

P-type ZnO thin films prepared by plasma molecular beam epitaxy using radical NO

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N-doped p-type ZnO thin films were grown by plasma molecular beam epitaxy (P-MBE) on *c*-plane sapphire (Al₂O₃) using radical NO as oxygen source and nitrogen dopant. The reproducible ZnO thin films have maximum net hole concentration ($N_A - N_D$) of $1.2 \times 10^{18} \text{ cm}^{-3}$ and minimum resistivity of 9.36 $\Omega \text{ cm}$. The influence of N incorporation on the quality of the ZnO thin films was studied using X-ray diffraction and absorption spectra. The photoluminescence spectra at 77 K of p-type ZnO thin films are dominated by the emission from donor–acceptor pair recombination. The formation mechanism of p-type ZnO is explained by the optical emission spectra of radical N₂ and radical NO.

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1 Introduction

Recently, wide gap semiconducting ZnO has attracted considerable attention because of its potential application in ultraviolet photoelectric devices [1]. Unintentionally doped ZnO usually shows n-type conduction, which is related to the presence of native donor defects, such as O vacancies (V_O) or Zn interstitials (Zn_i) [2]. It has been demonstrated that these native donor defects have lower formation energy than other native acceptor defects (vacancy Zn and interstitial O) [3]. Therefore, it is necessary to prepare ZnO thin films with fewer native donor defects. Among the various methods of preparation of ZnO thin films, such as magnetron sputtering [4], chemical vapour deposition (CVD) [5], plasma molecular beam epitaxy (P-MBE) [6], and pulse laser deposition (PLD) [7], P-MBE is considered to be suitable for preparing high-quality ZnO thin films [8–10] due to its controllability and the high purity of the background.

For the fabrication of p-type ZnO, N is predicted to be an outstanding dopant candidate [11, 12], where N is regarded as a shallow acceptor as an N atom on an oxygen site (N_O). The N can be generally supplied by N₂, NH₃, and nitrogen oxides, such as NO and N₂O, to realize p-type doping of ZnO. However, in most cases, N-doped ZnO film produced using an N₂ source leads to n-type, but not p-type conduction in ZnO [13, 14]. Yan et al. [12] predicted that it is difficult to break the N–N bond of N₂, which results in the existence of N₂ molecules in the gas source. The N₂ molecules are then very easily incorporated into ZnO thin films to form the shallow double donor (N_2)_o due to the lower formation energy in ZnO. This is the reason why doping with N₂ does not lead to p-type conduction in ZnO. In contrast, p-type ZnO films were successfully obtained by doping with nitrides [15–17]. In particular, some workers re-

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ported making p-type ZnO films using NO gas as the doping source [17, 18]. The N–O bond in NO molecules can be broken easily by thermal decomposition, even at lower temperature. That is, NO molecules can provide easily the single N atoms that substitute for O in the ZnO lattice. Therefore, it is concluded that NO should be a better N doping source for p-type ZnO than N₂. Moreover, when radical NO is used, the decomposition of NO will lead to an increase of N_O defects in ZnO comparing with normal NO gas.

In the work reported in this paper, we prepared p-type ZnO thin films by P-MBE using NO as both O and N dopant source. N and O atoms were produced by an rf atomic source to form easily NO defects. Hall effect measurements show that reproducible p-type ZnO was obtained with the lowest resistivity of 9.36 Ω cm and highest hole concentration of 1.2×10^{18} cm⁻³. Additionally, the possible formation mechanism of p-type ZnO is investigated by comparing optical emission spectra of radical N₂ and radical NO.

2 Experimental

The substrate used was c-plane sapphire (Al₂O₃). The substrate was treated with ethanol in an ultrasonic bath to remove surface contamination and etched in hot (160 °C) H₂SO₄:H₃PO₄ (3:1) solution for 10 min. It was then rinsed in deionized water (18.2 M Ω cm) and blown dry using high-purity nitrogen. To obtain a clean and highly crystallized surface, the substrate was heated in vacuum ($\leq 10^{-7}$ Pa) at 800 °C for 30 min in an MBE preparation chamber. A Knudsen effusion cell was used to evaporate elemental Zn of 99.9999% purity. The gas sources were activated by an Oxford Applied Research HD25 rf (13.56 MHz) atomic source with a power of 300 W. During growth, the Zn beam partial pressure, NO flow rate and substrate temperature were fixed at 4×10^{-4} Pa, 1.0 ml/min and 400 °C, respectively. To investigate the formation mechanism of p-type ZnO, ZnO N-doped using radical N₂ and undoped ZnO were prepared. In this case, the sources of N₂ and O₂ were supplied through completely separate paths to two different plasma chambers. The thickness of all the samples measured by ellipsometry was about 100 nm.

The electrical properties of as-grown samples were measured by Hall analysis in the Van der Pauw configuration at room temperature using a magnetic field of 3200 Gs and a current automatically set by the Hall system (Bio-Rad HL5500 PC). The results were averaged in order to compensate for various electromagnetic effects [19]. X-ray diffraction (XRD) was carried out using a Rigaku O/max-RA X-ray system with CuK α radiation ($\lambda = 1.5418$ Å). Absorption spectra were obtained using a Shimadzu UV-3101 PC spectrophotometer. The photoluminescence (PL) spectra were investigated using a He–Cd laser with the 325 nm line at liquid nitrogen temperature (77 K). The optical emission spectra (OES) of NO plasma and nitrogen plasma were detected through a fibre from a SiO₂ window of the rear part of the plasma cell to the optical spectrometer.

3 Results and discussion

Table 1 lists the growth parameters and the Hall data of the ZnO samples grown using the different gas sources. Sample A refers to the ZnO thin films prepared employing radical NO. Hall effect measurement results indicate that sample A shows p-type conduction with a high net hole concentration ($N_A - N_D$) of

Table 1 The preparation conditions and electronic properties of ZnO N-doped using radical NO (sample A) and radical N₂ (sample B), and undoped ZnO (sample C).

sample	gas	F_O^* (ml/min)	F_N^* (ml/min)	conduction type	resistivity (Ω cm)	mobility (cm V ⁻¹ s ⁻¹)	carrier concentration (cm ⁻³)
A	NO	0	1.0	p	9.36	0.53	1.26×10^{18}
B	N ₂	0.1	1.0	n	491.08	0.89	1.43×10^{16}
C	O ₂	1.0	0	n	0.043	5.34	2.74×10^{19}

* F_O and F_N are the flow rates of the O and N sources, respectively.

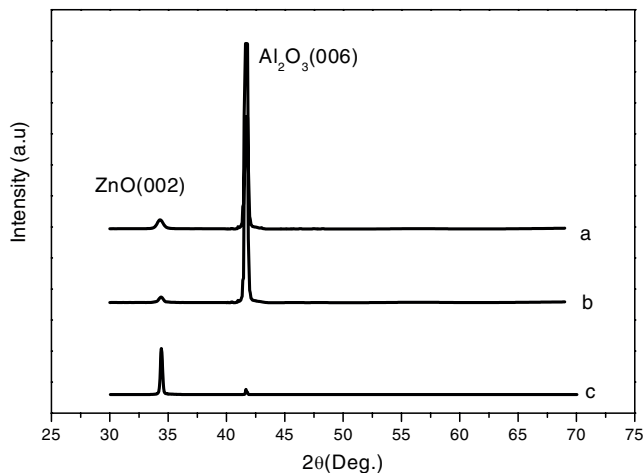


Fig. 1 XRD spectra: ZnO N-doped using (a) radical NO and (b) radical N_2 ; (c) undoped ZnO sample.

$1.2 \times 10^{18} \text{ cm}^{-3}$ and low resistivity of $9.36 \Omega \text{ cm}$. We note that the hole concentration of the p-type ZnO varies from 10^{15} to $1.2 \times 10^{18} \text{ cm}^{-3}$ under the different preparation conditions, such as growth temperature and flow rate of NO. In contrast, the N-doped ZnO thin film prepared using radical N_2 , sample B, shows a low carrier concentration of $1.43 \times 10^{16} \text{ cm}^{-3}$ and a high resistivity of $491.08 \Omega \text{ cm}$. It can be clearly seen that the radical NO can be incorporated into the ZnO films and compensate the native donor defects resulting in the trend towards p-type conductivity [20–22], but the attempts to obtain p-type ZnO by employing radical N_2 failed. For undoped ZnO thin film (sample C), the result shows typical n-type conduction with a carrier concentration of $2.74 \times 10^{19} \text{ cm}^{-3}$ and a low resistivity of $0.043 \Omega \text{ cm}$.

The crystalline structures of as-grown samples were investigated using XRD, as shown in Fig. 1. Besides the diffraction peak of Al_2O_3 (006), only one peak at 34.40° corresponding to the (002) orientation of ZnO can be observed for all samples. Although N-doped ZnO thin film is usually found to have increased tensile force and lattice constants [23], an obvious change in peak position is not observed in our work. From Fig. 1, we found that the intensity of the (002) diffraction peak for N-doped ZnO thin films is significantly reduced, and the full width at half maximum (FWHM) is broadened compared with the undoped ZnO thin film. The FWHM of the ZnO (002) diffraction peak is 0.25° for sample A, 0.34° for sample B and 0.15° for sample C. The broader FWHM implies that N-doped ZnO thin films have many defects related to N in the films, as reported by Li et al. [17].

Figure 2 shows the absorption spectra for N-doped and undoped ZnO thin films. The most visible difference (between the absorption spectra of doped and undoped samples) is the disappearance of the exciton-related peak in the spectra of the doped samples due to scattering by N impurity defects.

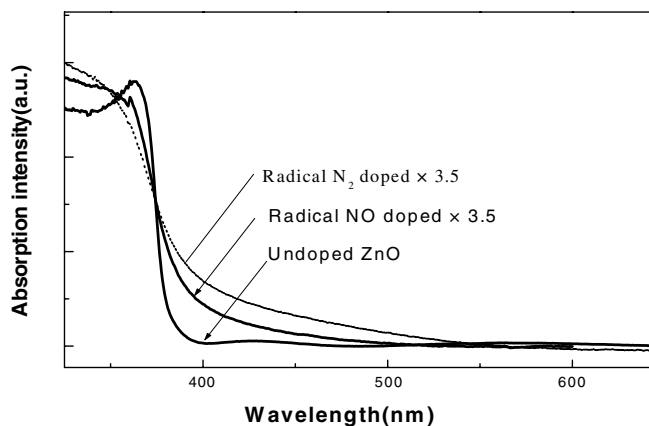


Fig. 2 Absorption spectra of N-doped and undoped ZnO samples, normalized and plotted for comparison.

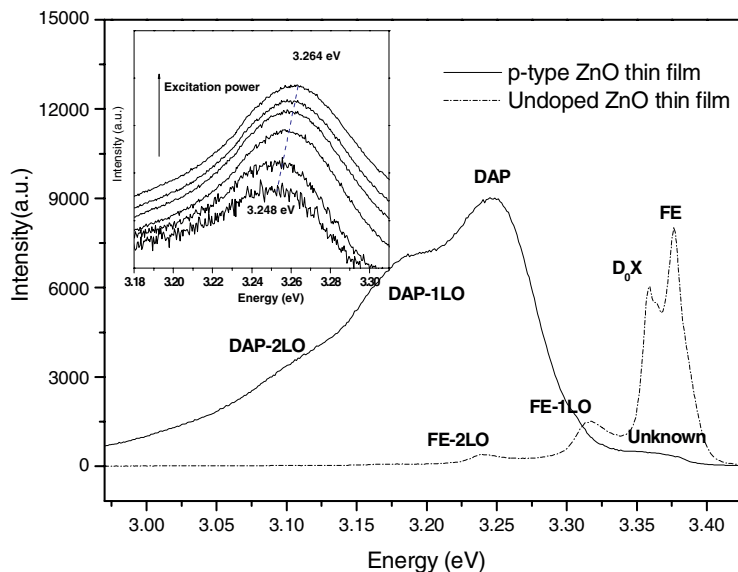


Fig. 3 Photoluminescence (PL) spectra of p-type ZnO and undoped ZnO thin films obtained at 77 K. The inset shows the excitation intensity-dependent PL spectra at 77 K (the dashed line in the inset is a guide for the eyes).

Sample C shows a very sharp absorption edge. The N-doped p- or n-type ZnO thin films show a much less sharp absorption edge. A similar result was also reported by Garces et al. [24] and Li et al. [17], from which they concluded that the existence of some subband gap levels associated with the N doping resulted in the difference in the absorption edges.

Figure 3 shows the PL spectra of p-type and undoped ZnO thin films measured at 77 K. The UV PL spectrum of the undoped ZnO (sample C) consists of a free exciton (FE) line at 3.377 eV, neutral donor bound exciton (D_0X) line at 3.360 eV and free exciton lines with first and second longitudinal optical (LO) phonon at 3.313 and 3.240 eV, respectively [25]. For the p-type ZnO (sample A), four peaks located at 3.358, 3.248, 3.178 and 3.105 eV are observed. The band at 3.358 eV is a new peak compared with the spectrum of undoped ZnO films. The origin of this peak is not clear and needs further investigation. The 3.248 eV line is dominant and this peak position depends on the N concentration, as reported by Tamura et al. [26], in which the peak origin was assigned to a donor–acceptor pair (DAP) transition. The inset of Fig. 3 shows that the emission peaks exhibit an obvious blue shift with increasing excitation intensity, which is characteristic of DAP emission. This is because the energy of the DAP emission (E_{DAP}) is represented as follows [27]: $E_{DAP} = E_{gap} - (E_D + E_A) + \frac{e^2}{4\pi\epsilon r}$, where E_{gap} , E_D and E_{DAP} are the band gap, binding energy of a donor and energy of DAP emission, respectively, ϵ is the dielectric constant of ZnO (8.6) and r is the pair separation. Due to increasing numbers of photoexcited DAPs, the DAP distance, r , decreases as the excitation intensity increases. Therefore, a DAP emission peak shows a blue shift. Hence the 3.248 eV line is considered as a DAP emission in this investigation. From Fig. 3, we note that these peaks have equal energy spacing of about 70 meV, which is in good agreement with the energy of the LO phonons of ZnO [28]. This implies that the peaks at 3.197 and 3.124 eV are the corresponding first and second LO phonon peaks of the DAP, respectively. The binding energy of an acceptor (E_A) can be calculated using the following equation:

$$E_A = E_{gap} - E_D - E_{DAP} + \frac{e^2}{4\pi\epsilon r} \quad (1)$$

The pair separation r can be very roughly estimated by $\langle r \rangle \sim (3/4\pi N_A)^{1/3}$. For the undoped ZnO thin films (see Table 1), the donor concentration (N_D) is estimated to be in the range 10^{19} – 10^{20} cm $^{-3}$, so the acceptor

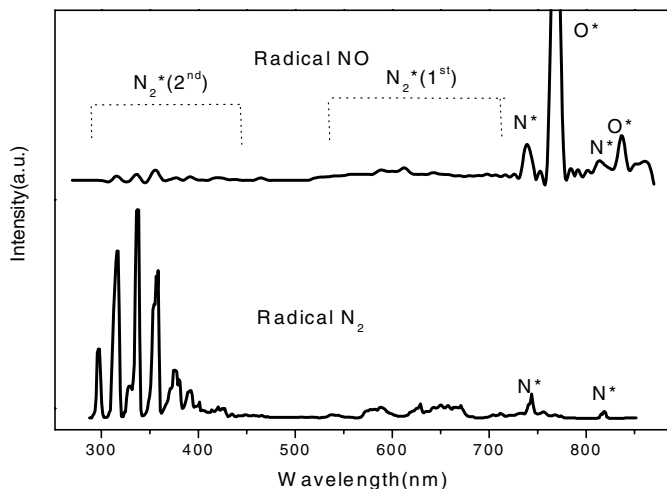


Fig. 4 Optical emission spectra of radical NO and radical N_2 .

concentration (N_A) is also in this range for the p-type sample. The donor binding energy is known to be about 60 meV [29, 30] and the energy gap at 77 K is $E_{\text{gap}} = 3.437$ eV according to the energy position of the free exciton transition. Thus, $E_A \approx 182\text{--}248$ meV can be obtained, which is close to the reported value of $E_A = 165 \pm 40$ meV [31].

To explain the formation mechanism of p-type ZnO, the optical emission spectra (OES) of the radical N_2 and radical NO are investigated (Fig. 4). The OES of NO consists of the emission peaks of atomic oxygen (O^*) located at 777 and 841 nm originating from $3p^5P\text{--}3s^5S^0$ and $3p^3P\text{--}3s^3S^0$ transitions, and emission peaks of atomic nitrogen (N^*) located at 744 and 821 nm originating from $3S^4P\text{--}3P^4S^0$ and $3S^4P\text{--}3P^4P^0$ transitions [32]. Furthermore, some weaker emission peaks of radical nitrogen molecules (N_2^*) originating from the second positive ($C^3\Pi_u\text{--}B^3\Pi_g$) and first positive ($B^3\Pi_u\text{--}A^3\Sigma_u^+$) transitions are also observed in the ultraviolet and visible light wavelength regions [30]. The OES of radical N_2 shows stronger emission of radical nitrogen molecules and weaker emission of atomic nitrogen (N^*). Because the chemical species in radical NO and radical N_2 are different, this would result in the difference in electrical properties of N-doped ZnO films produced using the two different dopants. Although the N_O acceptor in the ZnO thin film was formed by radical N_2 doping, $(N_2)_O$ defects were also introduced at the same times. These $(N_2)_O$ defects would compensate the N_O acceptor and could only lead to a trend of p-type conduction. Based on the above results, the production of N^* is responsible for p-type conduction of ZnO thin films. Similar results were also reported in Refs. [16, 17]. Therefore, we consider that NO is a good dopant for fabricating p-type ZnO.

4 Conclusion

P-type ZnO thin films were grown using radical NO as both nitrogen and oxygen source by P-MBE technology. The reproducible p-type ZnO has a minimum resistivity of $9.36 \Omega \text{ cm}$ and net hole concentration as high as $1.2 \times 10^{18} \text{ cm}^{-3}$. The binding energy of N acceptors is in the range 182–248 meV. From the OES of radical NO and radical N_2 it is concluded that atomic N is responsible for p-type ZnO. The success of the N doping to produce p-type ZnO demonstrates the feasibility of radical NO source as N dopant for the P-MBE method.

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