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D Wang[1], Y C Liu[1,2,4], R Mu[3], J Y Zhang[2], Y M Lu[2], D Z Shen[2] and X W Fan[2]

[1] Center for Advanced Optoelectronic Functional Material Research, Northeast Normal University, Changchun 130024, People's Republic of China
[2] Key Laboratory of Excited State Processes, Chinese Academy of Sciences, Changchun Institute of Optics, Fine Mechanics and Physics, CAS, Changchun 130021, People's Republic of China
[3] Nanoscale Materials and Sensors, Center for Photonic Materials and Devices, Fisk University, Nashville, TN 37208, USA

E-mail: ycliu@nenu.edu.cn

Abstract
Nitrogen doped ZnO films are directly fabricated by the thermal oxidation of Zn_3N_2 films. Zn_3N_2 films are prepared by plasma-assisted metal-organic chemical vapour deposition (PA-MOCVD). By comparing with undoped ZnO photoluminescence spectra, a much stronger bound exciton emission due to a neutral nitrogen acceptor (A^0X) is observed at low temperature. The neutral acceptor level is located at 130 meV above the valence band maximum. To demonstrate the quality of ZnO:N thin films as a p-type, a Zn_3N_2/n-Si heterojunction structure was first fabricated. With an increase of oxidation temperature, the structure has gradually shown p–n junction rectification characteristics from $I–V$ measurements.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO, a wide band gap semiconductor ($E_G(RT) = 3.36$ eV and excitonic binding energy $= 60$ meV), has attracted considerable attention as a potential candidate material for ultraviolet and blue light sources and detectors [1–4]. However, such applications are hampered

[4] Author to whom any correspondence should be addressed.

by the fact that ZnO semiconductor occurs naturally as an n-type. It is difficult to achieve p-type conduction through impurity doping due to the 'self-compensation' effect of various intrinsic donor defects, such as oxygen vacancies (V_o) or Zn interstitials (Zn_i) [5]. As a result, much effort have been made to obtain p-type ZnO. In one case, Kobayashi *et al* [6] have predicted that N would produce a shallow acceptor level in ZnO. This prediction is based on the theoretical study of the chemical trends in the defect energy levels when the substitutional impurities are considered in a number of wurtzite-structured semiconductors. There have been recent reports of p-type ZnO conduction achieved by growth of ZnO in the presence of excited N_2O [7] or by codoping N and H [8] or Ga [9]. However, the results show that it is not easy for N to be incorporated into the ZnO lattice because the chemical activity of oxygen is higher than that of nitrogen.

In this paper, we report on the use of an innovative method that can overcome the aforementioned nitrogen doping difficulties and achieve a p-type ZnO semiconductor through a thermal oxidation process of Zn_3N_2 films in an oxygen atmosphere. During the process, the majority of N atoms are replaced by O atoms. The residual nitrogen atoms left in the ZnO lattice serve as p-type acceptors in ZnO:N films.

2. Experimental details

The Zn_3N_2 thin films were fabricated by a plasma-assisted metal-organic chemical vapour deposition (PA-MOCVD). Dimethyl zinc (DMZn) and NH_3 were used as source materials. The flow rates of DMZn and NH_3 were fixed at 1.17×10^{-5} and 2.2×10^{-3} mol min^{-1}, respectively. The pressure in the growth chamber was maintained at 8 Torr. An n-type Si wafer was used as the substrate. The growth temperature was maintained at 450 °C. After deposition, the Zn_3N_2 samples were transferred in a tube furnace. Thermal oxidation was performed in an ultrapure oxygen environment at the temperatures from 500 to 800 °C for 1 h. As a comparison, an undoped thin film was also prepared by a two-step thermal oxidation process of metallic Zn and the detailed experimental procedure has been reported elsewhere [10]. To characterize the crystal structure of the films, x-ray diffraction (XRD) was measured using a D/max-rA x-ray diffraction spectrometer (Rigaku) with a Cu Kα line of 1.54 Å. The photoluminescence spectra of the films in the wavelength range 330–450 nm were obtained by using the UV Labran Infinity Spectrophotometer made by the Jobin Yvon Company, which is excited by the 325 nm line of a He–Cd laser with a power of 50 mW. The ZnO:N/n-Si heterojunction structure is fabricated. I–V measurements were conducted to evaluate the electrical properties of the ZnO:N/n-Si structure.

3. Results and discussions

Figure 1 shows XRD patterns of the films annealed at different temperatures. Two pronounced ZnO diffraction peaks (100) and (101) appear at $2\theta = 31.79°$ and $36.37°$, respectively. No peak from other compounds is detected beside those of ZnO. The XRD patterns indicate that the obtained ZnO thin films possessed a polycrystalline wurtzite structure without preferential orientation. As we know, ZnO films usually grow with *c*-axis orientation due to the low surface free energy for the (002) plane [11]. However, in our result, only a weak ZnO(002) diffraction peak can be observed. Nguyen *et al* has reported that if the deposition is performed at non-equilibrium conditions, such as low temperature or high deposition rate, another orientation can be achieved [12]. Hence, it may be responsible for our result. From figure 1 it can be seen that the full width at half maximum (FWHM) becomes narrower with increasing
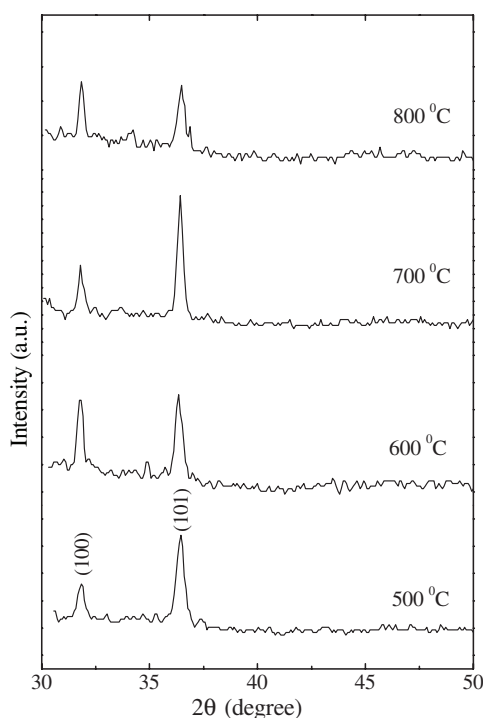
Figure 1. XRD patterns of the N-doped ZnO thin films annealed at 500, 600, 700 and 800 °C for 1 h.

annealing temperature, indicating the improvement of crystalline quality. While the annealing temperature is above 700 °C, the FWHM begins to broaden. This fact implies that the crystalline quality becomes worse due to the high annealing temperature.

Figure 2 shows the PL spectra in the excitonic emission region at 82 K. Figure 2(a) (denoted as nitrogen doped ZnO:N) is a PL spectrum of the Zn_3N_2 film oxidized at 700 °C for 1 h. Figure 2(b) (undoped ZnO) is a PL spectrum prepared via the oxidation of pure Zn metal. The sample doped with nitrogen shows a dominant peak at a photon energy of 3.350 eV. Three small shoulders known as phonon replicas are also observed at the low energy side. The dominant peak is known as the donor bound exciton (D^0X) emission [13]. The weak emission that appears as a shoulder at the high-energy side is attributed to the free exciton (FX) transition labelled with E_A, illustrated in an inset of figure 2. The 3.329 eV emission is the 1LO photon replica of FX. The broad line centred at 3.225 eV is composed of two emissions. They are 2LO phonon replicas of FX and the donor–acceptor pair transitions (D^0A^0) [14]. The peak located at 3.335 eV is due to the acceptor bound exciton (A^0X) emission [15]. In figure 2(b), the low-temperature PL spectrum shows a donor bound exciton emission at 3.351 eV and a weak shoulder on the high-energy side at 3.363 eV. This shoulder can be attributed to FX emission accompanied by 1LO and 2LO phonon replica emissions with a phonon energy of 72 meV. No emission peak is observed for the A^0X transition in this undoped sample. Thus, the A^0X emission present only in the nitrogen doped film originates from the nitrogen acceptors. It can be argued that the thermal oxidation process is able to have some nitrogen atoms in the film activated. These nitrogen atoms in the sample become the substitutional acceptors of the ZnO. To confirm the A^0X emission related to the nitrogen acceptors, other low temperature
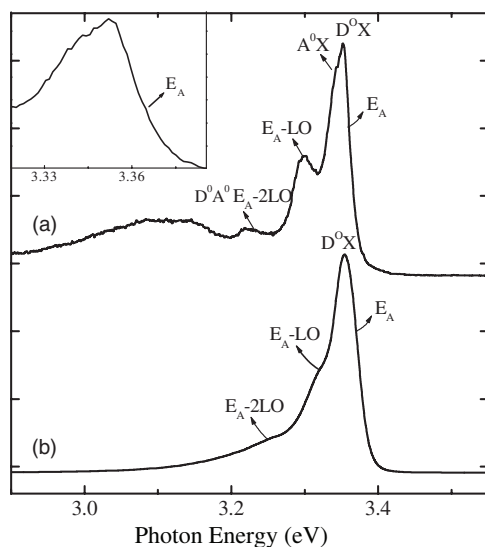
Figure 2. PL spectra. Curve (a): the N-doped ZnO thin film; curve (b): the undoped ZnO thin film, measured at 82 K.
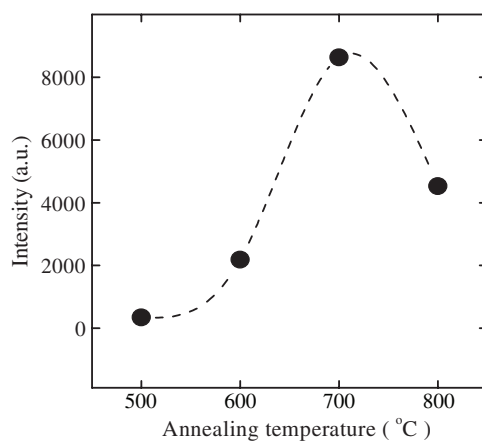

Figure 3. The PL intensity of peak A^0X versus annealing temperature.

PL spectra were also collected from the samples annealed at different temperatures. Figure 3 displays the oxidation temperature dependent PL intensity of A^0X emission at 82 K. Clearly, the A^0X emission intensity increases with the increase of the oxidation temperatures from 500 to 700 °C. This can be explained that as temperature increases, the crystalline properties of the films improve and the intrinsic donor defects, such as V_o or Zn_i, decrease. Then the donor defects are gradually insufficient to compensate for the N substitutional acceptor. Therefore it leads to an acceptor density increases. However, when the oxidation temperature is higher than 700 °C, the A^0X emission intensity starts to decrease, indicating that more nitrogen atoms in the film will be replaced by the oxygen atoms, which results in an acceptor concentration decrease.

Figure 4 shows the temperature dependent PL spectra from 82 to 301 K. When the sample temperature is increased, the intensities of all emissions are decreased. The intensity of the
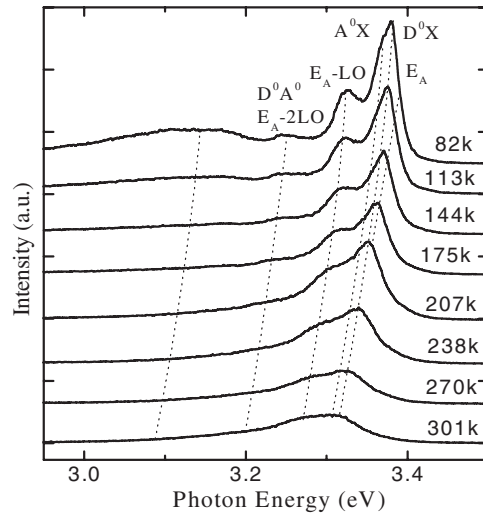
Figure 4. PL spectra measured at temperatures ranging from 82 to 301 K for the N-doped ZnO thin film.
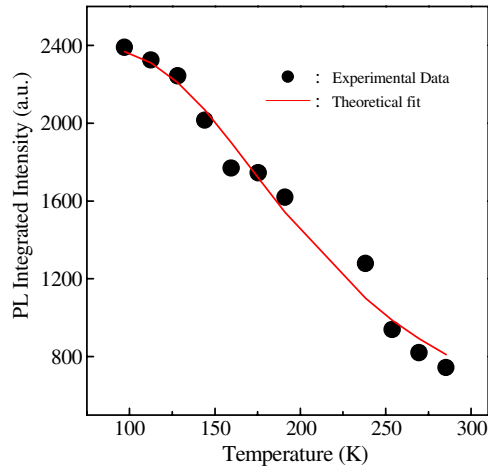

Figure 5. The PL integrated intensities of peak E_A as a function of measurement temperature from 82 to 301 K. Solid curve: the theoretical simulation; solid circles: the experimental data points.
$I(T) = \frac{I_0}{1 + A \exp(-E/k_B T)}$

bound exciton emission decreases more rapidly than that of the free exciton. The decrease in intensity is attributed to the thermal ionization of the bound excitons. The free exciton emission becomes dominant in the PL spectra when the sample temperature is above 175 K. For clarity, the PL integrated intensity of E_A quenches with temperature as displayed in figure 5. It is known that the temperature-dependent PL intensity can be expressed by the equation [16]

$$I(T) = \frac{I_0}{1 + A \exp(-E/k_B T)}$$

where E is the activation energy of the thermal quenching process, k_B is the Boltzman constant, I_0 is the emission intensity at 0 K, T is the thermodynamic temperature and A is a fitting
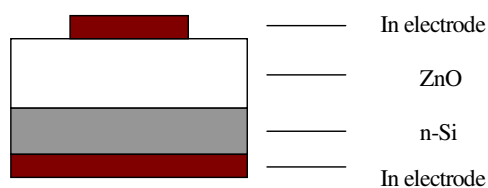
Figure 6. Schematic cross-section of the ZnO/n-Si junction.

parameter. From the fitting, a thermal activation energy of 62 meV is obtained. This value is very close to the exciton binding energy of 60 meV in a bulk ZnO crystal [17].

From the FX and A^0X peak positions, the acceptor energy level is estimated to be $\sim$130 meV above the valence band [18]. This value is consistent with the data reported in the literature. That is, 100 meV for p-ZnO [8, 19] and 110 meV in p-ZnSe [20, 21]. Theoretical modelling of the acceptor binding energy has also been reported in the past [15, 19] by assuming that the acceptor is a hydrogen-atom-like; the calculated value is 130 meV. In this calculation, the formula of $E = 13.6 \, m_h^*/m_0\varepsilon_0$ is used. The effective mass for hole $m_h^* = 0.73 \, m_0$. The relative low-frequency dielectric constant $\varepsilon_0 = 8.75$ [19]. Look *et al* [15] have suggested that the acceptor binding energy can be calculated by the D^0A^0 peak position. The D^0A^0 energy for a given pair will be described as $E_A = E_G - E_D - E_{DA} + e^2/4\pi\varepsilon r$, where E_G, E_D and E_A are the band gap, donor and accepter energies, respectively. ε is the dielectric constant and r is the pair separation. The average Coulomb energy $\Delta E = e^2/4\pi\varepsilon\langle r\rangle$ may be roughly estimated by letting $\langle r\rangle \sim (3/4\pi N_A)^{1/3}$. In these samples, N_A is very low. Thus, ΔE can be neglected. At 82 K, the band gap is 3.437 eV, and the donor energy is known to be about 60 meV [18, 22]. The calculated E_A (i.e. $E_G - E_D - E_{DA} = 3.437 - 0.06 - 3.225$) is, then, 152 meV. Clearly, the estimated theoretical values for the acceptor binding energy agree fairly well with our experimental value of 130 meV. Therefore it is suggested that the residual nitrogen atoms in the sample by incomplete oxidation are exhibited at the acceptor level of the PL spectra. Hence, the oxidized Zn_3N_2 can form p-type ZnO.

Hall effect measurement is simply a method to investigate the electrical properties of the films. In our previous paper [23], Li *et al* have observed p-type conduction by using Hall measurements of a similar material and explained it in detail. Hence we do not discuss these points again. In this paper, to further confirm the formation of p-ZnO:N thin film by thermal oxidation, a ZnO:N/n-Si structure was fabricated and is illustrated in figure 6. Two types of I–V measurements were carried out with this structure. (1) Ohmic contact testing and (2) junction testing across the ZnO:N/n-Si structure. To establish Ohmic contact, indium electrodes were deposited on both the ZnO:N thin film and the n-Si substrate via thermal evaporation. Figure 7(a) is an example plot of the I–V measurements conducted between any two indium electrodes on one side of the surface. That is, either on the ZnO:N thin film or on the n-Si substrate. A linear dependence of the I–V characteristic was observed to ensure a good Ohmic contact is established. Figure 7(b) shows the results of the I–V measurements across the ZnO:N/n-Si structure. Evidently, a rectifying behaviour is clearly illustrated for all three samples that were oxidized at three different temperatures of 500, 600 and 700 °C, respectively. However, the degree of the rectifying feature is strongly dependent on the oxidation temperature. When the sample is oxidized at 700 °C, the rectifying value reaches a maximum with a turn-on voltage of 2.44 V. As a result, it can be deduced that the rectifying characteristic is due to the p–n junction of ZnO:N/n-Si.

It is known that both intrinsic ZnO and Zn_3N_2 materials usually exhibit as n-type semiconductors due to their dominant donor defects, such as oxygen vacancies and Zn
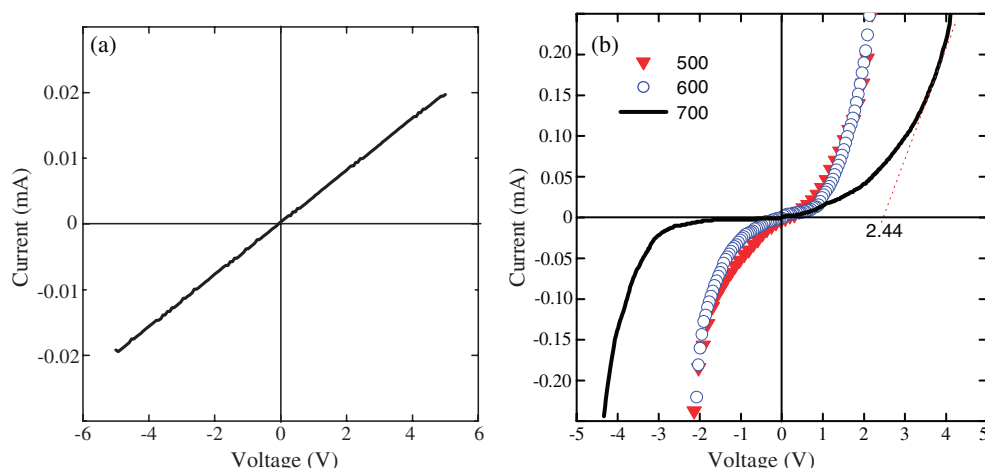
Figure 7. (a) The I–V curve for indium contacts on the ZnO thin film. (b) The I–V characteristics of the ZnO/n-Si annealed at different thermal oxidation temperatures.

interstitials [8]. At low annealing temperature, the thermal oxidation process takes place and a part of Zn_3N_2 transforms into ZnO:N with poor quality resulting from structural defects, high level of inactivated nitrogen, as well as deficiency of oxygen to form the correct ZnO structure in the sample. As a result, the sample may exhibit as an n-type. As the annealing temperature is increased, more oxygen atoms become available to eliminate the oxygen deficient sites. At the same time, more N atoms present in ZnO thin film can be activated as electron acceptors of the ZnO:N thin films, which, in turn, leads to the further pronounced p-type ZnO behaviour. When the oxidation temperature is above 700 °C, the acceptor density is decreased. The sample transforms from p-type conduction to n-type.

4. Conclusion

The study of both temperature dependent PL and I–V measurements has demonstrated that a p-type ZnO:N thin film can be successfully fabricated by the direct thermal oxidation of Zn_3N_2 thin film. It is shown that the oxidation temperature is a critical parameter to obtain a good quality p-type ZnO film. When the sample was oxidized at 700 °C, the maximum value of a rectifying characteristic is observed in the ZnO/n-Si structure. It suggests that a maximum concentration of nitrogen atoms present in the film become shallow electron acceptors by replacing oxygen atoms at the lattice sites.

Acknowledgments

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