

# The activation energy of the nitrogen acceptor in p-type ZnO film grown by plasma-assisted molecular beam epitaxy

J.W. Sun<sup>a,b</sup>, Y.M. Lu<sup>a,\*</sup>, Y.C. Liu<sup>a,c</sup>, D.Z. Shen<sup>a</sup>, Z.Z. Zhang<sup>a</sup>, B.H. Li<sup>a</sup>, J.Y. Zhang<sup>a</sup>,  
B. Yao<sup>a</sup>, D.X. Zhao<sup>a</sup>, X.W. Fan<sup>a</sup>

<sup>a</sup> Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics, and Physics, Chinese Academy of Science, Changchun 130033, People's Republic of China

<sup>b</sup> Graduate School of the Chinese Academy of Sciences, Beijing 100049, People's Republic of China

<sup>c</sup> Center for Advanced Optoelectronic Functional Material Research, Northeast Normal University, Changchun 130024, People's Republic of China

Received 14 April 2006; received in revised form 1 August 2006; accepted 1 September 2006 by J.W.P. Hsu

Available online 20 September 2006

## Abstract

The nitrogen-doped, p-type ZnO film was grown by plasma-assisted molecular beam epitaxy (P-MBE) on *c*-plane sapphire (*c*-Al<sub>2</sub>O<sub>3</sub>) using radical NO as oxygen and nitrogen sources. The activation energy of the nitrogen acceptor (AENA) was obtained by the temperature-dependent Hall effect and photoluminescence (PL) measurements, respectively. However, the values of AENA were rather different for the two methods, i.e., 75 meV for the Hall effect measurement and 145 meV for the photoluminescence measurement. In terms of the electrostatic interaction model, this energy difference was explained by the relationship between the Hall activation energy and the optical activation energy. According to these analyses, the reasonable value of the acceptor activation energy in nitrogen-doped p-type ZnO can be determined either by Hall experiments or by optical methods.

© 2006 Elsevier Ltd. All rights reserved.

PACS: 61.72.Vv; 78.55.Et; 71.55.Gs; 73.61.Ga; 81.05.Dz; 81.15.Hi

Keywords: A. Semiconductors; B. Impurities in semiconductors; C. Optical properties; D. Hall effect measurement

## 1. Introduction

ZnO, with a wide-band gap of 3.370 eV and a large exciton binding energy of 60 meV at room temperature, has stimulated substantial interest in the quest for blue/UV LED or LD, detectors, and other electronic devices [1,2]. However, one of the major obstacles in the development of this material is the difficulty in finding an efficient p-type dopant. Up to now, nitrogen (labeled N) has been proved to be the most successful dopant for the growth of p-type ZnO [3,4], especially since the observation of the electro-luminescence from the ZnO homojunction [5,6]. Nevertheless, in order to fully realize

ultraviolet light emitters based on this material, the quality of p-type ZnO must be improved. In this regard, the activation energy of N acceptor is one of the most important parameters in evaluating the performance of p-type doping process, because it controls the hole concentration and affects its mobility. In the previous studies, the reported values of the activation energy for N acceptor determined by optical methods varied over a wide range from 165 to 248 meV [3,4,7], while the values determined by temperature-dependent Hall effect (T-Hall) measurements were considerably lower than the former (90 meV [8], 100 meV [5]). The discrepancy between activation energies found by T-Hall and PL was explained by screening of carriers, as reported by Look et al. [9]. In fact, this phenomenon is always the case for most of the semiconductors [10–12] and is explained by the dependence of the thermal activation energy on the ionized acceptor concentration [12]. However, in the case of ZnO, this energy difference has not received a quantitative analysis, and a conclusive value still remains unavailable.

\* Corresponding address: Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics, and Physics, Chinese Academy of Science, 16-Dongnanhu Road, Changchun 130033, People's Republic of China. Tel.: +86 431 5682964; fax: +86 431 5682964.

E-mail address: [ymlu@mail.jl.cn](mailto:ymlu@mail.jl.cn) (Y.M. Lu).

Thus, a more comprehensive investigation combining T-Hall measurements with optical methods is required to obtain a reasonable value of N acceptor activation energy. To our knowledge, a systematic study has not been reported.

In this work, we show an N-doped p-type ZnO grown by P-MBE using radical NO as oxygen source and nitrogen dopant. The activation energy of N acceptor is deduced to be 75 meV by fitting the T-Hall data. On the other hand, it is estimated to be 145 meV from a donor–acceptor pair transition of 3.255 eV at 77 K. However, there is a considerable difference between the two values. This discrepancy is furthermore explained by the relationship between the Hall activation energy and the optical activation energy. According to these arguments, the reasonable value of the acceptor activation energy in N-doped p-type ZnO, determined either by the T-Hall measurement or by the optical method, has been proposed.

## 2. Experiments

The epitaxial ZnO thin film was grown by P-MBE. The substrate, *c*-Al<sub>2</sub>O<sub>3</sub>, was heated in vacuum ( $\leq 1 \times 10^{-7}$  Pa) at 800 °C for 30 min in the MBE preparing chamber after a cleaning process to obtain a clean and highly crystallized surface, which was introduced previously [4]. Pure zinc (99.9999%) was supplied by means of a Knudsen effusion cell. Oxygen and nitrogen were obtained to grow N-doped ZnO from the NO with 99.999% purity, flowing through an Oxford Applied Research Model HD25 r.f. (13.56 MHz) plasma source, operated at a power of 300 W. During growth, Zn beam partial pressure, NO flow rate and substrate temperature were fixed at  $2.5 \times 10^{-4}$  Pa, 0.5 ml/min and 425 °C, respectively. The thickness of the N-doped sample measured by ellipsometry was about 850 nm.

T-Hall measurements were carried out for the p-type ZnO film in van de Pauw configuration, by employing both positive and negative currents and magnetic fields, and the results were averaged in order to compensate for various electromagnetic effects [13]. The equipment was Lakeshore's 7707 Hall measurement system. The Ohmic contacts for electrical measurement were made by vacuum-sintering ( $\leq 5 \times 10^{-3}$  Pa) small indium dots at the four corners of square samples. The effect of persistent photoconductivity (PPC) was also considered and the electrical results of our samples were almost independent of the light. PL spectra were measured employing 325 nm He–Cd laser as the excitation source and collected with a microprobe system made by Jobin–Yvon Company in France.

## 3. Results and discussions

The p-type conduction of the N-doped ZnO film was confirmed by T-Hall measurements. The hole concentration  $p$  was derived from the Hall coefficient  $R_H$  by:

$$p = \frac{r_H}{qR_H}, \quad (1)$$

where the Hall scattering factor  $r_H$  is assumed to be of value unity and  $q$  is the electronic charge. The electrical results

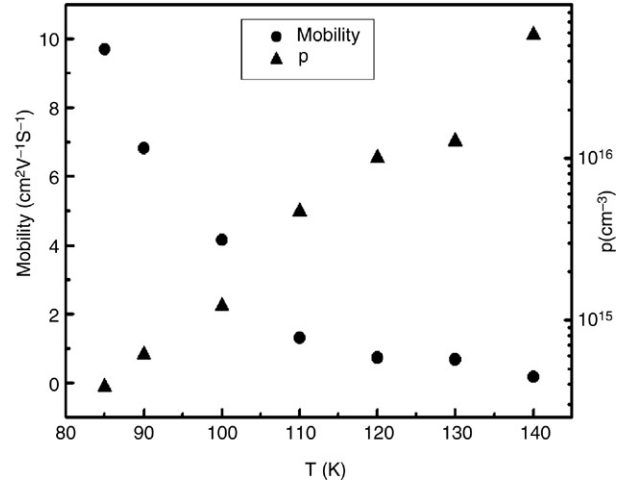


Fig. 1. The dependence of the hole concentration and mobility on the temperature from 85 to 140 K for N-doped p-type ZnO.

at room temperature are given: resistivity  $\rho(300 \text{ K}) = 78 \Omega \text{ cm}$ ; hole concentration  $p(300 \text{ K}) = 4.45 \times 10^{17} \text{ cm}^{-3}$ ; mobility  $\mu(300 \text{ K}) = 0.18 \text{ cm}^2/\text{V s}$ . Fig. 1 shows the temperature dependence of the hole concentration and Hall mobility ranging from 85 to 140 K. The Hall mobility decreases from 9.69 to 0.18  $\text{cm}^2/\text{V s}$ , while the hole concentration increases from  $3.87 \times 10^{14}$  to  $5.81 \times 10^{16} \text{ cm}^{-3}$  with the increasing temperature. It is roughly estimated that the decrease of the hole mobility in this temperature region is predominantly due to lattice scattering. The increase of the hole concentration with the temperature can be understood in terms of the native and foreign point defect model. Nitrogen primarily substitutes for oxygen and acts as acceptors. These acceptors may be partially compensated by native donors such as zinc interstitials or oxygen vacancies. With the increasing temperature, the acceptors can be gradually activated and thus the hole concentration increases. Therefore, it is rather reasonable to believe that the N-doping ZnO film behaves as a partially compensated p-type semiconductor. Based on the above analysis, the Hall activation energy of N acceptor (labeled  $E_A^H$ ) can be determined by a single-donor/single-acceptor model:

$$\frac{p(p + N_D)}{N_A - N_D - p} = \frac{N'_V}{g} T^{\frac{3}{2}} e^{-\frac{E_A^H}{kT}}, \quad (2)$$

where  $N_A$  and  $N_D$  are the acceptor and donor concentrations, respectively,  $g$  is the impurity level spin degeneracy factor,  $N'_V T^{\frac{3}{2}} = 2 \left( \frac{2\pi m_p^* kT}{h^2} \right)^{\frac{3}{2}}$  is the effective valence-band state density,  $T$  is the absolute temperature, and  $k$  is Boltzmann's constant.  $N'_V = 4.94 \times 10^{15} \text{ cm}^{-3} \text{ K}^{-3/2}$  and  $g = 4$  [3]. Furthermore,  $N_D$  can be roughly estimated from the electron concentration in undoped n-type ZnO films grown by the same conditions as in the case of p-type ZnO [20] and is about  $1 \sim 3 \times 10^{18} \text{ cm}^{-3}$ , and the value of  $N_A$  should be larger than that of  $N_D$  for the p-type ZnO films. Then the hole concentration in the temperature range 85–140 K is several orders of magnitude below the value of  $(N_A - N_D)$  or  $N_D$ , as shown in Fig. 1. Hence, we can conclude that  $p \ll N_D$  and  $p \ll (N_A - N_D)$ ,

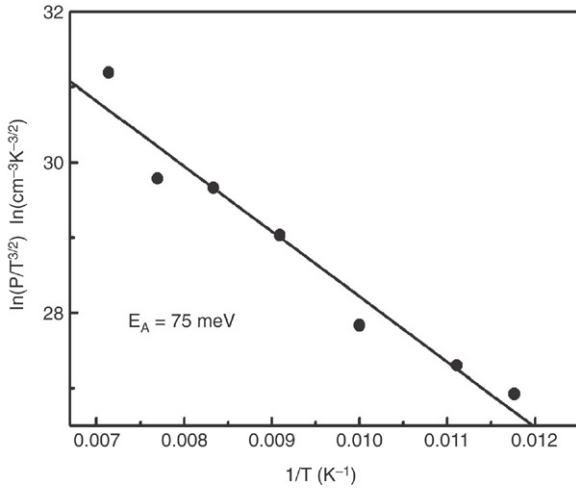


Fig. 2. The plot of  $\ln(p/T^{3/2})$  versus  $1/T$  in the temperature range 85–140 K for the N-doped p-type ZnO. The solid line is a least-squares fit of the data with Eq. (3).

when the temperature is below 140 K. Then, Eq. (2) can be approximated by

$$p = \left( \frac{N_A}{N_D} - 1 \right) \frac{N'_V}{g} T^{\frac{3}{2}} e^{-\frac{E_A^H}{kT}}. \quad (3)$$

Obviously,  $E_A^H$  could be deduced by a least-squares fit to the data of the natural logarithm of  $(p/T^{3/2})$  versus  $1/T$  using Eq. (3). As shown in Fig. 2,  $E_A^H = 75$  meV. The accuracy of  $E_A^H$ , at best, is limited to  $\pm 7$  meV, due to the limited temperature range of the ionization in the experimental curve as well as the experimental errors arising from the low mobility of the p-type sample [9].

On the other hand, in order to obtain the activation energy of N acceptor by an optical method (labeled  $E_A^O$ ), PL spectrum of p-type ZnO is investigated in detail. Fig. 3 shows PL results (77 K) of the undoped sample and N-doped p-type layer. The spectrum of undoped ZnO is typically dominated by a free exciton (FE) peak at 3.376 eV and a neutral donor-bound exciton ( $D^0X$ ) peak at 3.360 eV [14]. The two weaker lines centered at 3.313 and 3.240 eV are assigned to the first and the second longitudinal optical phonon (LO) replicas of the FE, respectively [14]. By comparing the undoped with p-type samples, as shown in Fig. 3, the most obvious difference is that the latter has a dominant line centered at 3.255 eV, with three gradually weaker broad lines centered at 3.185, 3.112 and 3.041 eV, respectively. Considering the fact that the line appearing in the range 3.245–3.264 eV has been assigned to a donor–acceptor pair (DAP) transition in our previous reports [4,15], the line centered at 3.255 eV is attributed to DAP recombination. The three shoulders located at the lower-energy side of DAP are assigned to DAP-LO, DAP-2LO and DAP-3LO, respectively, since the energy difference between them is close to the LO phonon energy of ZnO [16]. The higher-energy side peak centered at 3.366 eV is composed of the FE emission and ( $D^0X$ ) emission. The origin of the small peak at 3.311 eV is not very clear and needs further investigation.

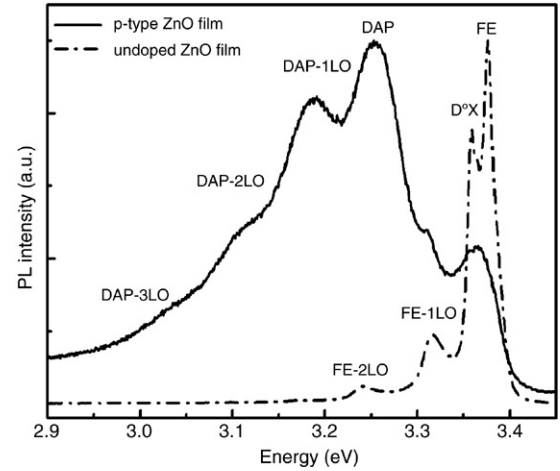


Fig. 3. Normalized PL spectra of undoped ZnO and N-doped p-type ZnO at 77 K.

Then, the activation energy of N acceptor for a given donor–acceptor pair will be given by  $E_A^O = E_G - E_{DAP} - E_D + \frac{e^2}{4\pi\epsilon r}$  [3], where  $E_G$ ,  $E_D$  and  $E_{DAP}$  are the band gap, donor binding energy, and DAP transition energy, respectively,  $\epsilon$  is the dielectric constant, and  $r$  is the average distance between the donor and acceptor. The average coulomb energy  $\frac{e^2}{4\pi\epsilon r}$  can be very roughly estimated to be 20 ~ 30 meV [9]. The donor energy is known to be about 60 meV [1,17]. At 77 K, the band gap  $E_G = 3.436$  eV, taking the energy position of FE as 3.376 eV and the free-exciton binding energy as 60 meV. Thus,  $E_A^O$  is estimated to be  $145 \pm 5$  meV, which coincides reasonably well with the reported value of  $165 \pm 40$  meV [7].

Now, we have obtained the acceptor activation energy in the N-doped p-type ZnO by the T-Hall and PL measurements, respectively, namely,  $E_A^H = 75$  meV for the former and  $E_A^O = 145$  meV for the latter. The Hall activation energy  $E_A^H$  is obviously smaller than the optical value  $E_A^O$ . However, it is not too surprising because this is always the case in group IV, III–V, and II–VI semiconductors [9–12,18]. A typical example is Mg-doped p-type GaN, with the optical energy of  $224 \pm 4$  meV [12] and the Hall activation energy varied over the range from 125 to 170 meV [12,19].

To be more quantitative, the relationship between  $E_A^H$  and  $E_A^O$  will be discussed in detail. Since the pioneering work of Pearson and Bardeen, it has been well known that the impurity activation energy determined by T-Hall measurements is proportional to the 1/3 power of the impurity concentration, which is attributed to the potential interaction between the free carriers and impurity ions [10]. On the other hand, the optical activation energy of an impurity is not known to vary with the impurity concentration [18]. Later, several models based on the electrostatic interaction have been proposed, and a detailed review can be found in the literature [12]. However, to our knowledge, no conclusive model has been proposed to explain the energy difference between  $E_A^H$  and  $E_A^O$  for various semiconductors. For p-type GaN, it has been demonstrated that the Hall activation energy  $E_A^H$  is given by [12]

$$E_A^H = E_A^O - \alpha (N_D + p)^{\frac{1}{3}}, \quad (4)$$

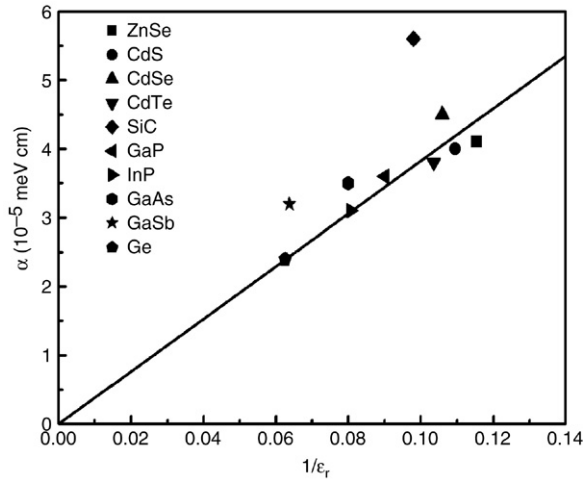


Fig. 4. Plot of the values of  $\alpha$  versus the reciprocal dielectric constant for various semiconductors. The solid line corresponds to  $\alpha\epsilon_r = 38.2 \times 10^{-5}$  meV cm. Data and plot from literature [11,12].

where  $E_A^O$  is the optical activation energy for the acceptor,  $\alpha$  is a parameter related to the static dielectric constant  $\epsilon_r$ . Pödör suggested that the values of  $\alpha$  for different semiconductors should be proportional to the reciprocals of the static dielectric constants, namely,  $\alpha = (40 \pm 5) \times 10^{-5}/\epsilon_r$  meV cm, as shown in Fig. 4 [11,12] ( $\epsilon_r = 8.12$  for ZnO [9]). Since ZnO has the same crystal structure, similar lattice constants and bandgap energy to that of GaN, it is rather reasonable to believe that Eq. (4) could be applicable to ZnO. If assuming that  $E_A^O = 145$  meV,  $N_D = 1 \sim 3 \times 10^{18}$  cm $^{-3}$  and  $p = 4.45 \times 10^{17}$  cm $^{-3}$ , as mentioned above, then  $E_A^H = 71 \sim 89$  meV according to the Eq. (4). This result is in excellent agreement with the value of  $E_A^H = 75$  meV obtained by the T-Hall measurement.

According to the above analyses, the reduction of the activation energy, as determined by the T-Hall measurement, is attributed to the potential interaction between free holes and ionized acceptors [10,12]. This suggests that the electrostatic interaction model is suitable for the N-doped p-type ZnO film, as served in other semiconductors [11,12]. Therefore, the energy difference between  $E_A^H$  and  $E_A^O$  can be quantitatively explained by Eq. (4). Then, we can conclude that the activation energy of N acceptor, determined either by the T-Hall measurement or by the optical method, are comparatively reasonable.

#### 4. Conclusions

We have produced N-doped p-type ZnO on *c*-Al $_2$ O $_3$  by P-MBE using radical NO as oxygen source and nitrogen dopant. The value of N acceptor activation energy, as deduced by fitting the T-Hall data, have been compared with that derived from the PL spectra. Furthermore, the energy difference between

them has been given a quantitative analysis on the basis of the available model. Thus, the reasonable value of acceptor activation energy has been proposed. It is hoped that these results provide a further understanding about properties of the nitrogen acceptor and thus speedup the progress of ZnO-based ultraviolet light emitters.

#### Acknowledgements

This work is supported by the Key Project of National Natural Science Foundation of China under Grant No. 60336020, the Innovation Project of Chinese Academy of Sciences, the National Natural Science Foundation of China under Grant No. 60278031, No. 60376009, No. 50402016, No. 60506014, No. 60576040 and No. 60501025.

#### References

- [1] D.C. Look, Mater. Sci. Eng. B 80 (2001) 383.
- [2] Z.K. Tang, G.K.L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, Y. Segawa, Appl. Phys. Lett. 72 (1998) 3270.
- [3] D.C. Look, D.C. Reynolds, C.W. Litton, R.L. Jones, D.B. Eason, G. Cantwell, Appl. Phys. Lett. 81 (2002) 1830.
- [4] H.W. Liang, Y.M. Lu, D.Z. Shen, Y.C. Liu, J.F. Yan, C.X. Shan, B.H. Li, Z.Z. Zhang, J.Y. Zhang, X.W. Fan, Phys. Status Solidi A 202 (2005) 1060.
- [5] A. Tsukazaki, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, M. Kawasaki, Nat. Mater. 4 (2005) 42.
- [6] J. Nause, M. Pan, V. Rengarajan, W. Nemeth, S. Ganesan, A. Payne, N. Li, I. Ferguson, Proc. SPIE Int. Soc. Opt. Eng. 5941 (2005) 59410D.
- [7] A. Zuener, H. Alves, D.M. Hofmann, B.K. Meyer, A. Hoffmann, U. Habocek, M. Strassburg, M. Dworzak, Phys. Status Solidi B 234 (2002) R7.
- [8] D.C. Look, B. Claffin, Ya.I. Alivov, S.J. Park, Phys. Status Solidi A 201 (2004) 2203.
- [9] D.C. Look, Semicond. Sci. Technol. 20 (2005) s55.
- [10] G.L. Pearson, J. Bardeen, Phys. Rev. 75 (1949) 865.
- [11] B. Pödör, Semicond. Sci. Technol. 2 (1987) 177.
- [12] B. Pödör, Proc. SPIE Int. Soc. Opt. Eng. 4412 (2001) 299.
- [13] D.C. Look, Electrical Characterization of GaAs Materials and Devices, Wiley, New York, 1989.
- [14] H.J. Ko, Y.F. Chen, T. Yao, K. Miyajima, A. Yamamoto, Goto, Appl. Phys. Lett. 77 (2000) 537.
- [15] S.J. Jiao, Y.M. Lu, D.Z. Shen, Z.Z. Zhang, B.H. Li, B. Yao, J.Y. Zhang, D.X. Zhao, X.W. Fan, Abstracts of the 14th International Conference on Luminescence, TUE.P.P.150 (ICL'05, Beijing, 2005).
- [16] F. Decremps, Julio Pellicer-Porres, A.M. Saitta, Jean-Claude Cheervin, A. Polian, Phys. Rev. B 65 (2002) 092102.
- [17] D.C. Reynolds, D.C. Look, B. Jogai, C.W. Litton, T.C. Collins, W. Harsch, G. Cantwell, Phys. Rev. B 57 (1998) 12151.
- [18] J. Monecke, W. Siegel, E. Ziegler, G. Kuhnel, Phys. Status Solidi B 103 (1981) 269.
- [19] T. Tanaka, A. Watanabe, H. Amano, Y. Kobayashi, I. Akasaki, S. Yamazaki, M. Koike, Appl. Phys. Lett. 65 (1994) 593.
- [20] O. Lopatiuk-Tirpak, W.V. Schoenfeld, L. Chernyak, F.X. Xiu, J.L. Liu, S. Jang, F. Ren, S.J. Pearton, A. Osinsky, P. Chow, Appl. Phys. Lett. 88 (2006) 202110.