Formation Mechanisms of Electrical Conductivity and Optical Properties of ZnO:N Film Produced by Annealing Treatment

2008 Chinese Phys. Lett. 25 2993

(http://iopscience.iop.org/0256-307X/25/8/070)

CHIN.PHYS.LETT. Vol. 25, No. 8 (2008) 2993

Formation Mechanisms of Electrical Conductivity and Optical Properties of ZnO:N Film Produced by Annealing Treatment *

WANG Xiang-Hu(王相虎)[1,2], YAO Bin(姚斌)[1**], WEI Zhi-Peng(魏志鹏)[1], SHEN De-Zhen(申德振)[1], ZHANG Zhen-Zhong(张振忠)[1], LU You-Ming(吕有明)[1], ZHANG Ji-Ying(张吉英)[1], FAN Xi-Wu(范希武)[1]

[1]*Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033*

[2]*Shanghai Dianji University, Shanghai 200240*

(Received 21 January 2008)

The effects of annealing on the chemical states of N dopant, electrical, and optical properties of N-doped ZnO film grown by molecular beam epitaxy (MBE) are investigated. Both the as-grown ZnO:N film and the film annealed in N_2 are of n-type conductivity, whereas the conductivity converts into p-type conductivity for the film annealed in O_2. We suggest that the transformation of conductivity is ascribed to the change in ratio of the N molecular number on O site $(N_2)_O$ to the N atom number on O site (N_O) in ZnO:N films under the various annealed atmosphere. For the ZnO:N film annealed in N_2, the percentage content of $(N_2)_O$ is larger than that of N_O, i.e. the ratio > 1, resulting in the n-type conductivity. However, in the case of the ZnO:N film annealed in O_2, the percentage content of $(N_2)_O$ is fewer than that of N_O, i.e., the ratio < 1, giving rise to the p-type conductivity. There is an obvious difference between low-temperature (80 K) PL spectra of ZnO:N film annealed in N_2 and that of ZnO:N film annealed in O_2. An emission band located at 3.358 eV is observed in the spectra of the ZnO:N film after annealed in N_2, this emission band is due to donor-bound exciton (D^0X). After annealed in O_2, the PL of the donor-bound exciton disappeared, an emission band located at 3.348 eV is observed, this emission band is assigned to acceptor-bound exciton (A^0X).

PACS: 71. 55. Gs, 78. 20. Ek

Wurtzite ZnO is a remarkable Ⅱ-Ⅵ semiconductor with a wide band gap of 3.37 eV and a large excitonic binding energy of 60 meV at room temperature, which makes it a promising material in applications of ultraviolet light-emitting diodes, laser diodes, and photodetectors.[1] However, one important problem should be overcome before ZnO could potentially make inroads into the world of optoelectronics devices: the growth of p-type-conductivity ZnO crystals. Among the various growth methods and various group-V dopant elements (N, P, As, and Sb), N is widely used as acceptor dopant to fabricate p-type-conductivity ZnO (ZnO:N), because the covalent bond length of Zn-N (1.88 Å) is close to that of Zn-O (1.93 Å).[2−8] In the fabrication process of N-doped p-type ZnO, the formation of N molecular on O site $(N_2)_O$, which is a double donor, is more easier than that of the N atom on O site (N_O) which is an acceptor in ZnO. As a result, the amount of $(N_2)_O$ is larger than that of N_O in the ZnO:N film,[4] giving rise to an n-type conductivity rather than a p-type conductivity. It is well known that the annealing treatment has an important effect on the electrical and optical properties of semiconductor thin film, because it can not only improve the crystal quality of semiconductor thin film but also lead to the changes of chemical states and percentage content of dopant.[9] With this notion in mind, we have examined the effects of annealing treatment on the chemical states of N dopant, electrical conductivity, and optical properties of the ZnO:N film prepared by means of molecular beam epitaxy (MBE). We find that the ZnO:N film annealed in O_2 can substantially enhance the peak at N_O leading to the appearance of p-type conductivity, and the origin of the formation mechanisms is also discussed.

The N-doped ZnO film was grown on a *c*-plane sapphire (Al_2O_3) substrate by MBE. A Knudsen effusion cell was used to evaporate elemental zinc (6N). The mixed-gas of O_2 and N_2 with a ratio of 1:1 was used as the oxygen and nitrogen sources, and the mixed gas was activated by an Oxford Applied Research model HD25 rf (13.56 MHz) atomic source. In the growth process, the radio frequency power of the mixed-gas plasma was 300 W and the flow rate controlled by a leak valve was kept at 1.0 sccm. The zinc source temperature was 245°C. In order to obtain a clean fresh surface, the substrates were chemically etched in a hot solution of H_2SO_4:H_3PO_4=3:1 at 160°C for 15 min. Before growth, the substrates were thermally pretreated at 700°C for 30 min. The ZnO:N film was grown at 425°C. The thickness of film is measured to be approximately 400 nm. After the growth of ZnO:N

*Supported by the Hundred Talents Programme of Chinese Academy Sciences, the Key Project of the National Natural Science Foundation of China under Grant No 60336020 and 50532050, and Outstanding Overseas Chinese Young Scholar Foundation under Grant No 60429403, and the Direct Allocation Grant of Research Committee of Hong Kong under Grant No DAG04/05.SC24.

**Email: binyao@jlu.edu.cn

film, the as-grown film was annealed in the O_2 and N_2 flow at 500, 600, and 700°C for 5 min, respectively. The electrical properties of the samples were measured by Hall analysis in the Van der Pauw configuration at room temperature by using a magnetic field of 15000 Gauss and a current automatically set by the Hall system (Lakeshore). The crystal structure of the samples was characterized by x-ray diffraction (XRD) using a D/max-RA x-ray diffractometer with Cu-$K\alpha(\lambda = 1.5418\,\text{Å})$. The elements chemical states and content in the ZnO:N films were measured by x-ray photoelectron spectrum (XPS) and secondary ion mass spectrometry (SIMS). The photoluminescence (PL) spectra were conducted on a He–Cd laser with 325 lines at the liquid nitrogen temperature.

Table 1. Electrical properties of as-grown ZnO:N and annealed in different atmospheres at various temperatures.

Temperature (°C)		Type	Resistivity (Ω cm)	Mobility $cm^2/(Vs)$	Carrier concentration (cm^{-3})
As-grown		n	4.1939	7.6415×10^{-1}	1.9600×10^{18}
Annealed in O_2	500	p	3.7966×10^{4}	1.9309×10^{-1}	9.4203×10^{14}
	600	p	1.0184×10^{5}	6.6981	1.7637×10^{13}
	700		High		
Annealed in N_2	500	p/n	1.7150×10^{1}	1.9016	1.9564×10^{17}
	600	n	3.8983×10^{3}	3.1301×10^{-1}	5.4680×10^{15}
	700	n	9.7700×10^{7}	2.9640	2.3177×10^{10}

The electrical properties of both as-grown and annealed ZnO:N films are listed in Table 1. It can be seen that the electrical properties are strongly influenced by annealing atmosphere and temperature. The as-grown ZnO:N film shows n-type conductivity with a carrier concentration of $1.96 \times 10^{18}\,\text{cm}^{-3}$, whereas the films annealed in O_2 and N_2 exhibit p-type and n-type conductivity, respectively. Moreover, the carrier concentration decreases with the increasing annealing temperature.

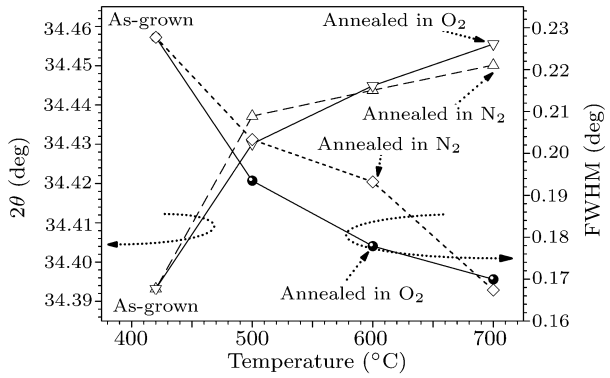

Fig. 1. Characteristics of 2θ of (002) diffraction peaks and FWHM as a function of the annealing temperature.

In order to investigate the conversion mechanism of the electrical conductivity induced by the annealing treatment, we carried out the measurements of XRD, SIMS, and XPS. The variations of (002) diffraction peak and full width at half maximum (FWHM) versus the annealed temperature are shown in Fig. 1. It can be seen that the (002) diffraction peaks shift towards the higher angle and the values of FWHM decrease with the increasing annealing temperature for both cases annealed in N_2 and O_2. From Fig. 1, it is found that the values of FWHM annealed in O_2 are smaller than those annealed in N_2 at the same annealing temperature. The change in (002) diffraction peak induced by the annealing treatment can be ascribed to the N molecular on O site ($(N_2)_O$)[10] or stress[11] in the ZnO:N film. It is worth noting that the band gap of a semiconductor is affected by the residual stress in the film. A tensile stress results in a decrease of the band gap, whereas a compressive stress causes an increase in the band gap.[12] In our samples, the measurements of the absorption spectra show that the band gap change little after the annealing process, indicating that the annealing treatment has little effect on the stress in the ZnO:N film grown by MBE. The change in (002) diffraction peaks and values of FWHM are mainly produced by the N molecule on O site, which are due to the facts that $(N_2)_O$ changes the lattice constants and decrease the crystallization quality of the ZnO film,[10] leading to increase of values of the FWHM.

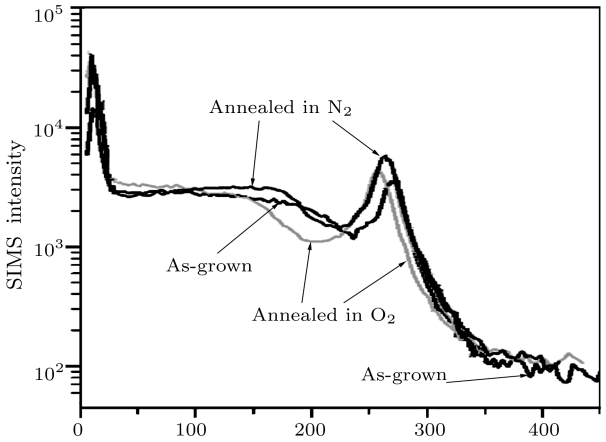

Fig. 2. N amount in the as-grown film and annealed in O_2 and N_2 at 600°C.

Figure 2 shows the amount of nitrogen element measured by SIMS in the as-grown film and films annealed in O_2 and N_2 at 600°C. The intensities of N

element were almost kept at the same level before and after annealing, indicating no change in the amount of nitrogen element after the annealing treatment. The results of SIMS suggest that N element cannot escape from the ZnO:N film after the annealing treatment. However, SIMS can only measure the total number of N element, and it cannot detect chemical state of N in the ZnO:N film. The N element in ZnO film has two chemical states, i.e., $(N_2)_O$ and N_O. $(N_2)_O$ is a double donor which produces electron carrier, whereas N_O is an acceptor which produces hole carrier.[4] As a result, the conversion of electrical conductivity induced by the annealing treatment may be associated with the change of percentage content of $(N_2)_O$ and N_O in the ZnO:N film.

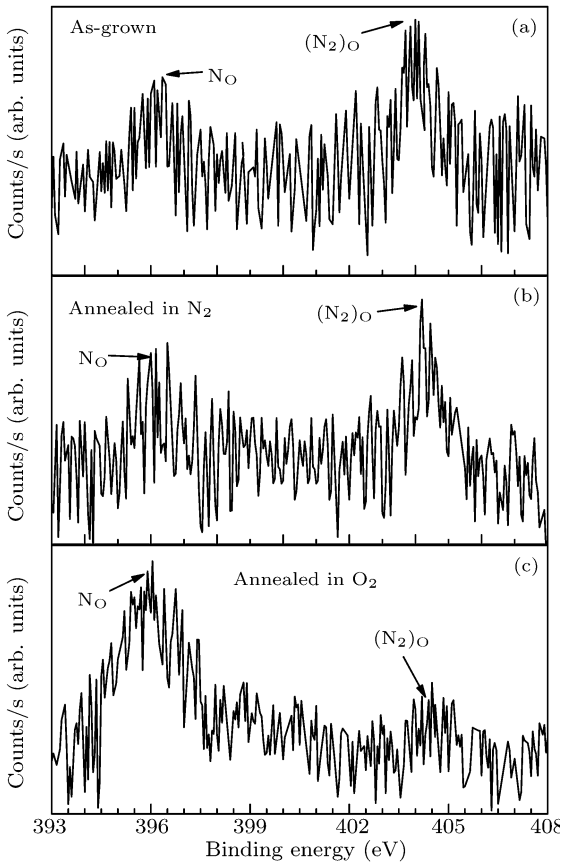

Fig. 3. XPS spectra of N 1*s*: (a) as-grown, (b) annealed in N_2, and (c) annealed in O_2 at 600°C.

To study the chemical states of N in the as-grown film and the films annealed in O_2 and N_2 at 600°C, XPS were measured. Prior to the measurement, the films were sputtered by Ar^+ for 10 min to remove the surface contamination, such as C element. Figure 3(a) shows the result of the as-grown film, two N 1*s* peaks are observed at the binding energy of 396.3, and 404.3 eV, which correspond to N_O and $(N_2)_O$,[13] respectively. It is noted that the intensity of $(N_2)_O$ is larger than that of N_O in the as-grown film, implying that the percentage content of $(N_2)_O$ is larger than that of N_O, i.e., the electron concentration produced by $(N_2)_O$ exceeding the hole concentration generated by N_O. Therefore, the n-type conductivity was observed in the as-grown ZnO:N film, which is consistent with the result in Table 1. Figure 3(b) and 3(c) are the measured results of the films annealed in N_2 and O_2. Two peaks at 396.3 and 404.3 eV corresponding to N_O and $(N_2)_O$ still exist in the case of annealing treatment, whereas the ratio in two peaks shows a remarkable change under the various annealed atmosphere. In the case of the ZnO:N film annealed in N_2, the peak of N_O is lower than that of $(N_2)_O$, which implies that the percentage content of N_O is fewer than that of $(N_2)_O$ giving rise to n-type conductivity. However, for the ZnO:N film annealed in O_2, the peak at N_O becomes more obvious and the peak at $(N_2)_O$ becomes weaker indicating p-type conductivity. It is shown that the annealing ZnO:N film in O_2 can substantially enhance the peak at N_O leading to the appearance of p-type conductivity, which is consistent with the results listed in Table 1.

The results of SIMS and XPS measurements suggest that the amount of N element in the film has no change after annealing and N element in the ZnO:N films contains two chemical states of $(N_2)_O$ and N_O. The ratio in two chemical states keeps constant in the as-grown film, but the percentage content of $(N_2)_O$ and N_O are changed after the annealing treatment. Paul *et al.*[14] reported that N_2 bubble will be formed in ZnO:N grown by MBE after the annealing process. Thus, it can be supposed that the thermal annealing induces the diffusion of N from $(N_2)_O$ and N_O to form the N_2 bubble in the film, but the diffusion velocity of N from $(N_2)_O$ and N_O is different in various annealing atmosphere, originating from the different diffusion barrier. When the as-grown film is annealed in O_2, the diffusion velocity of N from $(N_2)_O$ is faster than that of N from N_O, which causes the percentage content of $(N_2)_O$ to be fewer than that of N_O and result in the p-type conductivity. However, in the case of the as-grown film annealed in N_2, the diffusion velocity of N from $(N_2)_O$ will be reduced, which produces the percentage content of $(N_2)_O$ to be larger than that of N_O and make the ZnO:N film show n-type conductivity.

Figure 4 shows the PL spectra at 80 K for the ZnO:N films annealed in O_2 and N_2 at 600°C. It can be seen that the emission bands located at 3.310, 3.231, and 3.160 eV were detected in both the films. The obvious differences between two films are the emission bands located at 3.348 and 3.358 eV. As will be shown later, the emission band located at 3.348 eV in the ZnO:N film annealed in O_2 corresponds to the acceptor-bound exciton. The emission band located at 3.358 eV in the ZnO:N film annealed in N_2 is due

to the donor-bound exciton.[15]

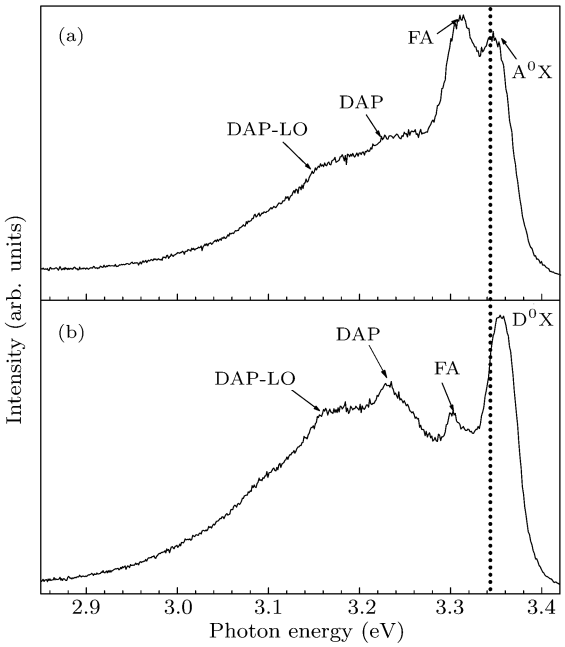

Fig. 4. PL spectra at 80 K for the ZnO:N films annealed in (a) O_2 and (b) N_2 at 600°C.

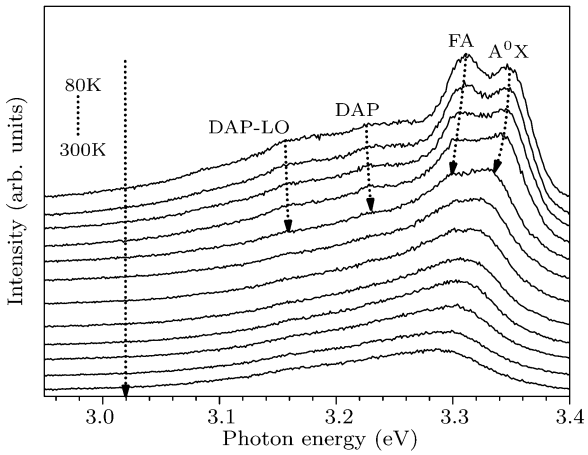

Fig. 5. Temperature-dependent PL of the ZnO:N film annealed in O_2 at 600°C measured at temperatures from 80 K to 300 K.

In order to investigate the origin of the emission bands of p-type ZnO:N film annealed in O_2 at 600°C, the temperature-dependent PL measurements were performed, the spectra are shown in Fig. 5. With the increasing temperature, the peak at 3.310 eV exhibits red shift, whereas the emission band at 3.231 eV shows blue shift, which are indicative of transition between free-to-neutral acceptor transition (FA) and donor-acceptor pair (DAP).[16] Therefore, these two emission bands at 3.310 and 3.231 eV are identified as FA and DAP transitions, respectively. The emission band located at 3.160 eV shows similar evolution to the emission band at 3.231 eV with the increasing temperature. Since the energy difference between 3.160 eV and 3.231 eV is 71 meV, equivalent to the longitudinal optical (LO)-phonon energy of ZnO, the emission band located at 3.160 eV can be ascribed to DAP-1LO. The emission band at 3.348 eV distinctly shows the characteristic of red shift and the emission intensity decreases with the increasing temperature, which is due to the fact that acceptor-bound exciton turns into the free exciton-1LO gradually with temperature.[17] Thus, this emission band at 3.348 eV is attributed to acceptor-bound exciton.

In summary, the effects of annealing on the chemical states of N dopant, electrical, and optical properties of N-doped ZnO film grown by MBE have been investigated. The characteristic of n-type conductivity for the as-grown ZnO:N film is still kept after annealed in N_2, however, the n-type conductivity of the as-grown ZnO:N film converted into p-type conductivity after annealed in O_2. The conversion of conductivity originates from the change in the amount of $(N_2)_O$ and N_O, which is due to different diffusion velocity of N from $(N_2)_O$ and N_O in different annealed atmosphere. The diffusion velocity of N from $(N_2)_O$ is faster than that of N from N_O in ZnO:N film annealed in O_2, which causes the amount of $(N_2)_O$ to be less than that of N_O and result in the p-type conductivity. When the as-grown film is annealed in N_2, the diffusion velocity of N from $(N_2)_O$ will be reduced leading to the amount of $(N_2)_O$ larger than that of N_O, which makes the ZnO:N film show n-type conductivity.

The PL spectra at 80 K for the ZnO:N films annealed in O_2 and N_2 at 600°C are also investigated. The emission bands located at 3.310, 3.231, and 3.160 eV are detected in both films annealed in O_2 and N_2. The obvious difference between PL spectra of the ZnO:N films annealed in O_2 and N_2 is the emission bands located at 3.348 and 3.358 eV, which are ascribed to acceptor-bound exciton and donor-bound exciton, respectively.

References

[1] Krtschil A et al 2005 *Appl. Phys. Lett.* **87** 262105
[2] Kobayashi A et al 1983 *Phys. Rev.* B **28** 946
[3] Iwata K et al 2000 *J. Crystal. Growth* **209** 526
[4] Yan Y and Zhang S B 2001 *Phys. Rev. Lett.* **86** 5723
[5] Li X et al 2003 *J. Vac. Sci. Technol.* A **21** 1342
[6] Xu W Z et al 2004 *J. Crystal Growth* **265** 133
[7] Liang H W et al 2005 *Phys. Status Solidi* A **202** 1060
[8] Matsushita T et al 1997 *Jpn. J. Appl. Phys.* **36** L1453
[9] Ji Z G et al 2004 *Chin. Phys.* **13** 561
[10] Yao B et al 2006 *J. Appl. Phys.* **99** 123510
[11] Teresa M. B et al 2005 *Appl. Phys. Lett.* **86** 112112
[12] Zhao D G et al 2003 *Appl. Phys. Lett.* **83** 677
[13] Craig L P et al 2005 *J. Appl. Phys.* **97** 034907
[14] Paul F et al 2006 *Phys. Rev. Lett.* **96** 045504
[15] Meyer B K et al 2004 *Phys. Status Solidi* B **241** 231
[16] Tamura K et al 2003 *Solid State Commun.* **127** 265
[17] Wang X H et al 2007 *Solid State Commun.* **141** 600