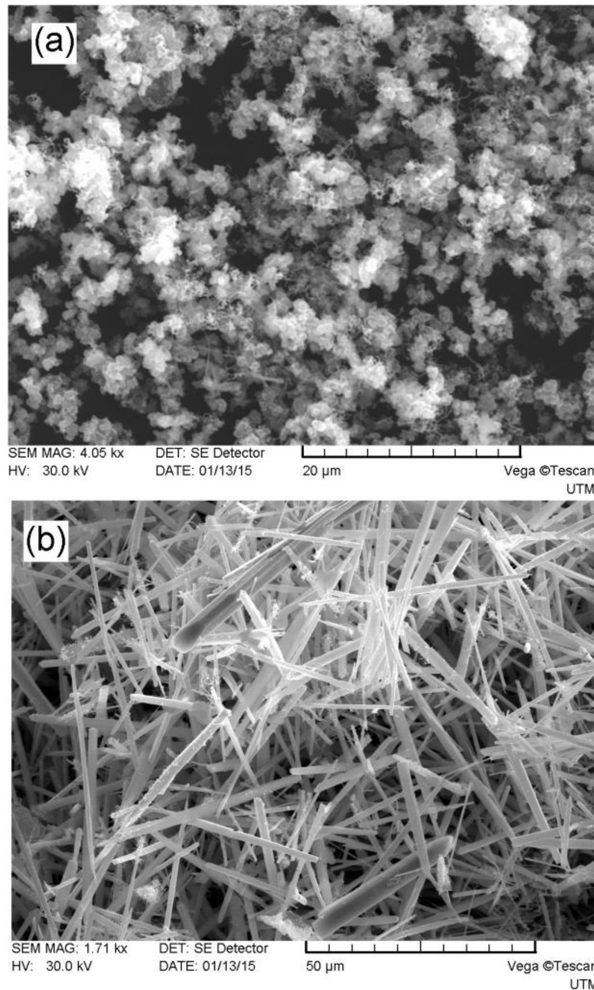

Fig. 1. SEM image of the Ga_2O_3 powder produced with 5 hours (a) and 24 hours (b) hydrothermal process.

Good quality GaN nanoparticles have been produced from Ga_2O_3 nanocrystals under flowing ammonia with a subsequent nitridation in a mixture of NH_3 and H_2 with flow rates of 0.35 and 2.5 l/min, respectively. The Ga_2O_3 powder was placed into a horizontal tube furnace with a quartz boat and heated at temperature of 900-950 °C during 90-150 min. After annealing, the furnace was switched off, and cooling down occurred in a natural fashion.

III. XRD Analysis

The obtained powder was studies by means of XRD spectroscopy which demonstrated the presence of a single β - Ga_2O_3 phase after the hydrothermal process (Fig. 2a).

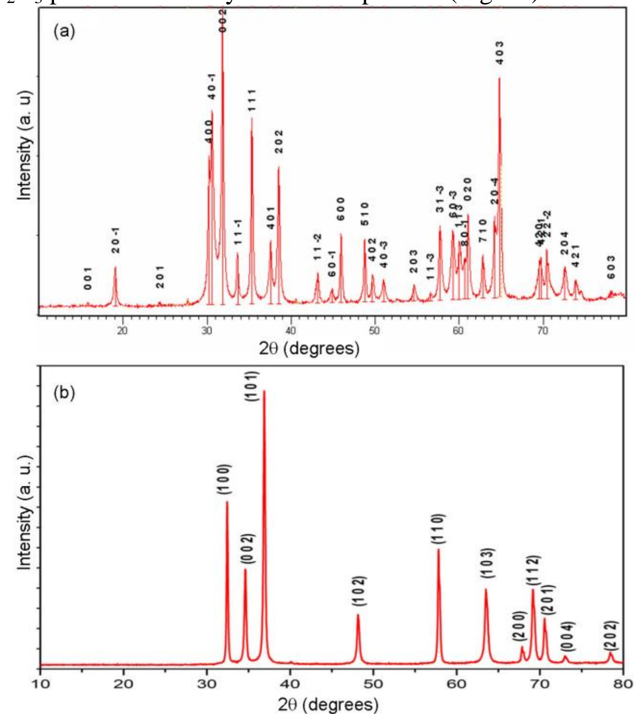

Fig. 2. XRD pattern of Ga_2O_3 nanoparticles obtaining by hydrothermal method (a) and GaN produced by nitridation (b).

The diffraction peaks observed in the XRD pattern of the material produced by nitridation can be indexed to a hexagonal wurtzite GaN structure (Fig. 2b), while the morphology of the GaN powder is similar to that of the Ga_2O_3 one. The sizes of the produced high crystallinity GaN nanoparticles deduced from the XRD spectra according to Sherrer formula are around 28.6 nm, while the length and diameter of GaN wires was 20-50 µm and 3-0,5 µm, respectively That means that the GaN nanowires are composed of smaller nanoparticles.

IV. Raman Scattering and FTIR Spectroscopy

The produced GaN powder was also characterized by means of Raman scattering (Fig. 3) and FTIR spectroscopy (Fig. 4).

The Raman spectrum measured in the wavenumber range from 300 to 800 cm^{-1} shown the presence of peaks at 534 cm^{-1}, 561 cm^{-1} and 569 cm^{-1} assigned to A_1(TO), E_1(TO), and E_2-high vibration modes, respectively, as well as a weak band at 730-740 cm^{-1} assigned to the A_1(LO) and E_1(LO) modes. The low intensity of the LO modes is likely due to the presence of a high free carrier concentration in the nanoparticles. A Raman scattering band was also observed at 420 cm^{-1}, which has been previously assigned to an acoustic overtone [13]. The symmetry of vibration modes in wurtzite GaN is summarized in Table 1.

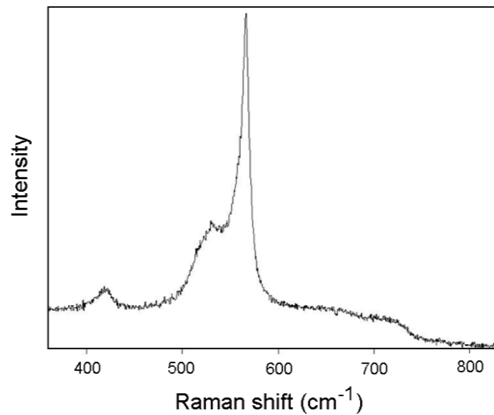

Fig. 3. Raman spectrum of GaN nanoparticles.

TABLE I. SYMMETRY OF VIBRATION MODES IN WURTZITE GAN

Symmetry	Active in	Raman Shift (cm^{-1})
E_2 low	Raman	144
A_1(TO)	Raman, IR	533
E_1(TO)	Raman, IR	561
E_2 high	Raman	569
A_1(LO)	Raman, IR	735
E_1(LO)	Raman, IR	743
B_1 low	silent	
B_1 high	silent	

FTIR spectra demonstrated the formation of β-Ga_2O_3 nanoparticles after the hydrothermal process (Fig. 4, curve 1). The spectrum is dominated by the absorption bands at 455 cm^{-1} and 684 cm^{-1} which have been previously assigned to vibration modes of the Ga-O bonds in the β-Ga_2O_3 structure (A_u modes) [14]. Other peaks observed at 528 cm^{-1}, 624 cm^{-1}, 748 cm^{-1} are related to B_u modes.

No absorption bands related to the Ga_2O_3 phase are observed in the FTIR spectra of the prepared GaN nanoparticles (Fig. 4, curve 3). The spectrum is dominated instead by two absorption bands at 565 cm^{-1} and 634 cm^{-1}. The first one has been previously attributed to the Ga–N stretching vibration (E_1(TO) mode) in the hexagonal type GaN crystals [15], while the second one is related to a local vibration mode (LVM) attributed to nitrogen and gallium vacancies.

For the purpose of comparison, FTIR spectrum of Li_3N is presented in Fig. 4 (curve 2). The shift o the band at 501 cm^{-1} observed in Li_3N to 565 cm^{-1} in the case of GaN is probably due to the fact that bonding in Li_3N is mainly ionic, while in GaN it is more covalent.

In order to dope the Ga_2O_3 nanopowder with Eu^{3+} ions, $EuCl_3$ with concentration from 0.3 to 3 at% was added to the 0.05M $Ga(NO_3)_3$ solution which was subjected to stirring with a magnetic stirrer during 30 minutes. The pH of the solution was adjusted to 9.5 by means of 25% NH_4OH under additional stirring for 30 minutes. The obtained suspension was introduced in a teflon autoclave with a steel shell for thermal treatment as described above. The incorporation of the Eu^{3+} ions into the powder was investigated by means of photoluminescence (PL) spectroscopy. The PL spectra were excited by 355 nm or 532 nm of a Nd:YAG laser, or by the 405 nm line of a mercury lamp at room temperature. The PL spectrum of a Ga_2O_3 sample doped with a 2% concentration of Eu is shown in Fig. 5.

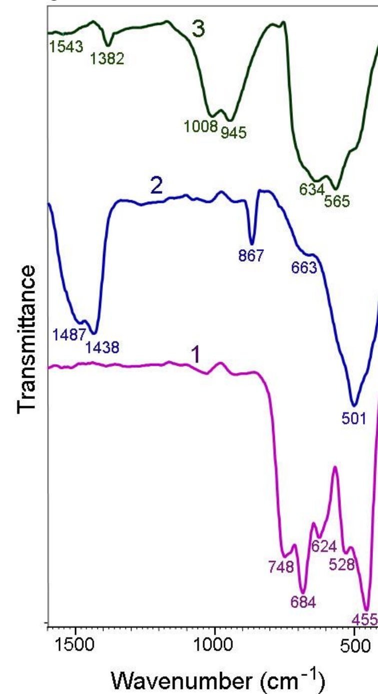

Fig. 4. FTIR spectrum of Ga_2O_3 nanoparticles (1), Li_3N (2) and GaN nanoparticles (3).

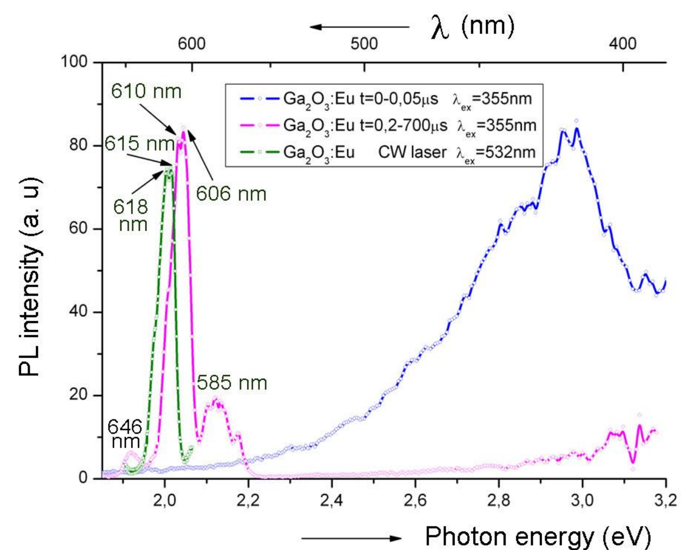

Fig. 5. PL spectrum of Eu-doped Ga_2O_3 nanoparticles under various excitation.

V. Luminescence of Eu Doped Powders

The spectrum measured with a short delay of 0 - 0.05 μs after the excitation laser pulse consists of a broad luminescence band at 420 nm. A model has been put forward for the blue luminescence in gallium oxide many years ago [16,17], which suggests that an electron in a donor is captured by a hole on an acceptor to form a trapped exciton. The donor should be formed by oxygen vacancies and the acceptor would contain gallium vacancies or gallium–oxygen vacancy pairs. The recombination of the electron and the hole should emit a blue photoluminescence. The blue luminescence is quenched with a larger delay of 0.2 - 700 μs after the excitation laser pulse, and the luminescence spectrum is dominated by the red emission coming from Eu^{3+}-related radiative electron transitions. All the observed lines are consistent with Eu^{3+}-related radiative electron transitions, namely with ${}^5D_0 \rightarrow {}^7F_j$ (J = 1,2,3) transitions. The PL band at 585 nm comes from ${}^5D_0 \rightarrow {}^7F_1$ transitions. The lines at 606-818 nm are related to ${}^5D_0 \rightarrow {}^7F_2$ transitions, while the luminescence at 646 nm comes from ${}^5D_0 \rightarrow {}^7F_3$ transitions. With cw excitation, the luminescence lines are slightly shifted to longer wavelengths.

The structure of β-Ga_2O_3 is monoclinic with a space group of C2/m, and Ga^{3+} ions occupy either tetrahedral or octahedral crystallographic sites. With regular tetrahedrons and octahedrons, the local site symmetry of Eu^{3+} ions substituting Ga^{3+} ions would be T_d or O_h, respectively. However, the tetrahedrons and octahedrons are distorted in the real β-Ga_2O_3 structure, and the point-group of these sites should be lower than T_d and O_h. In fact, both these sites have the same site symmetry of C_s [18]. Since the ionic radii of the Ga^{3+} ions are 0.047 and 0.062 nm for tetrahedral and octahedral coordination, respectively [19,20], taking into account the ionic radius of the Eu^{3+} ions (0.095 nm), the distorted octahedral site should be more suitable for Eu^{3+} ions. The incorporation of Eu^{3+} ions in this site symmetry was previously confirmed in Eu^{3+}-doped β-Ga_2O_3 nanophosphors annealed at 1100°C, where sharp and well-resolved transition lines were observed [21]. On the other hand, the broader lines observed in spectrum presented in Fig. 5 suggest that a small portion of Eu^{3+} ions is incorporated into the crystal lattice, while the main signal comes from the Eu^{3+} ions that occupied a surface or near surface site of nanoparticles. As a result, the emission lines associated with crystal field levels of Eu^{3+} ions are poorly resolved due to the inhomogeneous broadening of the spectra.

Eu^{3+} ions are also well incorporated into the wurtzite GaN lattice produced from Ga_2O_3 as a result of nitridation, as demonstrated by the PL spectrum presented in Fig. 6. The lines related to ${}^5D_0 \rightarrow {}^7F_2$ transitions are narrower as compared to those observed in the Ga_2O_3 nanoparticles, suggesting that the Eu^{3+} ions are most probably incorporated into GaN nanoparticles rather than occupying a surface or near surface site.

VI. Conclusions

The results of this paper demonstrate preparation of monoclinic Ga_2O_3 nanoparticles and nanowires by hydrothermal method with gallium nitrate as a source material, and obtaining of wurtzite GaN nanoparticles by conversion of Ga_2O_3 in a flow of NH_3 and H_2. The SEM images demonstrate that the morphology of the produced nanomaterial depends upon the duration of the hydrothermal process, while the high crystal quality has been confirmed by the presence of sharp and narrow peaks in the XRD spectrum, as well as by Raman scattering and FTIR spectroscopy. The analysis of emission lines related to Eu^{3+} radiative electron transitions in the PL spectra of Ga_2O_3 and GaN nanoparticles demonstrates their efficient doping through the addition of $EuCl_3$ to the $Ga(NO_3)_3$ solution during the hydrothermal growth process.

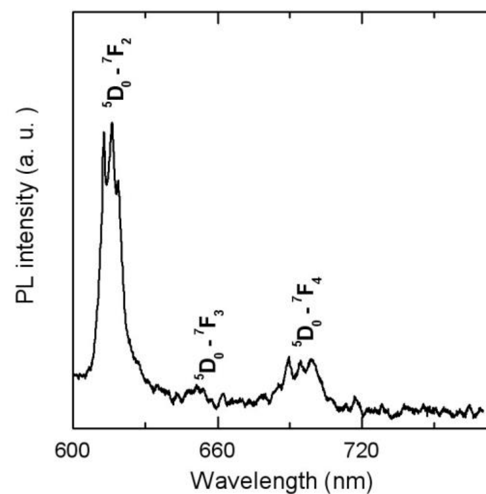

Fig. 6. PL spectrum of Eu-doped GaN nanoparticles excited by the 405 nm line of a mercury lamp at room temperature.

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