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Synthesis and luminescent properties of GaN and GaN-Mn blue nanocrystalline thin-film phosphor for FED

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ABSTRACT

The technologies of fabrication of thin film phosphors based on gallium nitride using rf-magnetron sputtering are developed and the structural properties of these films are studied. Luminescence and electron spin resonance (ESR) spectra of GaN and GaN-Mn thin films are obtained. A correlation between cathodo-luminescence intensity and conductivity of GaN films is found. The nature of emission centers in GaN and GaN-Mn thin films is discussed and a mechanism of luminescence in these films is proposed.

INTRODUCTION

Gallium nitride, well known in light emitting diode (LED) applications, is also a very promising material for use as an active luminescent layer in field emission displays (FED) [1-3]. Although efficient luminescence can be obtained with zinc sulfide, this material is not sufficiently stable. The crystallo-chemical analysis conducted by us has revealed the possibility of activation of GaN and AlN with luminescent dopants of Mn^{2+} and Cr^{3+}. In the case of stabilization of 3-valent state in tetrahedral neighborhood, the isomorphic substitution of Ga(Al) by Cr^{3+} can create a stable high-spin state for the d^3 configuration. Activation of GaN with Mn may result in stabilization of high- and low- spin states with a stable crystal structure configuration. Also the heterovalent substitution of Ga(Al) for Mn^{2+} in low concentrations is possible in the case of partial substitution of nitrogen atoms for oxygen or in the case of a nitrogen defect sublattice in GaN. Therefore, GaN and AlN doped with Mn^{2+} and Cr^{3+} are good candidates for FED applications. There are several substantial differences between LED and FED devices – the latter have relatively large emitting surface, and their light emission is more efficient if polycrystalline layers are used [4]. Thus, the magnetron-sputtering technique is suitable for deposition of thin film phosphors. The present work investigates luminescence of nano / polycrystalline GaN thin films synthesized by rf-magnetron sputtering.

2. EXPERIMENTAL

Metallic gallium was used as the target for rf-magnetron sputtering, [5]. The deposition substrates were monocrystalline sapphire, amorphous quartz with ZnO and $MgAl_2O_4$ buffer layers [6] as well as mica sheets. Sputtering was conducted in a pure nitrogen atmosphere at

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pressures from $5\cdot10^{-3}$ to $5\cdot10^{-2}$ Torr. Substrate temperature was varied from 450°C to 650°C. The rf-discharge power was in the 50 ÷ 200 W range.

The quality of thin films is dependent on deposition conditions and was assessed by absorption edge position, refractive index, and transparency of the films in the visible region obtained from optical measurements. The film structure was investigated using an HZG-4A X-ray powder diffractometer (Cu $_{K\alpha}$ radiation, θ-2θ scan mode, step 0.05°, t=10 s per point). The Rietveld profile refinement method of analysis of experimental XRD data was used [7, 8]. Specified parameters were unit cell parameters and a texture parameter [8, 9]. The X-band ($\nu\cong$9.4 GHz) ESR spectra were recorded using a computer controlled commercial AE-4700 radio frequency spectrometer with 100 kHz magnetic field modulation at room temperature. The microwave frequency was controlled by means of diphenylpicrylhydrazyl (DPPH) *g*-marker (*g*=2.0036±0.0001). For ESR study, the thin films were prepared on the mica sheets. Cathodoluminescence spectra were measured at 300 K and with e-beam excitation energy between 1 and 6 keV at a current density of 3 mA cm^{-2}.

3. RESULTS AND DISCUSSION

3.1. Technology and structure of the GaN thin films

One of the main factors which affects formation of gallium nitride films is the efficiency of ionization of nitrogen molecules. With this in mind, the rf-discharge plasma emission from nitrogen was spectrally analyzed and used as a monitor. It was found that the most efficient formation of GaN takes place when the most intense line in the emission spectrum is at 391.4 nm which corresponds to ionized nitrogen molecules N_2^+.

rf-magnetron sputter deposition of nitride-based thin films depends on the working gas composition, rf-discharge power, and substrate temperature. It was found that the deposition rate increases with increased rf-discharge power and decreases with both increasing substrate temperature and nitrogen pressure. The decrease of deposition rate with the increase of nitrogen pressure may be connected with the shortened mean free path of gallium atoms.

The dependence of the crystal structure parameters of GaN thin films (figure 1) on substrate

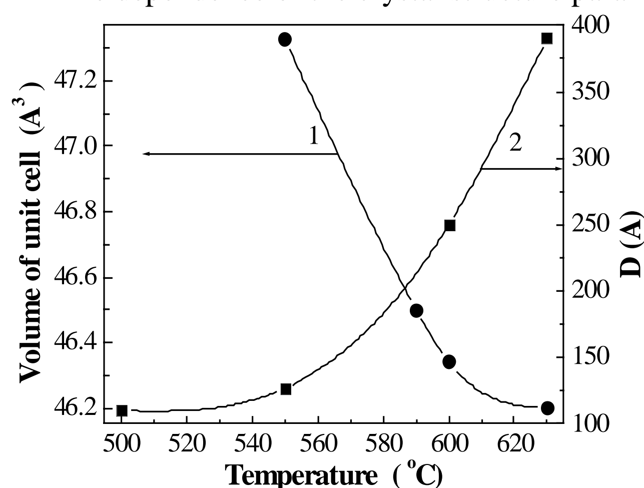

Figure 1. Dependence of the unit cell volume (curve 1) and crystallite size (curve 2) on the substrate temperature for GaN thin films, deposited on [0001] sapphire substrates.

temperature during deposition were investigated. As the substrate temperature is increased from 500 to 650°C, the lattice parameter, a, of the GaN films gradually decreases from 3.225 Å to

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3.208 Å, and the parameter c decreases from 5.281 Å to 5.217 Å. It was found that the unit cell volume decreases exponentially with an increase of temperature (figure 1, curve 1) tending to the value characteristic of polycrystalline GaN (~46 $Å^3$). This suggests a reduction of defects in close-packed layers of Ga and N atoms in "hexagonal-cubic" layering. The nanocrystallite size grows exponentially from 10 nm to 40 nm as substrate temperature is increased from 450 to 600°C, Figure 1, curve 2.

Auger profiling showed minor non-stoichiometry of the GaN film composition in the near-surface region (~200 Å) caused by the presence of oxygen, carbon and excess gallium atoms, whereas at depths greater than 300 Å, the composition of the thin films was stoichiometric.

3.2. Luminescent properties of the GaN and GaN-Mn thin films

GaN films showed cathodoluminescence in the blue region of the spectrum with a peak at 450 nm and with color coordinates x=0.198, y=0.206 (figure 2, curve 1). When doping gallium nitride with manganese, the increase of intensity of blue emission is observed together with emergence of emission in the red region of the spectrum with a maximum at approximately 690 nm (figure 2, curve 2). The additional band in the red region can be assigned to the $^4T_{1g} \Rightarrow {}^6A_{1g}$ transition of the Mn^{2+} ions in lattice sites with trigonally distorted octahedral and/or cubic local symmetry [10]. The Mn^{2+} emission band is characterized by inhomogeneous broadening caused by a distribution of crystal field parameters in low-symmetry (trigonally distorted octahedral) and high-symmetry (cubic) sites of the GaN film structure. In films of GaAlN-Mn the intensity of cathodoluminescence (figure 2, curve 3) is twice that of the GaN-Mn films.

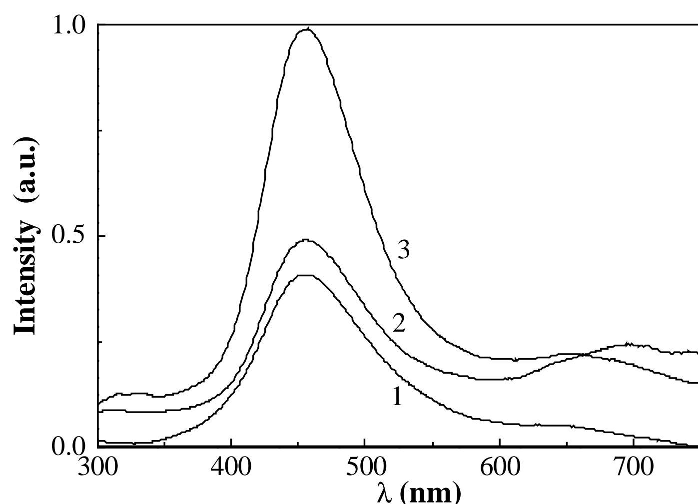

Figure 2
Cathodoluminescence spectra for thin films of GaN (1), GaN-Mn (2) and GaAlN-Mn (3) recorded at 300K and at 3.5 keV excitation energy.

3.3. ESR spectra of the Mn-doped GaN thin films

For confirmation of the incorporation of Mn into the GaN lattice, the ESR spectra of as-grown films were investigated. In the undoped GaN films no ESR spectra could be detected, whereas GaN-Mn films show a complex ESR spectrum, with intensity increasing with film thickness (figure 3). The observed ESR spectrum consists of three absorption bands with effective g-values: g_{eff}=6, g_{eff}=4.3, and g_{eff}=2.0 and is characteristic of Mn^{2+} ions in complex

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compounds [11]. On the basis of these ESR spectra, the Mn^{2+} impurity is incorporated into the lattice of the GaN films as Mn^{2+} in both low-symmetry (resonance lines with g_{eff}=6 and g_{eff}=4.3) and high-symmetry (resonance line with ge_{ff}=2.0) sites.

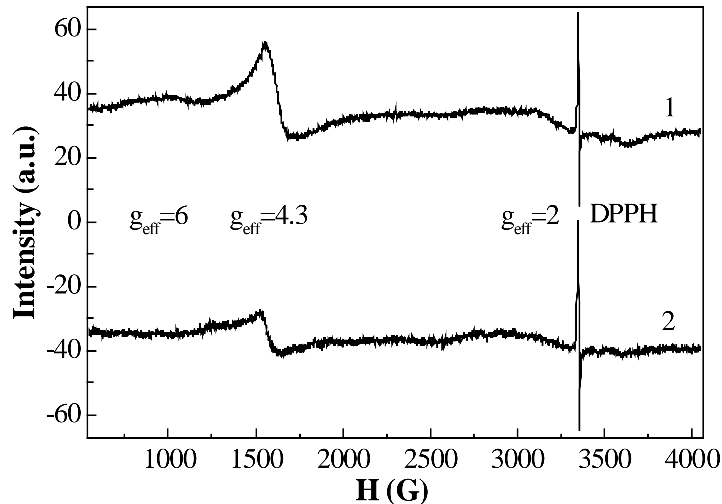

Figure 3. ESR spectra of the as-growth GaN-Mn films with thickness 0.55 µm (1) and 0.40 µm (2), recorded at 300 K.

3.4 Mechanism and nature of the luminecscence of GaN films

Investigations of the electro- and photo-conductivity of gallium nitride thin films in relationship with the conditions of their synthesis show that intrinsic defects are primarily responsible for the observed luminescence in the visible region of the spectrum. We established that the nitrogen vacancies are the most probable donor-type defects in the undoped gallium nitride [12, 13].

A correlation has been found between the luminescence intensity and the density of shallow level donors. These donors are nitrogen vacancies and determine the conductivity of the GaN films. The luminescence intensity increases with conductivity (figure 4). This correlation is in agreement with the donor-acceptor nature of the luminescence center. Evidently the luminescent center is formed by pairs which consist of shallow-level donors and deep-level acceptors

The shallow donors are nitrogen vacancies, and deep acceptors are probably related to magnesium- or zinc type dopants. The proposed model is in agreement with literature data [14, 15] obtained on optically-detected magnetic resonance in GaN:Mg crystals which show that shallow-level donors are included in centers responsible for blue luminescence in GaN doped with magnesium. The higher intensity of cathodoluminescence in GaAlN-Mn films may be caused by the magnification of efficiency of formation of donor-acceptor centers of luminescence in these films.

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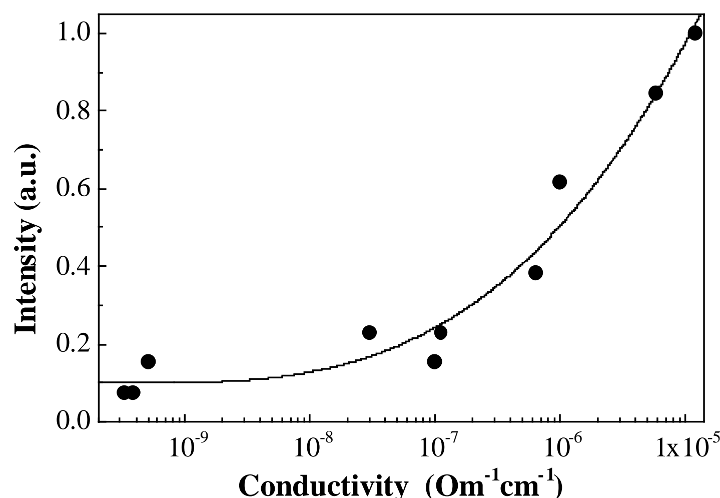

Figure 4. Luminescence intensity vs. conductivity of GaN thin films at 300K.

4. CONCLUSIONS

The technologies of fabrication of thin film phosphors based on nitrides GaN using the rf-magnetron method are developed. It was found that the volume of the unit cell in GaN thin films decreases with increase in substrate temperature. This can be associated with the reduction of the density of defects in the Ga and N close-packing layers. The GaN thin films obtained show cathodoluminescence in the blue region of the spectrum with a peak at 450 nm. In the GaN-Mn films, an additional weak emission band peaked at 690 nm has been observed. It can be assigned to the $^4T_{1g} \Rightarrow {}^6A_{1g}$ transition of the Mn^{2+} ions. The presence of the Mn^{2+} ions in both low- and high-symmetry sites in the GaN film structures is confirmed by ESR spectroscopy. A correlation has been found between the luminescence intensity and the density of shallow level donors (nitrogen vacancies which determine the conductivity of the GaN films). Such correlation is in agreement with the donor-acceptor nature of luminescence centers in GaN.

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