Optical Properties of Nitrogen-Doped Epitaxial ZnO Layers

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Abstract

Epitaxial nitrogen-doped ZnO (ZnO:N) films are obtained by the method of radical beam gettering epitaxy. Their optical properties are examined by means of transmission and photoluminescence (PL) spectroscopy. The as-grown ZnO:N films show high transmittance (about 90%) in the visible range. A peak at 3.31 eV is seen in the low-temperature PL spectrum of the N-doped ZnO films, which is probably due to a neutral acceptor-bound exciton N_O. Post-thermal annealing is performed on ZnO:N films in the atomic oxygen conditions. The PL of the annealed samples shows a strong response improvement, when compare with the non-annealed samples. The nature of the donor-acceptor band located at 3.23 eV and the 'green' band at 2.56 eV is discussed.

Key words: ZnO, N-doping, PL, intrinsic defects.

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Introduction

Zinc oxide is one of the most popular semiconductor materials applied in many devices that utilize surface acoustic waves, integrated optical elements, gas sensors and solar cells. Moreover, of a particular interest are applications of ZnO as a basic material for obtaining diode and laser structures radiating in 'blue' and ultraviolet spectral regions [1,2]. As for the characteristics of wide-gap semiconductor compounds, the optical and electro-physical properties of II-VI ZnO, whose band gap is equal to 3.437 eV at 2 K, are similar to those of GaN [3]. The main advantage of ZnO is a large binding energy of exciton (60 meV, while the corresponding parameter for GaN is only 24 meV). This allows one to get efficient exciton luminescence at the room temperature. In order to create light-emitting devices on the basis of ZnO, it would be necessary to obtain the material of both *n*- and *p*-types. There is a number of reports on obtaining the *n*-type ZnO with the aid of group III elements, such as Al and Ga [4,5]. Up to now, however, obtaining of the *p*-type material is a complex technological problem [6]. This is associated with the fact that both the films and single crystals of ZnO exhibit the *n*-type conductivity, owing to a large number of donor intrinsic defects, such as interstitial zinc (Zn_i) or oxygen vacancies (V_O) [1,2,7]. In the recent years the interest in ZnO has significantly grown because of reports on a success achieved in obtaining the *p*-type ZnO by means of doping it with the acceptors of group V (N, As and P) [8-11], including the case of co-doping [12-14]. In this paper we study the structural and photoluminescence (PL) properties of ZnO:N.

Experimental

N-doped thin films of ZnO were obtained by an original technique of radical beam gettering epitaxy employed at the substrate temperature T_{sub} = 500–700ºC [15]. The essence of the method consists in thermal annealing of ZnSe substrate in the atomic (radical) oxygen.

Atomically clean surfaces (220) of ZnSe obtained by chipping in vacuum were used as a substrate. In the process of annealing, growing of surface layers on a crystalline matrix takes place and one of the components (oxygen) comes from the gas phase, whereas the zinc atoms diffuse towards the surface from the substrate. While obtaining the N-doped ZnO, 99.99% pure NO gas was used as a source of atomic oxygen and nitrogen as a dopant. Atomic oxygen and nitrogen were obtained in RF-discharge with the power of 100 W at the pressure of 0.1–10 Pa. Separation of charged particles was carried out with the help of strong direct-current magnetic field. The flow of the atomic (radical) oxygen close to the substrate surface was $J_O = 10^{18}$ cm^{-2}s^{-1}. The films ZnO:N were annealed at 600ºC for 60 min in the atomic oxygen.

The optical properties were investigated using the setup KSVU-12 that incorporated MDR-23 grating monochromator. The spectra of PL were measured at liquid-helium temperatures. The luminescence was excited by a nitrogen laser (the wavelength of 337 nm).

Result and discussion

The thicknesses of typical as-grown layers employed in this work are about 0.5 μm. An X-ray diffraction peak in the angular region of $2\theta \sim 34.45^{\circ}$ can be clearly seen. This suggests that ZnO:N films exhibit preferential orientation (002), with the *c* axis perpendicular to the substrate. Fig. 1 shows typical optical transmission spectra of both ZnO:N and the undoped ZnO films measured at the room temperature. The fundamental absorption starts at about 350 nm. The transmission of ZnO:N films is almost identical to that of the undoped films. Let us stress that the transmittance for the majority of films in the visible range is more than 90%.

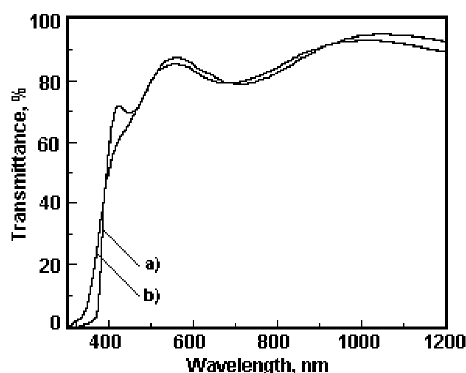


Fig. 1. Optical transmission spectra of N-doped (a) and undoped (b) thin ZnO films.

Fig. 2 presents the low-temperature PL spectra of the undoped and ZnO:N films grown at 600ºC. An ultraviolet peak at 3.36 eV prescribed to a neutral donor-bound exciton (D^0, X) [1,2] and a wide band with the maximum located at 2.4 eV are seen in the spectrum of the undoped ZnO films. Notice also that the structural and PL properties of the undoped ZnO films have been studied in detail in our earlier works [16-18].

To some extent, the nature of the band at 2.4 eV still remains debatable. It might be linked to the oxygen vacancy (V_O), interstitial zinc (Zn_i) and the zinc vacancy (V_{Zn}) [1,2,7,19,20]. The PL spectrum of ZnO:N (see Fig. 2b) includes the bands located at 3.31, 3.24 and 2.23 eV. It is possible to relate the band observed at 3.31 eV to the radiation of (A^0, X), where the nitrogen dope N_O acts as acceptor. At present there is no unequivocal identification of the given band. For the case of N-doped ZnO films grown with the molecular beam epitaxy, Look et al. [21] have suggested that the peak at 3.315 eV is associated with the radiation of (A^0, X). At the same time, Vaithianathan et al. [11] have connected the

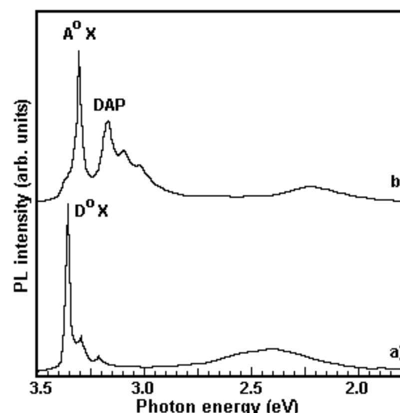


Fig. 2. PL spectra of undoped (a) and N-doped (b) thin films of ZnO measured at 4.2 K.

peak at 3.2568 eV with various technological conditions of obtaining ZnO:N films. The peak observed at 3.24 eV is related to recombination on donor-acceptor pairs (DAP) [21-23]. The energy of the shallow acceptor activation may be determined from the peak position of the DAP band, using the following relation [23]: $E_A = (E_g - E_{DA}) - E_D + \frac{\varepsilon e}{r}$, where E_A means the energy of acceptor ionization, E_D the energy of donor ionization (≈60 meV), E_g the band gap, E_{DA} the DAP radiation peak and $\frac{\varepsilon e}{r}$ the term that takes the Coulomb interaction between the donor and acceptor into account (≈10 meV [23]). The calculation of the acceptor ionization energy gives the value ≈140 meV that agrees well with the results [11,23] and is close to the corresponding theoretical value [24].

The radiation associated with the deep levels in the region of 2.23 eV could be also linked to the nitrogen dopant. The given band has been observed in many works [21,25]. According to those authors, it should be prescribed to the presence of nitrogen as an acceptor. In order to study the role of intrinsic defects in formation of the given band, we have annealed the ZnO:N films in the atmosphere of atomic oxygen. It has turned out that the annealing causes substantial changes in the PL spectrum (see Fig. 3).

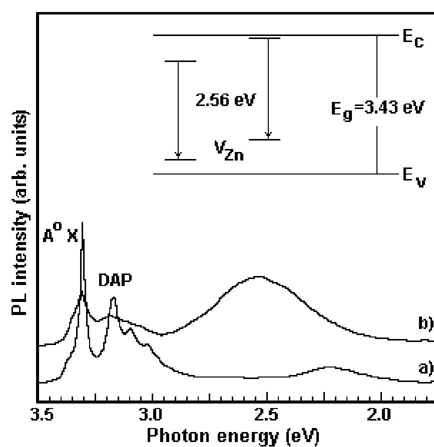
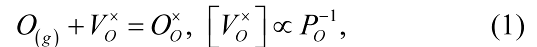
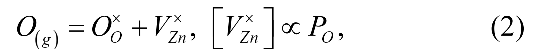


Fig 3. PL spectra of ZnO:N films measured at 4.2 K: (a) as-grown film and (b) film annealed in the atomic oxygen at 600ºC.

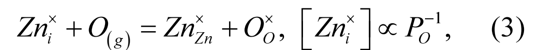
A decrease in the intensity of peaks at 3.31 and 3.24 eV and a shift of the 2.23 eV band towards a short-wavelength spectral region (its final location being at 2.56 eV) are then observed. The following reactions are possible under the conditions of thermal treatment and the increased content of atomic oxygen:



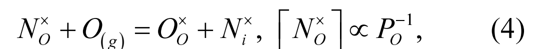
$$O_{(g)} + V_O^{\times} = O_O^{\times},\ \left[V_O^{\times}\right] \propto P_O^{-1}, \qquad (1)$$



$$O_{(g)} = O_O^{\times} + V_{Zn}^{\times},\ \left[V_{Zn}^{\times}\right] \propto P_O, \qquad (2)$$



$$Zn_i^{\times} + O_{(g)} = Zn_{Zn}^{\times} + O_O^{\times},\ \left[Zn_i^{\times}\right] \propto P_O^{-1}, \qquad (3)$$



$$N_O^{\times} + O_{(g)} = O_O^{\times} + N_i^{\times},\ \left[N_O^{\times}\right] \propto P_O^{-1}, \qquad (4)$$

where $\left[V_O^{\times}\right]$ and $\left[V_{Zn}^{\times}\right]$ are respectively the concentrations of neutral vacancies of oxygen and zinc, while $\left[Zn_i^{\times}\right]$ and $\left[N_O^{\times}\right]$ represent the concentrations of interstitial zinc and nitrogen in the sublattice of oxygen, respectively.

Taking into account the reactions (1)–(4), one can infer that the concentrations of $\left[V_O^{\times}\right]$, $\left[Zn_i^{\times}\right]$ and $\left[N_O^{\times}\right]$ would decrease with increasing oxygen pressure and the quantity $\left[V_{Zn}^{\times}\right]$ would then increase. Obviously, the observed changes in the PL spectrum should be caused by a redistribution of composition of the intrinsic defects. Some discrepancies are available in the literature concerning the energy position of zinc vacancy in ZnO. Most of the authors are inclined to consider that the zinc vacancy has the local level at E_V+0.8 eV [19] and a 'green' band in the region of 2.4–2.6 eV is related to that level [19,20]. However, the recent paper [26] has demonstrated that the zinc vacancy creates a level at E_V+0.3 eV. In case when the 'green' band is observed in the PL spectra, the existence of such a 'shallow' level must suppose the existence of a donor level ~ 0.5 eV below the bottom of the conduction band. It is possible to connect the intrinsic defect Zn_i with the given level [26,27]. We have shown in the work [28] that the concentration of zinc vacancies is equal to 10^{18} cm^{-3} under the atomic

oxygen flow $J_O=10^{18}$ cm^{-2}s^{-1}. This allows us to assume that the band located at 2.56 eV is caused by the transitions between the shallow donor and deep acceptor V_{Zn} (see the insert in Fig. 3).

Conclusions

We have grown ZnO:N films on ZnSe substrates, using the method of radical beam gettering epitaxy. The bands at 3.31, 3.23 and 2.56 eV caused by nitrogen dopant could be seen in the PL spectra of ZnO:N films. The optical depth of bedding of the acceptor centre N_O is equal to ≈140 meV. The observed shift of the deep-level transitions after the treatment of ZnO:N films in atomic oxygen is originated from the changing composition of intrinsic defects. We assume that the band at 2.56 eV is associated with the deep-level transitions related to zinc vacancy, whose level is located at E_V+0.8 eV.

References

1. Look D.C., Claflin B., Alivov Ya.I. and Park S.J. Phys. Stat. Sol. (a) **201** (2004) 2203.
2. Özgür Ü., Alivov Ya.I., Liu C., Teke A., Reshchikov M., Doğan S., Avrutin V., Cho S.-J. and Markoç H. J. Appl. Phys. **98** (2005) 041301.
3. Kaprpina V.A., Lazorenko V.I., Lashkarev C.V., Dobrowolski V.D., Kopylova L.I., Baturin V.A., Pustovoytov S.A., Karpenko A.Ju., Eremin S.A., Lytvyn P.M., Ovsyannikov V.P. and Mazurenko E.A. Cryst. Res. Technol. **39** (2004) 980.
4. Myong S.Y., Baik S.J., Lee Ch.H., Cho W.Y. and Lim K.S. Jpn. J. Appl. Phys. **36** (1997) L1078.
5. Hiramatsu M., Imaeda K., Horio N. and Nawata M. J. Vac. Sci. Technol. A **16** (1998) 669.
6. Look D.C., Jones R.L., Sizelove J.R., Garces N.Y., Giles N.C. and Halliburton L.E. Phys. Stat. Sol. (a) **195** (2003) 171.
7. Zang S.B., Wei S.-H. and Zunger A. Phys. Rev. **B63** (2001) 075205.
8. Minegishi K., Koiwai Y., Kikuchi K., Yano K., Kasuga M. and Shimizu A. Jpn. J. Appl. Phys. **36** (1997) L1453.
9. Liang H.W., Lu, Y.M. Shen D.Z., Liu Y.C., Yan J.F., Shan C.X., Li B.H., Zhang Z.Z., Zhang J.Y. and Fan X.W. Phys. Stat. Sol. (a) **202** (2005) 1060.
10. Ryu Y.R., Zhu S., Look D.C., Wrobel J.M., Jeong H.M. and White H.W. J. Cryst. Growth. **216** (2000) 330.
11. Vaithianathan V., Lee Y.H., Lee B.-T., Hishita S. and Kim S.S. J. Cryst. Growth. **287** (2006) 85.
12. Joseph M., Tabata H. and Kawai T. Jpn. J. Appl. Phys. **38** (1999) L1205.
13. Nakahara K., Takasu H., Fons P., Yamada A., Iwata K., Matsubara K., Hunger R. and Niki S. J. Cryst. Growth. **237-239** (2002) 503.
14. Ye Z.-Z., Zhu-Ge F., Lu J.-G., Zhang Z.-H., Zhu L.-P., Zhao B.-H. and Huang J.-Y. J. Cryst. Growth. **265** (2004) 127.
15. Georgobiani A.N., Kotlyarevsky (Kotlyarevskii) M.B. and Rogozin I.V. Inorganic Materials **41** Sppl. **1** (2004) S1.
16. Georgobiani A.N., Kotlyarevsky M.B. and Rogozin I.V. Nucl. Phys. B (Proc. Suppl.). **78**, (1999) 484.
17. Georgobiani A.N., Kotlyarevskii M.B., Kidalov V.V., Lepnev L.S. and Rogozin I.V. Inorganic Materials **37** (2001) 1095.
18. Kotlyarevskii M.B., Georgobiani A.N., Rogozin I.V. and Marakhovskii (Marakhovsky) A.V. J. Appl. Spectr. **70** (2003) 95.
19. Kohan A.F., Ceder G., Morgan D. and Van de Walle C.G. Phys. Rev. **B61** (2000) 15019.
20. Yang X., Du G., Wang X., Wang J., Liu B., Zhang Y., Liu D., Liu D., Ong H.C. and Yang S. J. Cryst. Growth. **252** (2003) 275.
21. Look D.C., Reynolds D.C., Litton C.W., Jones R.L., Eason D.B. and Cantwell G. Appl. Phys. Lett. **81** (2002) 1830.

22. Tonke K., Gruber Th., Teofilov N., Schonfelder R., Waag A. and Sauer R. Physica B **308-310** (2001) 945.
23. Yamauchi S., Goto Y. and Hariu T. J. Cryst. Growth. **260** (2004) 1.
24. Park C.H., Zang S.B. and Wei S.-H. Phys. Rev. **B66** (2002) 073202.
25. Iwata K., Fons P., Yamada A., Matsubara K. and Niki S. J. Cryst. Growth. **209** (2000) 526.
26. Xu P.S., Sun Y.M., Shi C.S., Xu F.Q. and Pan H.B. Nucl. Instrum. & Methods Phys. Res. **B199** (2003) 286.
27. Simpson C. and Cordaro J.F. J. Appl. Phys. **63** (1988) 1781.
28. Kotlyarevsky M.B., Rogozin I.V. and Marakhovsky A.V. NATO Sci. Ser. II: Math., Phys. and Chem. **194** (2005) 25.