

# Optical and electrical properties of p-type ZnO fabricated by NH<sub>3</sub> plasma post-treated ZnO thin films

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## Abstract

In this paper, a simple method is reported to obtain nitrogen-doped p-ZnO film. In this method NH<sub>3</sub> plasma, generated in a plasma-enhanced chemical vapor deposition system, was employed to treat ZnO thin film. By Hall-effect measurement, a p-type conductivity was observed for the treated film with the hole density of  $2.2 \times 10^{16} \text{ cm}^{-3}$ . X-ray photoelectron spectroscopy (XPS) results confirmed that nitrogen was incorporated into ZnO film during the treatment process to occupy the oxygen positions. In low temperature photoluminescence spectra, an emission peak corresponding to acceptor–donor pair was observed. From this emission peak we calculated the N-related acceptor binding energy to be 130 meV. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** p-type ZnO; Nitrogen doping; NH<sub>3</sub> plasma

## 1. Introduction

ZnO as a wide band gap semiconductor, having a direct band gap of 3.37 eV and a large exciton binding energy of 60 meV, has been recognized as a promising material for use in ultraviolet (UV) light emission devices and laser diodes. For the achievement of a practical ZnO based light emission diode (LED) or laser diode (LD), it is imperative to fabricate the p-type ZnO. But the growth of the p-type ZnO is very difficult. Considerable efforts have been made in preparing p-type ZnO, such as by doping with N, P, As, Sb, Li and so on [1–5]. However, a reproducible low resistance and high mobility p-type ZnO has not been successfully obtained.

Efforts have been made to obtain p-type ZnO films by using acceptor dopants such as nitrogen, arsenic, and phosphorus. Both As and P are deep acceptors and make few contributions to p-type conduction, which leaves nitrogen as the relatively better

choice for the acceptor dopant in p-type ZnO [6]. So a lot of research has been developed about p-type nitrogen-doped ZnO films by many methods such as molecular beam epitaxy (MBE), ion-implantation, magnetron sputtering, pulsed-laser deposition (PLD) and so on [7–12]. In this report, a NH<sub>3</sub> plasma post-treatment method was used to realize p-type conductivity of ZnO film. The optical properties and the electrical characterization of N-doped p-type ZnO film are discussed in the paper.

## 2. Experiments

ZnO films were grown on the c-Al<sub>2</sub>O<sub>3</sub> substrate by molecular beam epitaxy (MBE) [13]. NH<sub>3</sub> plasma post-treatment was carried out in plasma enhanced chemical vapor deposition (PECVD) system with high-purity NH<sub>3</sub> serving as the nitrogen source. The treatment was carried out for 1 h under a power of 10 W at 100 °C. The flux of NH<sub>3</sub> was 10 sccm and the pressure was maintained at 250 Pa.

X-ray diffraction (XRD) measurement was taken on a Siemens D500 diffractometer using Cu K $\alpha$  radiation of

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1.5418 Å. The electrical properties of all the samples were measured by Hall-effect measurements at room temperature with van der Pauw sample configuration using the Lakeshore's 7707 Hall measurement system. The Ohmic contacts were made by an indium electrode, which was operated at a pressure of  $10^{-3}$  Pa for 20 min at near 300 °C. The chemical nature of surfaces was analyzed by X-ray photoelectron spectroscopy (VGESCALAB MK II XPS, VG Co., East Grinstead, UK). The binding energies were calibrated by centring the aliphatic carbon peak at 284.6 eV. Surface morphology of the ZnO was studied by atomic force microscopy (AFM) in a contact mode using a Veeco's Instrument Dimension 3100 system. PL spectra were measured employing a He–Cd laser with the laser line at 325 nm as the excitation source and collected with a microprobe system made by Jobin–Yvon Company. The temperature was controlled by Linkam Scientific Instruments Ltd. LNPQ312 system.

### 3. Results and discussion

The XRD spectra of ZnO sample before and after treatment by  $\text{NH}_3$  plasma are shown in Fig. 1. The XRD patterns showed that *c*-axis preferred orientation ZnO were fabricated which had the wurtzite structure. No additional diffractive peaks are observed, which means there were no impurity phases in the samples. The full-width at half-maximum (FWHM) of peak (0 0 2) is  $0.200^\circ$  and  $0.233^\circ$  for undoped and  $\text{NH}_3$ -treated samples, respectively. It can be seen that the intensity is weak after the treatment, which indicates that the crystal quality of the treated ZnO is inferior to the undoped sample. The thicknesses of the samples were all around 200 nm obtained by scanning electron microscope (SEM).

Electrical transport properties of ZnO films are summarized in Table 1. Based on the Hall-effect measurement, the as-grown film has n-type conductivity. After the  $\text{NH}_3$  plasma post-treatment the Hall coefficient is inverted to positive, which indicates a hole-dominant transport effect and the film converts to the p-type conductivity. The carrier concentration increases by two orders of magnitude, from  $3.9 \times 10^{14}$  to  $2.2 \times 10^{16} \text{ cm}^{-3}$ .

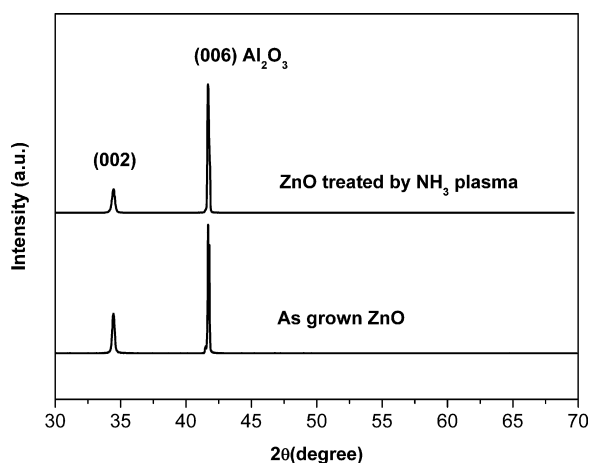


Fig. 1. The XRD spectra of the sample before and after treatment by  $\text{NH}_3$  plasma.

The resistivities of the samples drop more than two orders of magnitude. This result shows that  $\text{NH}_3$  plasma treatment is an efficient method to obtain p-ZnO thin film. During the treatment process nitrogen atoms could incorporate into ZnO film to occupy oxygen positions, partly compensating some donors induced from non-stoichiometric composition. Therefore, the N-acceptors in ZnO are activated. The density of acceptors will be dominant, leading to the ZnO inverted from n-type to p-type. This conductivity transformation can be confirmed by the structural and compositional analyses.

Fig. 2 shows  $5 \times 5 \mu\text{m}^2$  AFM images of the films. The N-doped ZnO film, shown in Fig. 2(b), consists of slender-shaped grains having roughness of approximately 50–80 nm, while the undoped ZnO film, shown in Fig. 2(a), has relatively flat surface. Because the treated temperature is quite low, the variety of surface morphology is thought due to the chemical reaction between ZnO and  $\text{NH}_3$  plasma. The detailed discussion will be given below.

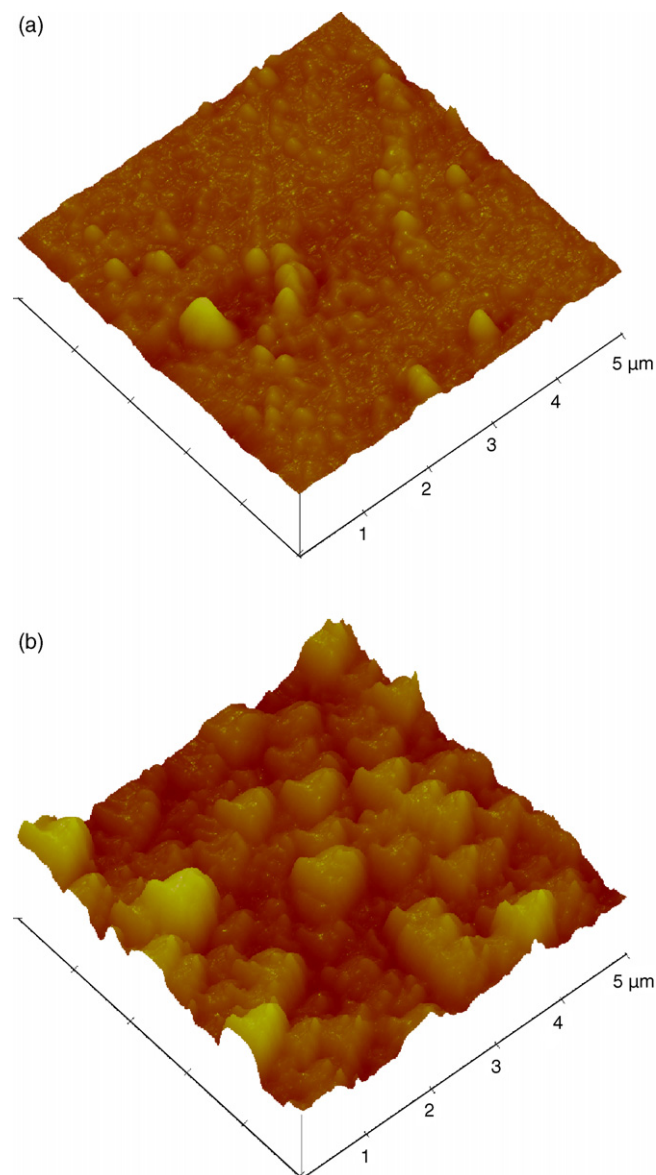


Fig. 2. The AFM spectra of (a) n-type ZnO and (b) p-type ZnO.

Table 1  
Electrical properties of the sample before and after treatment by NH<sub>3</sub> plasma

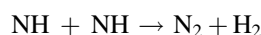
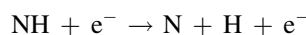
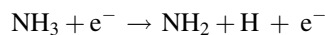
Sample	Conductivity type	Carrier density (cm <sup>-3</sup> )	Resistivity (Ω cm)	Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
ZnO	n	$3.9 \times 10^{14}$	$2.5 \times 10^4$	0.46
NH <sub>3</sub> plasma treated ZnO	p	$2.2 \times 10^{16}$	$3.3 \times 10^2$	0.82

In order to investigate the chemical state of N in ZnO, the XPS measurements were performed as shown in Fig. 3. The insert of Fig. 3(a) shows the XPS signals under different ion etching depths of NH<sub>3</sub> plasma treated sample. There were no N related XPS peaks on the sample surface and at the depth of 10 nm. When the ion etching depth was 20 nm, a broad XPS peak centered at 399.6 eV was observed. With etching depth increasing to 100 nm, the center of the XPS peak shifts to 398.5 eV. From the Fig. 3(b), it can be seen that the binding energy of the Zn 2p<sub>3/2</sub> peak of the sample after the treatment is slightly larger than the as-grown one. The absolute position of the Zn 2p<sub>3/2</sub> core level generally reflects the charge and the

chemical environments around the Zn atom. For samples after the treatment, the symmetry of the crystal lattice was degraded because of nitrogen doping. The electrical cloud around the Zn atom becomes asymmetric, resulting in the increase of the binding energy of the Zn 2p<sub>3/2</sub> peak for p-type ZnO [14]. With the ion etching depth increasing, the blue-shift is also increased. The lower binding energy indicates that there are a few Zn–N bonds of the surface, which confirms that the nitrogen was incorporated into ZnO films during the treatment process to occupy oxygen positions. The blue-shift of the binding energy indicates that Zn–N bonds increased with the etching depth increasing, which is similar to the results shown for N 1s.

Based on these results, a diffusion and departure process for N ions was assumed during the NH<sub>3</sub> plasma treatment. Firstly, N could substitute O position in ZnO thin film by diffusion process. Secondly, because the N–Zn bond is much weaker than O–Zn bond [14], the N–Zn bonds at the surface were destroyed by the energy of the NH<sub>3</sub> plasma during the treatment process. Due to this reason, N atoms could not stay stable on film surface. With the increasing depth, the influence of the NH<sub>3</sub> plasma energy became weak gradually, so the N–Zn bond can be found under a certain depth.

Fig. 3(a) is an enlarged XPS spectrum at this depth. By Gauss fitting, three distinct forms of nitrogen are revealed. The binding energies, located at 398.5, 399.6, and 403.5 eV, could be attributed to N–Zn bonds, N–H bonds and weakly bound nitrogen, respectively [14,15]. From the literatures, the binding energy of N–Zn bond was given by two different values, located at around 396.6 and 398 eV [14,15]. In our case the value is preferred to the larger one. To explain this point, the NH<sub>3</sub> plasma treatment process was considered. NH<sub>3</sub> fragmentation and recombination reactions in the discharge produce N<sub>2</sub> and H<sub>2</sub> molecules as stable species, as well as NH<sub>2</sub>, NH, N, and H fragments, both in ground and excited states [16,17]:



The active H could react with ZnO to form H<sub>2</sub>O and release oxygen vacancies (V<sub>O</sub>). Then N fills in these vacancies to substitute the O sublattice. Because both of the steps concern the surface etching and reforming process, the surface morphology changes dramatically after NH<sub>3</sub> plasma treatment. And since the treated temperature was as low as 100 °C and in the treated process the Zn atoms could not escape by forming some low melting point complexes, Zn sublattice keeps integrity. The binding energy peaks near 396.5 eV compare

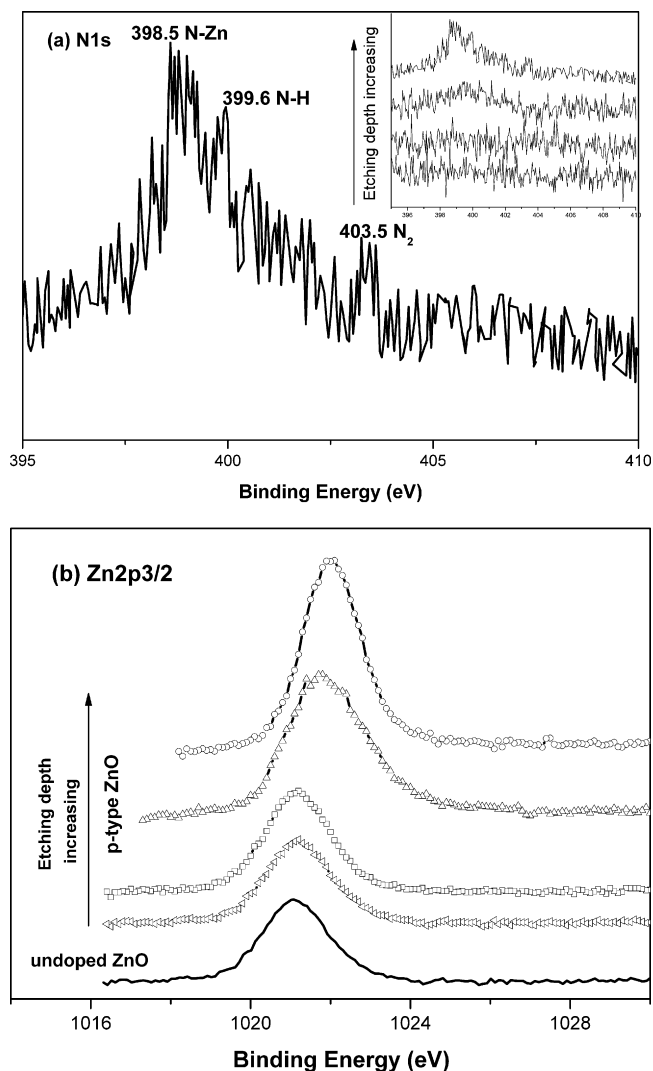


Fig. 3. (a) N 1s and (b) Zn 2p<sub>3/2</sub> spectra for the samples before and after the NH<sub>3</sub> plasma treatment. The inset of (a) shows the N 1s XPS signals under different ion etching depths of NH<sub>3</sub> plasma treated sample.

favorably with values found for  $N^{3-}$  in metal nitrides in which the N atom has received substantial charge from the surrounding metal atoms [18]. For oxygen-rich nitrogen compounds, the binding energy could be found in high-energy side, around 400 eV [18,19]. In the case of N substitution of O sublattice (No) in ZnO crystal, the chemical surroundings of N are only O and Zn, in which the number of oxygen atoms is larger than Zn atoms. Therefore, the binding energy of No should be between 396.5 and 400 eV, and prefer higher energy side. Based on the above discussion and the Hall-effect measurement result, we can deduce that the binding energy of 398.5 eV in our experiment is originated from No, which induces efficient acceptor doping. For other growth method, especially direct growth by molecular epitaxy method, the nitrogen concentration in ZnO thin film could achieve  $10^{20} \text{ cm}^{-3}$ . But hole concentration in p-ZnO is only  $10^{16} \text{ cm}^{-3}$  [20], which means that only 0.01% of N substitutes O sublattice in ZnO to generate holes. Because nitrogen in ZnO could form different complexes, it is not easy to distinguish the XPS emission peak of No in this kind of sample [21].

Since the formation energy of the NH is lower than ‘pure’ NO defects, a weak XPS emission peak originating from NH could also be observed. As a result, the free hole generated by NO acceptor is neutralized by hydrogen. In this instance, the NO acceptor defects are electrically inactive owing to a so-called hydrogen passivation [15]. From the XPS spectra (the insert of Fig. 3(b)), it should be noticed that this hydrogen passivation effect is prominently close to the film surface. But when the ion etching depth was 100 nm, this effect is neglected. The peaks at 403.7 eV is due to  $(N_2)_o$  defects [15], which is a double donor: the  $(N_2)_o$  represents substitution of  $N_2$  for O sublattice.

In order to further investigate the behavior of No in ZnO thin film, low-temperature (81 K) PL spectra of undoped ZnO and p-type ZnO post-treated by PECVD were performed. The measured UV PL spectra measured at 81 K are shown in Fig. 4. The UV PL spectrum of the undoped ZnO consists of a free

exciton (FE) line at 3.375 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 [22]. For the p-type ZnO, five peaks located at 3.372, 3.360, 3.310, 3.232, and 3.160 eV are observed. The PL peak located at 3.372 eV is assigned as free exciton (FE), and the peak located at 3.310 eV is considered as first LO replica of free exciton [22]. The dominant PL emission peak appearing at 3.360 eV is attributed to neutral donor bound exciton ( $D_0X$ ) [23]. The band at 3.232 eV is a new peak compared with the spectrum of undoped ZnO film, which can probably be considered to be related with N doping. The peak position at 3.232 eV shifted towards higher energy with increasing the excitation power as shown in the inset, it is a characteristic of emission from donor–acceptor pairs (DAP) [24]. From Fig. 4, we note that the peaks at 3.232 and 3.160 eV have equal energy spacing of about 70 meV, which is in good agreement with the energy of the LO phonons of ZnO. This implies that the peak at 3.160 eV is the corresponding first LO phonon peak of the DAP, respectively. Therefore, based on the peak energy of DAP the energy level of the nitrogen acceptor in the band gap of ZnO was calculated by the formula:

$$E_A = E_g - E_D - E_{DAP} + \frac{e^2}{4\pi\epsilon r}$$

where  $E_g$  (3.437 eV) is the band gap energy at low temperature [24],  $E_D$  is donor binding energy of 60 meV, dielectric constant of ZnO is 8.6 [25],  $r$  is the distance of donor–acceptor pairs, can be calculated with the  $\langle r \rangle \sim (3/4\pi N_A)^{1/3}$  [26,27]. Since the donor concentration ( $N_D$ ) of the undoped ZnO is  $10^{14} \text{ cm}^{-3}$ , so the acceptor concentration ( $N_A$ ) is also in this range for the p-type sample [13]. Using this value, the acceptor bonding energy  $E_A$  can be obtained at 130 meV, which is almost consistent with the results of the literatures [28–30]. It proved that some N atoms have occupied the positions of O atom, and these acceptors can compensate all donor state, so the film yields p-type conductivity.

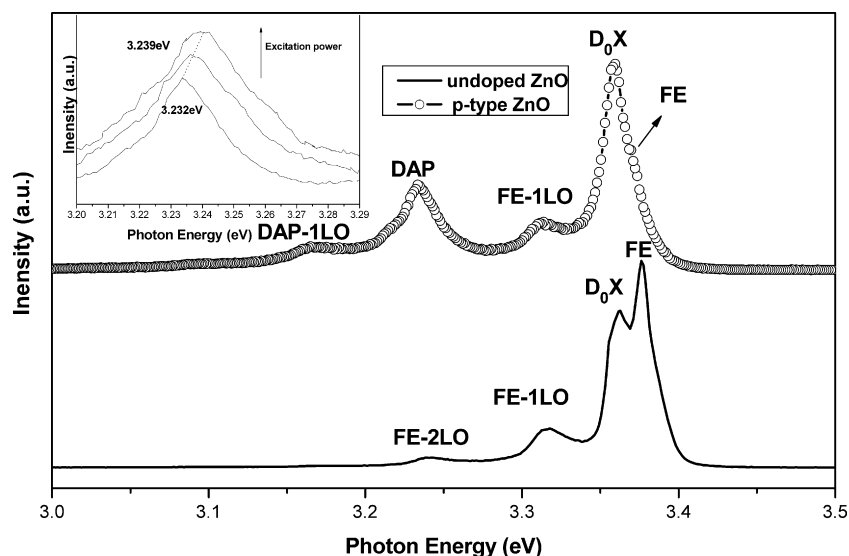


Fig. 4. Low temperature (81 K) PL UV-blue spectra of undoped and p-type ZnO post-treated by PECVD.

#### 4. Conclusions

In summary, p-type ZnO film was successfully prepared by post-treatment with PECVD at low temperature. Electrical and optical properties of N-doped ZnO were studied. The p-type ZnO with the hole density of  $2.2 \times 10^{16} \text{ cm}^{-3}$  was obtained. XPS result indicated that a part of N substitute O sublattices to form the acceptor-like defects. The binding energy of N could be established at 398.5 eV. The rational identification of the PL peak positions of the p-type ZnO was discussed. All results have elucidated the course of nitrogen being incorporated into film to compensate donors during the treatment process, resulting in the transformation from n-type to p-type.

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