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Growing the epitaxial undoped and N-doped ZnO films by radical beam gettering epitaxy

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Abstract. Epitaxial undoped and N-doped ZnO films were obtained using the method of radical beam gettering epitaxy. Structural and luminescent properties of the obtained films were researched. In both cases, there can be seen orientation of the films along *c*-axis. In the spectrum of low-temperature photoluminescence of N-doped ZnO films, observed was a peak 3.31 eV probably of a neutral acceptor-bound exciton N_O. The nature of donor-acceptor band 3.23 eV and green band 2.56 eV was discussed.

Keywords: ZnO, N-doping, photoluminescence, intrinsic defects.

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1. Introduction

Zinc oxide is one of the most popular semiconductor materials applied to produce the devices that use surface acoustic waves, elements of integrated optics, gas sensors and solar cells. However, ZnO application is of particular interest as a base material for obtaining diode and laser structures that radiate in blue and ultraviolet region [1, 2]. Among wide gap semiconductor combinations, the optical and electrophysical properties of II-VI ZnO with the width of the bandgap close to 3.437 eV at 2 K [3] are similar to GaN [3]. Large exciton binding energy (60 meV) as compared to GaN (24 meV) is the main advantage of ZnO, which allows to get effective exciton luminescence at the room temperature. In order to create light-emitting devices based on ZnO, it is necessary to obtain material of both *n*- and *p*-type. There are a number of reports on obtaining the *n*-type ZnO with the use of elements of group III, such as Al, Ga [4, 5]. However, at present obtaining *p*-type material is a complex technological problem [6]. It is connected with the fact that ZnO films and single crystals have *n*-type conductivity due to the large number of donor intrinsic defects, such as interstitial zinc Zn_i or oxygen vacancies V_O [1, 2, 7]. In recent years the interest to ZnO has grown because of reports on successful obtaining of *p*-type ZnO owing to doping by acceptors of group V (N, As, P) [8-11], including co-doping [12-14]. In the paper submitted by us, the structural and photoluminescent (PL) properties of the undoped and N-doped ZnO were researched.

2. Experimental

Thin undoped and N-doped ZnO films were obtained using the original method of radical beam gettering epitaxy at the temperature of 500 to 700 ºC [15, 16]. The essence of the method consists in the thermal annealing of ZnSe substrate in atomic (radicals) oxygen. Atomically clean surfaces of ZnSe (220) obtained by chipping in vacuum were used as a substrate. In the annealing process, the growth of surface layers on a crystalline matrix takes place, and one of the components (oxygen) comes from a gas phase, while zinc atoms diffuse to the surface from the substrate volume. Oxygen O_2 (99.999 %) and NO gases are used as sources of atomic oxygen and nitrogen dopants to obtain undoped and N-doped ZnO. Atomic oxygen and nitrogen were obtained in RF-discharge with the power 100 W at pressures from 0.1 up to 10 Pa. Separation of charged particles was carried out using a strong permanent magnetic field. The flux of atomic (radicals) oxygen close to the surface of the substrate was $J_O = 10^{17}\ \text{cm}^{-2}\text{s}^{-1}$.

The structure and crystalline orientation of the films were studied using an X-ray three-crystal diffractometer with the use of CuK_α radiation. The atomic force microscope was applied to study the morphology of the surface. The PL spectra were taken at helium temperatures. The N_2 laser (337.1 nm) was used as an excitation source.

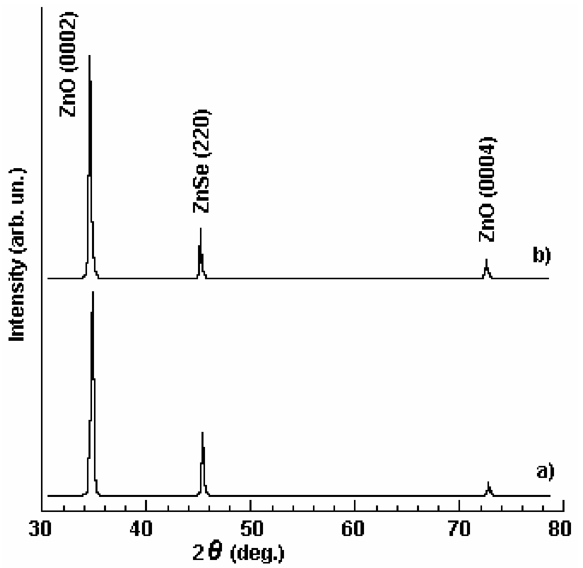

Fig. 1. X-ray diffraction data of the ZnO thin films: undoped (a) and N-doped (b). Both films were grown on ZnSe substrate at the temperature 600 ºC.

3. Results and discussion

The thicknesses of a typical as-grown layer employed in this work are about 0.5 µm. Fig. 1 shows the typical XRD profiles of the as-grown undoped (a) and N-doped (b) ZnO thin films at the substrate temperature 600 ºC. The peak at the angle $2\theta \approx 34.45°$ can be observed in both cases. It suggests that the ZnO films exhibit the (0002) preferential orientation with the *c*-axis perpendicular to the substrate. When the temperature is varied, the intensity of the (0002) peak increases and reaches the maximum value at 600 ºC. It can be expected that the ZnO films grown at 600 ºC possess better qualities. The full-width at half-maximum (FWHM) of the peak (0002) for undoped and N-doped ZnO films measures 0.154º and 0.136º, respectively. Wang *et al.* [17] also noted higher quality of the ZnO:N films obtained using the MOCVD method which agrees well with our results.

The surface morphology of undoped and N-doped ZnO films is shown in Fig. 2. In both cases, the films have smooth surfaces with the surface roughnesses 25 and 7 nm, respectively. It is obvious that the N-doped ZnO films have a higher surface quality, which agrees well with the results of XRD measurements. It is necessary to point out that with the increase in annealing temperature the degree of roughness increases, which can be probably caused by the increase in growth rate and desorption of film components from the surface.

Fig. 3 shows the low temperature PL spectra of undoped and N-doped ZnO films. In the spectrum of the undoped ZnO films, there is an ultraviolet peak 3.36 eV of a neutral donor-bound exciton (D^0, X) [1, 2] and a wide band with a peak at 2.4 eV. PL properties of the undoped ZnO films are studied in detail by us in our work [18]. The nature of the 2.4 eV band remains, to a great extent, debatable and is connected with the oxygen vacancy V_O, interstitial zinc Zn_i, and zinc vacancy V_{Zn} [1, 2, 7, 19, 20]. The PL N-doped ZnO spectrum (Fig. 3b) includes the bands 3.31, 3.24, and 2.23 eV. It is possible to connect the observed band at 3.31 eV with (A^0, X) radiation, where the nitrogen dopant N_O acts as an acceptor. At present, there is certain identification of the position for the given band. In the case of MBE growth of N-doped ZnO films, Look *et al.* [21] observed the peak at 3.315 eV that was connected with (A^0, X) radiation. Vaithianathan *et al.* [11] observed the peak at 3.2568 eV that can be connected with various technological conditions of obtaining N-doped ZnO films. The observed peak at 3.24 eV is connected with recombination on donor-acceptor pairs (DAP) [21-23]. The energy of activating the shallow acceptor can be

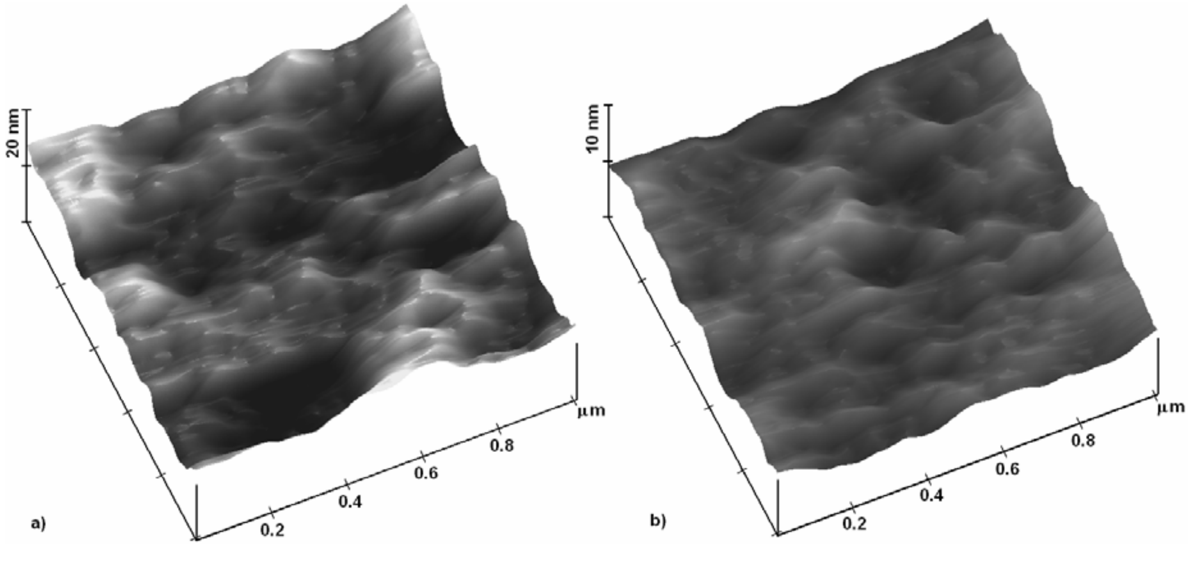

Fig. 2. AFM 3D images surface undoped (a) and N-doped (b) films ZnO grown on ZnSe substrate at the temperature 600 ºC.

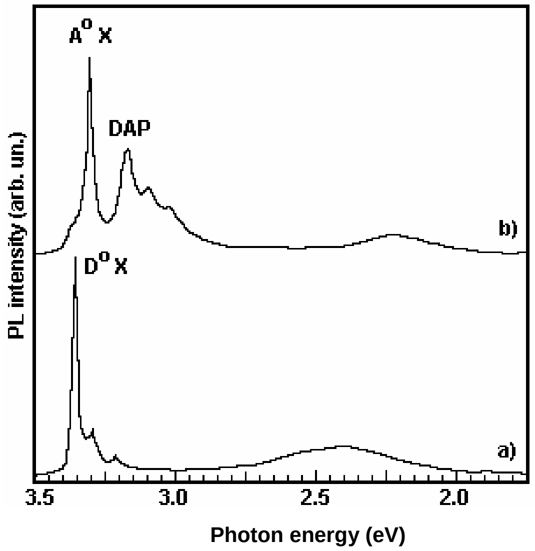

Fig. 3. PL spectrum of the undoped (a) and N-doped (b) thin films ZnO measured at 4.2 K with N_2 laser excitation.

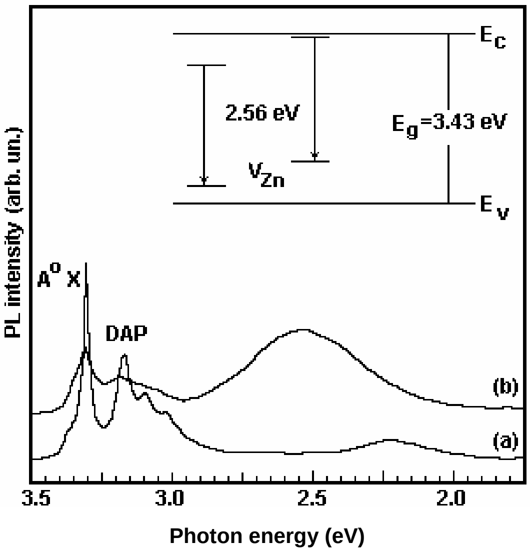

Fig. 4. PL spectrum and N-doped thin films ZnO after annealing in atomic oxygen at 600 °C; annealing time 1 h.

determined from the peak position of DAP band using the correlation [23]: $E_A = (E_g - E_{DA}) - E_0 + \frac{\varepsilon e}{r}$, where E_A is the energy of acceptor ionization, E_D is the energy of donor ionization (≈ 60 meV), E_g is the bandgap, E_{DA} is the peak of DAP radiation, and $\frac{\varepsilon e}{r}$ is the member taking into account the Coulomb interaction between the donor and acceptor (≈10 meV [23]). The calculation value of acceptor ionization energy makes ≈140 meV, which agrees well with the papers [11, 23] and is close to the theoretical value [24].

Radiation from the deep levels close to 2.23 eV can be also connected with the nitrogen dopant. The given band was observed in many works [6, 17, 21], which in opinion of the authors, is connected with the presence of nitrogen as an acceptor. With the purpose to determine the intrinsic defects role in forming the given band, the N-doped ZnO films were annealed in the atmosphere of atomic oxygen. The annealing caused the substantial changes in the PL spectrum (Fig. 4).

There is a decrease of the intensity of the peaks 3.31 and 3.24 eV as well as the shift of the 2.23 eV band into the short-wave region 2.56 eV. In the conditions of heat treatment with the increased content of atomic oxygen, the following reactions are possible:

$$\mathrm{O}_{(g)} + \mathrm{V}_\mathrm{O}^\times = \mathrm{O}_\mathrm{O}^\times,\ \left[\mathrm{V}_\mathrm{O}^\times\right] \propto P_\mathrm{O}^{-1}, \qquad (1)$$

$$\mathrm{O}_{(g)} = \mathrm{O}_\mathrm{O}^\times + \mathrm{V}_\mathrm{Zn}^\times,\ \left[\mathrm{V}_\mathrm{Zn}^\times\right] \propto P_\mathrm{O}, \qquad (2)$$

$$\mathrm{Zn}_i + \mathrm{O}_{(g)} = \mathrm{Zn}_\mathrm{Zn} + \mathrm{O}_\mathrm{O},\ \left[\mathrm{Zn}_i\right] \propto P_\mathrm{O}^{-1}, \qquad (3)$$

$$\mathrm{N}_\mathrm{O} + \mathrm{O}_{(g)} = \mathrm{O}_\mathrm{O}^\times + \mathrm{N}_i,\ \left[\mathrm{N}_\mathrm{O}\right] \propto P_\mathrm{O}^{-1}, \qquad (4)$$

where $\left[\mathrm{V}_\mathrm{O}^\times\right]$ and $\left[\mathrm{V}_\mathrm{Zn}^\times\right]$ are the concentrations of oxygen and zinc neutral vacancies, $\left[\mathrm{Zn}_i\right]$ and $\left[\mathrm{N}_\mathrm{O}\right]$ are the concentrations of interstitial zinc and nitrogen in the oxygen sublattice, respectively.

Taking into account the reactions (1)-(4) the concentration of $\left[\mathrm{V}_\mathrm{O}^\times\right]$, $\left[\mathrm{Zn}_i\right]$, and $\left[\mathrm{N}_\mathrm{O}\right]$ will decrease with the increase in oxygen pressure, and $\left[\mathrm{V}_\mathrm{Zn}^\times\right]$ will increase. Obviously, the observed changes in the PL spectrum are caused by redistribution of composition of intrinsic defects. With regard to the power position of the zinc vacancy in ZnO, there are certain divergences in literature. Most authors inclined to think that the zinc vacancy has the local level of E_V+ 0.8 eV [19], with which they associate the green band in the region of 2.4 to 2.6 eV [19, 20]. However, the recent paper [25] shows that the zinc vacancy creates the level E_V+ 0.3 eV. The existence of such a "shallow" level in a case of the green band in PL spectra must suppose the existence of a donor level ≈0.5 eV below the bottom of the conduction band. It is possible that the given level causes the intrinsic defect Zn_i [25, 26]. As was shown in our paper [27], at the flux of atomic oxygen J_O= 10^{18} cm^{-2}s^{-1} the concentration of zinc vacancies makes 10^{18} cm^{-3}. It allows to assume that the band 2.56 eV is caused by the transitions shallow donor-deep acceptor V_Zn (insert of Fig. 4).

4. Conclusions

We researched the growth of the undoped and N-doped ZnO films on ZnSe substrates by using the method of radical beam gettering epitaxy. In the PL spectra of N-doped ZnO films, there can be seen the bands 3.31, 3.23, and 2.56 eV caused by the nitrogen dopant. The optical depth of the N_O acceptor centre location makes

≈ 140 meV. The observed shift of deep-level transitions after the treatment of N-doped ZnO films in atomic oxygen is caused by the change of composition of intrinsic defects. We assume that the band 2.56 eV is caused by the deep-level transitions connected with the zinc vacancy that has the level E_V + 0.8 eV.

References

1. D.C. Look, B. Claflin, Ya.I. Alivov, and S.J. Park, The future of ZnO light emitters // *Phys. status solidi* (*a*) **201**, p. 2203-2212 (2004).
2. Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Markoç, A comprehensive revive of ZnO materials and devices // *J. Appl. Phys.* **98**, p. 041301-041404 (2005).
3. V.A. Kaprpina, V.I. Lazorenko, C.V. Lashkarev *et al.*, Zinc oxide – analogue of GaN with new perspective possibilities // *Cryst. Res. Technol.* **39**, p. 980-992 (2004).
4. S.Y. Myong, S.J. Baik, Ch.H. Lee, W.Y. Cho and K.S. Lim, Extremely transparent and conductive ZnO:Al thin films prepared by photo-assisted metalorganic chemical vapor deposition (photo-MOCVD) using $AlCl_3(6H_2O)$ as new doping material // *Jpn J. Appl. Phys.* **36**, p. L1078-L1081 (1997).
5. M. Hiramatsu, K. Imaeda, N. Horio, and M. Nawata // *J. Vac. Sci. Technol. A* **16**, p. 669 (1998).
6. K. Iwata, P. Fons, A. Yamada, K. Matsubara, S. Niki, Nitrogen-induced defects in ZnO:N grown on sapphire substrate by gas source MBE // *J. Cryst. Growth* **209**, p. 526-531 (2000).
7. S.B. Zang, S.-H. Wei, and A. Zunger, Intrinsic n-type versus p-type doping asymmetry and the defect physics of ZnO // *Phys. Rev. B* **63**, p. 075205-075211 (2001).
8. K. Minegishi, Y. Koiwai, K. Kikuchi, K. Yano, M. Kasuga and A. Shimizu, Growth of p-type zinc oxide films by chemical vapor deposition // *Jpn J. Appl. Phys.* **36**, p. L1453-L1455 (1997).
9. H.W. Liang, Y.M. Lu, D.Z. Shen, Y.C. Liu, J.F. Yan, C.X. Shan, B.H. Li, Z.Z. Zhang, J.Y. Zhang, X.W. Fan, P-type ZnO thin films, prepared by plasma molecular beam epitaxy using radical NO // *Phys. status solidi* (*a*) **202**, p. 1060-1065 (2005).
10. Y.R. Ryu, S. Zhu, D.C. Look, J.M. Wrobel, H.M. Jeong, H.W. White, Synthesis of p-type ZnO films // *J. Cryst. Growth* **216**, p. 330-334 (2000).
11. V. Vaithianathan, Y.H. Lee, B.-T. Lee, S. Hishita, and S.S. Kim, Doping of As, P and N in laser deposited ZnO films // *J. Cryst. Growth* **287**, p.85-88 (2006).
12. M. Joseph, H. Tabata and T. Kawai, *p*-type electrical conduction in ZnO thin films by Ga and N codoping // *Jpn J. Appl. Phys.* **38**, p. L1205-L1207 (1999).
13. K. Nakahara, H. Takasu, P. Fons, A. Yamada, K. Iwata, K. Matsubara, R. Hunger and S. Niki, Growth of N-doped and Ga+N-codoped ZnO films by radical source molecular beam epitaxy // *J. Cryst. Growth* **237-239**, p. 503-508 (2002).
14. Z.-Z. Ye. F. Zhu-Ge, J.-G. Lu, Z.-H. Zhang, L.-P. Zhu, B.-H. Zhao, J.-Y. Huang, Preparation of p-type ZnO films by Al+N-codoping method // *J. Cryst. Growth* **265**, p. 127-132 (2004).
15. A.N. Georgobiani, M.B. Kotlyarevsky, and I.V. Rogozin, Phase content and photoluminescence of ZnO layers obtained on ZnSe substrates by radical-beam gettering epitaxy // *Nucl. Phys. B (Proc. Suppl.)* **78,** p. 484-487 (1999).
16. A.N. Georgobiani, M.B. Kotlyarevsky, and I.V. Rogozin, Methods of high-energy chemistry in the technology of wide-gap chalcogenide semiconductors // *Inorganic Materials* **41,** Suppl. **1**, p. S1-S18 (2004).
17. X. Wang, S. Yang, J. Wang, M. Li, X. Jiang, G. Du, X. Liu, R.P.H. Chang, Nitrogen doped ZnO film grown by the plasma-assisted metal-organic chemical vapor deposition // *J. Cryst. Growth* **226**, p. 123-129 (2001).
18. A.N. Georgobiani, M.B. Kotlyarevskii, V.V. Kidalov, L.S. Lepnev, I.V. Rogozin, Luminescence of native-defect p-type ZnO // *Neorganich. Mater.* **37**, p. 1095-1098 (2001).
19. A.F. Kohan, G. Ceder, D. Morgan, and C.G. Van de Walle, First-principles study of native point defects in ZnO // *Phys. Rev. B* **61**, p. 15019-15027 (2000).
20. X. Yang, G. Du, X. Wang *et al.*, Effect of post-thermal annealing on properties of ZnO thin film grown on c-Al_2O_3 by metal-organic chemical vapor deposition // *J. Cryst. Growth* **252**, p. 275-278 (2003).
21. D.C. Look, D.C. Reynolds, C.W. Litton, R.L. Jones, D.B. Eason, G. Cantwell, Characterization of homoepitaxial *p*-type ZnO grown by molecular beam epitaxy // *Appl. Phys. Lett.* **81**, p. 1830 (2002).
22. K. Tonke, Th. Gruber, N. Teofilov, R. Schonfelder, A. Waag, R. Sauer, Donor-acceptor pair transitions in ZnO substrate material // *Physica B* **308-310**, p. 945-948 (2001).
23. S. Yamauchi, Y. Goto, T. Hariu, Photoluminescence studies of undoped and nitrogen-doped ZnO layers grown by plasma-assisted epitaxy // *J. Cryst. Growth* **260**, p. 1-6 (2004).
24. C.H. Park, S.B. Zang, and S.-H. Wei, Origin of p-type doping difficulty in ZnO: The impurity perspective // *Phys. Rev. B* **66**, p. 073202-073204 (2002).
25. P.S. Xu, Y.M. Sun, C.S. Shi, F.Q. Xu, H.B. Pan, The electronic structure and spectral properties of ZnO and its defects // *Nucl. Instrum. & Meth. Phys. Res. B* **199**, p. 286-290 (2003).
26. C. Simpson and J.F. Cordaro, Characterization of deep levels in zinc oxide // *J. Appl. Phys.* **63**, p. 1781-1783 (1988).
27. M.B. Kotlyarevsky, I.V. Rogozin, and A.V. Marakhovsky, Kinetics of high-temperature defect formation in ZnO in the stream of oxygen radicals // *NATO Sci. Ser. II: Math., Phys. and Chem.* **194**, p. 25-34 (2005).