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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 structural properties of films are studied. Luminescence and electron spin resonance (ESR) spectra of GaN and GaN-Mn thin films have been studied. The correlation between cathodoluminescence intensity and conductivity of GaN films has been found. The nature of emission centers in GaN and GaN-Mn thin films is discussed as well as mechanism of luminescence in these films is proposed.

INTRODUCTION

Gallium nitride besides light emission diode (LED) applications also is very prospective material for using as an active luminescent layer in field emission displays (FED) [1-3]. In the case of obtaining efficient impurity luminescence it can substitute zinc sulfide which shows the efficien_ luminescen__, however is not stable enough. The crystallochemical 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) for Cr^{3+} with creation of high-spin stable state for d^3 configuration can take place. Activation of GaN with Mn may result in stabilization of high- and low- spin states with stable crystal structure configuration. Also the heterovalent substitution of Ga(AL) for Mn^{2+} in low concentrations is possible in the cases of partial substitution of nitrogen atoms for oxygen or creation of 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 external light efficiency is higher if polycrystalline layers are used [4] so the magnetron-sputtering technique is suitable for thin film phosphors deposition. The present work is directed on an investigation of luminescence of nano / polycrystalline GaN thin films synthesized by rf-magnetron sputtering.

2. EXPERIMENTAL

As a target for rf-magnetron sputtering the metallic gallium was used [5]. As substrates for deposition monocrystalline sapphire, amorphous quartz with ZnO and $MgAl_2O_4$ buffer layers [6] as well as mica sheets were used. Sputtering was conducted in the pure nitrogen atmosphere under pressures from $5 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ Torr. Substrate temperature was varied from 450°_ to 650°_. The rf-discharge power was in the 50 ÷ 200 W range.

The quality control of thin films dependent on deposition conditions was made by absorption edge position, refraction index, and transparency of the films in 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 registered 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 dipheny lp icry lhydrazyl (DPPH) *g*-marker (g=2.0036±0.0001). For ESR study the samples of thin films were prepared in the mica sheets. Cathodoluminescence spectra at e-beam energy exitation beetwen 1 and 6 KeV and current density 3 mA cm^{-2} were measured at 300 K.

3. RESULTS AND DISCUSSION

3.1. Technology and structure of the GaN thin films

One of the main factors, which affect formation of gallium nitride films is efficiency of ionization of nitrogen molecules. With this purpose the spectral parameters of rf-discharge plasma emission of nitrogen used as a working gas were investigated. It was found that the most efficient formation of GaN takes place when the most intensive line in emission spectra is 391.4 nm which correspond to ionized nitrogen molecules N_2^+.

The technological conditions of rf-magnetron sputtering of nitride-based thin films dependent on working gas composition, rf-discharge power, and substrate temperature were investigated. It was found that deposition rate increases with increasing of rf-discharge power and decreases with both increasing of substrate temperature and nitrogen pressure during deposition. The decreasing of deposition rate with the increasing of nitrogen pressure may be connected with the shortening of a free path length of gallium atoms.

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

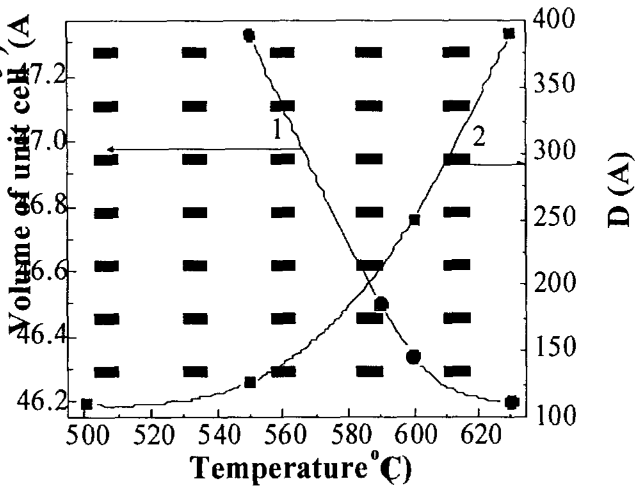

Figure 1. Dependencies of the unit cell volume (curve 1) and crystallite size (curve 2) on the substrate temperature for the GaN thin films, deposited on the [0001] sapphire substrate.

temperature during deposition were investigated. While increasing of the substrate temperature from 500 to 650°C the lattice parameter a of GaN films gradually decreases from 3.225 Å to 3.208 Å, the parameter c decreases from 5.281 Å to 5.217 Å, and the ratio c/a – from 1.636 to 1.629, which corresponds to calculated values. It was found that the value of unit cell volume decreases exponentially with increasing of temperature (figure 1, curve 1) tending to the value characteristic for the polycrystalline GaN samples (~46 $Å^3$). It can indicate on the reducing of close-packing defects of Ga and N atoms in film layers and its "hexagonal-cubic" layering. The nanocrystallyte size grows exponentially from 10 nm to 40 nm with increasing of substrate temperature at deposition from 450 to 600°_ (figure 1, curve 2).

The Auger-profiling analysis showed minor non-stoichiometry of the GaN films composition in the near-surface region (~200 Å) caused by the presence of oxygen, carbon and excessive gallium atoms, whereas at the depths more than 300 Å the composition of 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 spectrum with a peak at 450 nm and color coordinates x=0.198, y=0.206 (figure 2, curve 1). When dopping gallium nitride with manganese, the increase of intensity of blue emission is observed together with emerging of emission in the red region of spectrum with maximum about 690 nm. (figure 2, curve 2). This additional band in the red region can be assigned to the $^4T_{1g} \Rightarrow {}^6A_{1g}$ transition of the Mn^{2+} ions in the lattice sites with trigonally distorted octahedral and/or cubic local symmetry [10]. The Mn^{2+} emission band are characterized by ingomogeneous broadening caused by distribution of crystal field parameters in low-symmetry (trigonally distorted octahedral) and high-symmetry (cubic) sites of the GaN film structure. In films GaAlN-Mn the intensity of a cathodoluminescence (figure 2, curve 3) is incremented twice as contrasted to by films GaN-Mn.

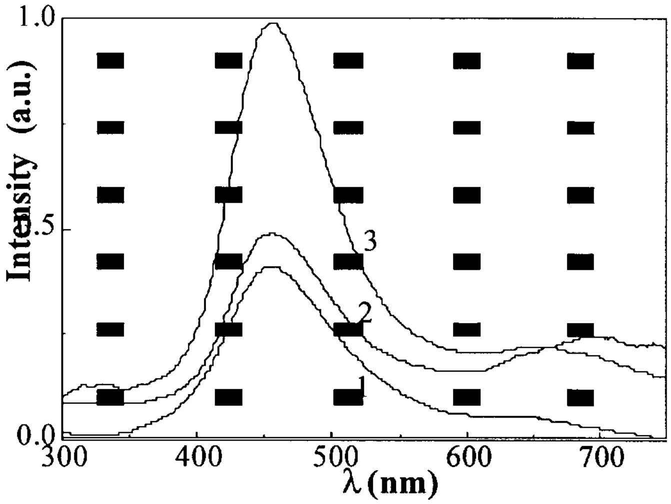

Figure 2 Cathodoluminescence spectra at 3.5 kev of GaN (1), GaN-Mn (2) and GaAlN-Mn (3) thin films, registered at 300K.

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

For confirmation of the Mn incorporation into the GaN lattice the ESR spectra of as-grown films were investigated. In the undoped GaN films any ESR spectra have not been detected, whereas the GaN-Mn show complex ESR spectrum, intensity of which increases with increasing of 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 for Mn^{2+} ions in the complex compounds [11]. On the basis of ESR spectra analysis it was shown, that the Mn^{2+} impurity is incorporated into the lattice of GaN films as Mn^{2+} ions 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.

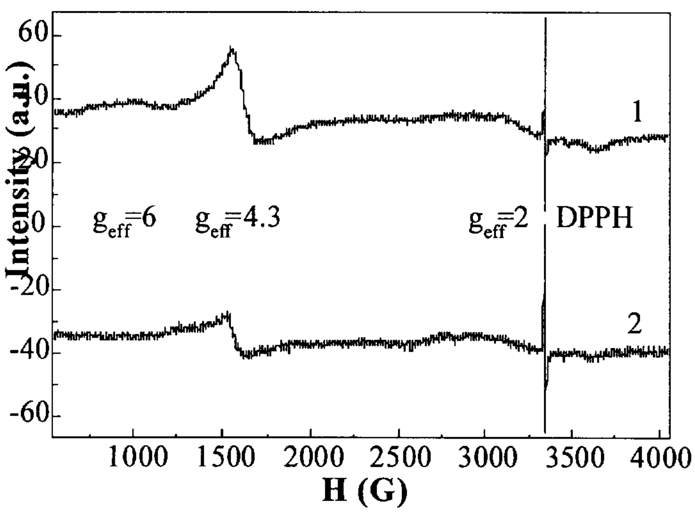

Figure 3. ESR spectra of the as-growth GaN-Mn films with thickness 0.55 μm (1) and 0.40 μm (2), registered at 300 K.

3.4 Mechanism and nature of luminecscence of GaN films

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

The correlation between luminescence intensity and shallow level donors density – nitrogen vacancies, which determine the value of GaN films conductivity, has been found. The luminescence intensity increases with increasing of conductivity (figure 4). Such correlation is in agreement with donor-acceptor nature of luminescence center. Evidently, the center of luminescence form the donor-acceptor pairs consisting 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 showed that shallow-level donors are included in centers responsible for blue luminescence in GaN doped with magnesium. The higher intensity of a cathodoluminescence in films GaAlN-Mn may be caused the magnification of efficiency of formation of donor-acceptor centers of luminescence in these films.

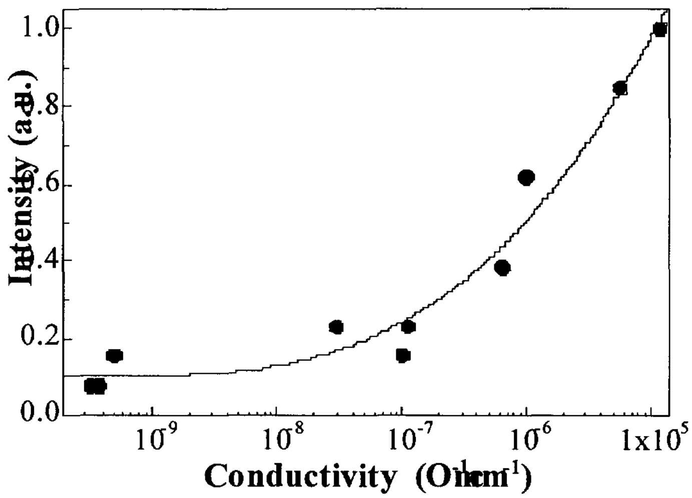

Figure 4. Luminescence intensity vs. conductivity of GaN thin films at 300K.

4. CONCLUSIONS

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

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REFERENCES

1. S.Okamoto, Y.Kanemitsu, K.Abbe, S.Kobayashi and S.Nonomura. *The Third International Conference on the Science and Technology of Display Phosphors*. Huntington Beach, CA, pp. 159-162, Nov. 3-5, 1997.
2. V.Bondar, M.Grytsiv, A.Groodzinsky and M.Vasyliv, Cathodoluminescent characteristics and light technical parameters of thin film screens based on oxides and oxisulfides of rare-earth elements, *Proc. SPIE*, **2648**, 339-342 (1996).
3. V.Bondar, M.Grytsiv, A.Groodzinsky and M.Vasyliv, A.Chakhovskoi, C.Hunt, M.Malinowsky and T.Felter, Thin film energy-control variable color cathodoluminecscent screens, *J. Electrochem. Soc.* **144**, No. 2, 704-707 (1997).
4. V.Bondar, Electrical properties of microstructural thin film oxide phosphors, *Materials Science and Engineering B*, **69**, 223-225 (1999).
5. V.Bondar, I.Kucharsky, B.Simkiv, L. Axelrud, V.Davydov, Yu.Dubov and S.Popovich, Low-temperature synthesis of gallium nitride thin films using reactive rf-magnetron sputtering, *Phys. Stat. Solidi (a)*, **176**, 329-332 (1999).
6. V.Bondar, Properties of nanocrystalline gallium nitride thin films grown on monocrystalline substrates and buffer layers, *Phys. Stat. Solidi (a)*, **176**, 635-638 (1999).
7. V.Lysoivan, S.Gromilov. *Aspects of accuracy in polycrystalline diffractometry*, (Nauka, Novosibirsk, 1989 (in Russian)).
8. V.K.Pecharski, L.D.Axelrood and P.Yu.Zavalii, On the method of accounting of preferred orientation (texture) in powder samples while investigation of atomic structure of materials, *Crystallography*, **32**, No. 6, 874-877 (1987).
9. A.Segmuller, Characterization of epitaxial thin films by X-ray diffraction, *J. Vac. Sci. Technol.* **A 9**, No. 4, 2477-2480 (1991).
10. D.T. Sviridov, R.L. Sviridova and Yu.F. Smirnov, *Optical spectra of transition metalIons in crystals*, (Nauka, Moscow, 1976 (in Russian)).
11. J. Kliava, EPR spektroskopia neuporiadochennych tverdych tel (EPR spectroscopy of disordered solids), (Zinatne, Riga, 1988 (in Russian)).
12. V.Bondar, V.Vasyltsiv, I.Kucharsky and B.Simkiv, The influence of intrinsic defects on electrophysical properties of gallium nitride films, *J. Physical Studies*, **3**, No. 4, 498-501 (1999). (in Ukranian).

13. V.Bondar, V.Vasyltsiv, I. Kucharsky and Yu. Dubov, *The Third International Conference on Nitride Semiconductors (ICNS3),* Montpellier, France, Mo-P072, p.31, July 5-9 1999.
14. P.Perlin, T. Suski, H. Teisseyre, M. Leszczynski, I. Grzegory, J. Jun, S. Porowski, P. Boguslawski, J. Bernholc, J. C. Chervin, A. Polian and T. D. Moustakas, Towards the identification of the dominant donor in GaN, *Phys. Rev. Letters,* **75**, No. 2, 296-299 (1995).
15. M.W. Bayerl , M.S. Brandt , E.R. Glaser , A.E. Wickenden , D.D. Koleske , R.L. Henry , M. Stutzmann, The origin of red luminescence from Mg-doped GaN, *Phys. Stat. Solidi (b),* **216**, 547-550 (2000).