

# Temperature-dependent photoluminescence of undoped, N-doped and N-In codoped ZnO thin films

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## Abstract

Temperature-dependent photoluminescence properties of undoped, N-doped and N-In codoped p-type ZnO thin films have been investigated in detail. The yielded temperature dependences of ultraviolet peak energy, width and intensity for several resolved emissions exhibit the different carrier recombination processes associated with doping mechanisms. We have revealed the acceptor binding energy of 113 meV, 140 meV and 112 meV and donor one of 56 meV, 82 meV and 112 meV for undoped, N-doped and N-In codoped ZnO, respectively, together with the broadening of the acceptor levels in N-doped and N-In codoped ZnO. We have also clarified the origin of the ZnO deep-level visible emission.

As a wide band gap (3.37 eV at room temperature) semiconductor with a large exciton binding energy (about 60 meV), ZnO has recently attracted much attention for optoelectronic devices, such as light-emitting diodes and laser diodes [1]. Due to the asymmetric doping limitations in ZnO [2], a great deal of effort has been made to realize the p-type doping of ZnO. Many groups have reported the fabrication of p-type ZnO by intentionally undoping [3], single-doping with Li [4], N [5,6], P [7], As [8,9] and Sb [10], as well as codoping techniques [11–13]. In contrast to the growth interest, the understanding of fundamental properties in p-type ZnO is still relatively incomplete, especially for the doping mechanisms and the acceptor and donor levels.

It is essential to understand the carrier recombination processes and the role of defects in p-type ZnO to fabricate the optoelectronic devices. Photoluminescence (PL) properties have been studied for p-ZnO of undoped [3] and single-doped with N [5], P [7], As [8] and Sb [10]. Recently, there is also a report on the compared PL study between P-doped and P-In codoped p-ZnO [13]. However, owing to the lack of

effective methods to resolve the experimental emission spectra, the exact mechanisms of ultraviolet (UV) emission in ZnO and the corresponding carrier recombination processes are still subjects of considerable debates. Furthermore, compared with the interest in UV emission properties, the temperature-dependent behaviour of the visible emission in ZnO is rarely studied and the responsible defects remain controversial.

In this paper, we have presented a comprehensive investigation of temperature-dependent PL properties of undoped, N-doped and N-In codoped p-type ZnO thin films grown by ultrasonic spray pyrolysis (USP). Through multi-Gaussian fittings to the experimental spectra, the temperature dependences of UV peak energy, width and intensity have been obtained and fitted to reveal the different carrier recombination processes and doping mechanisms. In addition, the mechanism of the deep-level visible emission in ZnO has also been discussed.

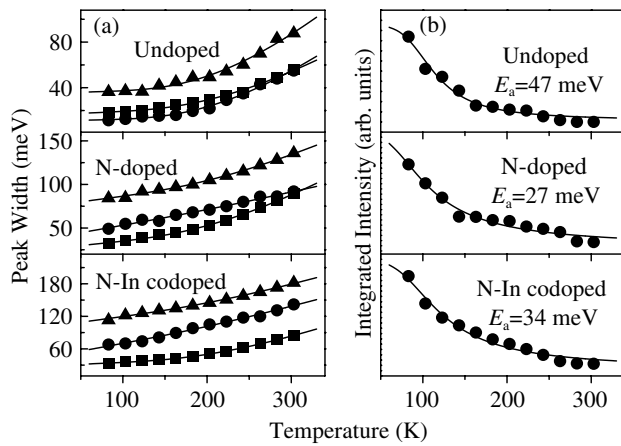
The studied undoped, N-doped and N-In codoped ZnO thin films were deposited by USP at atmosphere [11]. The  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (AR,  $0.5 \text{ mol l}^{-1}$ ),  $\text{CH}_3\text{COONH}_4$  (AR,  $2.5 \text{ mol l}^{-1}$ ) and  $\text{In}(\text{NO}_3)_3$  (AR,  $0.5 \text{ mol l}^{-1}$ ) were chosen as the sources of Zn, N and In, respectively. The atomic

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**Table 1.** Results of fitting peak energy and width for bands 1 (FX), 2 (A<sup>0</sup>X) and 3 (eA<sup>0</sup>) in undoped, N-doped and N-In codoped ZnO. Here  $E_g(0) = 3.437$  eV.

Sample	Band	$E(0)$ (eV)	$\alpha$ ( $10^{-4}$ eV K <sup>-1</sup> )	$E_g(0) - E(0)$ (meV)	$\Gamma_0$ (meV)	$\gamma_{ph}$ (meV K <sup>-1</sup> )	$\Gamma_{LO}$ (meV)
Undoped ZnO	1	3.379	9.20	58	16	0.033	435
	2	3.361	8.96	76	11	0.017	594
	3	3.324	7.38	113	35	0.022	690
N-doped ZnO	1	3.375	9.09	62	25	0.101	502
	2	3.346	8.12	91	36	0.171	61
	3	3.297	8.55	140	74	0.128	339
N-In codoped ZnO	1	3.379	7.28	58	28	0.066	539
	2	3.373	8.75	64	42	0.287	171
	3	3.325	10.00	112	98	0.212	267


**Figure 3.** (a) Temperature-dependent peak widths and the fitting curves for bands 1 (■), 2 (●) and 3 (▲) in undoped, N-doped and N-In codoped ZnO. (b) Integrated PL intensity and the fitting curves for the band 2 (●) as a function of temperature. Bands 1, 2 and 3 are assigned to FX, A<sup>0</sup>X and eA<sup>0</sup>, respectively.

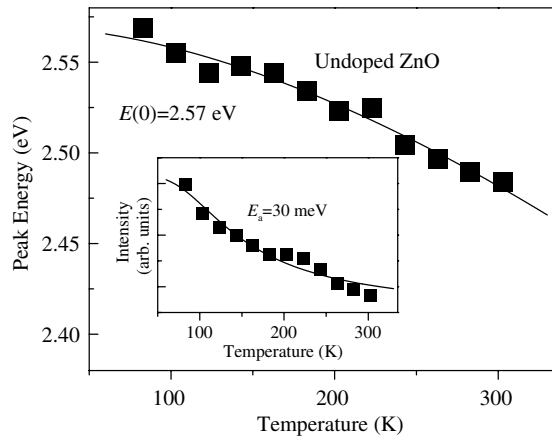
binding energy  $E_D$  can be estimated from the equation  $E_D = E_g - E_A - E_{DAP} + \sqrt[3]{4\pi/3}(e^2/4\pi\epsilon\epsilon_0)N_{A,D}^{1/3}$  [6], where  $N_{A,D}$  is the majority impurity concentration,  $\epsilon = 8.656$  is the specific dielectric constant and  $\epsilon_0$  is the dielectric constant in a vacuum. Making  $N_{A,D}$  approximately equal to the hole density, we have  $E_D$  of 56 meV, 82 meV and 112 meV for undoped, N-doped and N-In codoped ZnO, respectively. In addition, the weak emission of band 5 at 3.143 eV in undoped ZnO is attributed to the zinc vacancy ( $V_{Zn}$ )-related defect [3]. Although the nature of shallow acceptor is difficult to identify in undoped ZnO, the obtained  $E_D$  of 56 meV is in good agreement with the reported 56–58 meV [19].  $E_A$  of 140 meV in N-doped film corresponds to  $N_O$  acceptor while the smaller  $E_A$  of 112 meV in N-In codoped ZnO is attributed to  $2N_O$ -In<sub>Zn</sub> acceptor complex, which complies with the theoretical prediction of reduced acceptor transition energy due to the codoping technique [20]. On the other hand, the N-doping and N-In codoping in ZnO result in the deeper and deeper donor level according to  $E_D$ . Thus fewer and fewer free electrons can be activated to compensate holes. The enhanced hole density from Hall measurements in N-doped and N-In codoped ZnO is the best demonstration.

Figure 3(a) displays the temperature dependence of peak width  $\Gamma(T)$  of bands 1 (squares), 2 (circles) and 3 (triangles) for undoped, N-doped and N-In codoped ZnO. The smaller peak width of bands 1 and 2 (FX and A<sup>0</sup>X) than that of band 3 (eA<sup>0</sup>)

is due to the excitonic properties, which further supports the above assignments. The solid curves are least-square fits using the equation  $\Gamma(T) = \Gamma_0 + \gamma_{ph}T + \Gamma_{LO}/[\exp(\hbar\omega_{LO}/k_B T) - 1]$  [21], where  $\hbar\omega_{LO} = 72$  meV is the energy of a longitudinal optical (LO) phonon,  $\Gamma_0$  is the intrinsic line width at 0 K,  $\gamma_{ph}$  is the exciton-acoustic phonon coupling constant and  $\Gamma_{LO}$  represents the exciton-LO phonon (Fröhlich) coupling strength. The fitting parameters are also listed in table 1. Among them, the values of  $\Gamma_{LO}$  are much larger than those of  $\gamma_{ph}$ , which is mainly owing to the high Fröhlich constant and the LO energy. For the values of  $\Gamma_0$ , the ratios between N-doped and undoped ZnO are 1.56, 3.27 and 2.11 for FX, A<sup>0</sup>X and eA<sup>0</sup>, respectively, while the corresponding ratios are 1.75, 3.82 and 2.80 in codoped film. This broadening behaviour is attributed to the doping mechanisms. With the enhanced hole density by N-doping and N-In codoping, more temperature-independent mechanisms including hole-hole interaction and impurity will be introduced to broaden  $\Gamma_0$ . On the other hand, the N-doping and N-In codoping will broaden the acceptor level in the band gap [20], which directly leads to the stronger broadening of A<sup>0</sup>X and eA<sup>0</sup> emissions than FX.

Figure 3(b) shows the integrated intensity of A<sup>0</sup>X (band 2) emission as a function of temperature for the three samples. The observed overall temperature-quenching behaviour can be well described by the equation  $I(T) = I_0/[1 + A \exp(-E_a/k_B T)]$  [22], where  $I_0$  is the emission intensity at zero temperature,  $A$  is a parameter and  $E_a$  is the activation energy in the thermal quenching process. The good fits (solid curves) yielded  $E_a$  of 47 meV, 27 meV and 34 meV for undoped, N-doped and N-In codoped ZnO, respectively. In order to understand the thermal quenching process, the localization energy  $E_{loc}$  (FX-A<sup>0</sup>X) of 18 meV, 29 meV and 6 meV for undoped, N-doped and N-In codoped ZnO, respectively, has been obtained to compare with  $E_a$ . We identify the dissociation process of A<sup>0</sup>X to a FX and a neutral acceptor in N-doped ZnO because of the comparable values of the activation and localization energy. For undoped and codoped ZnO, the difference between  $E_a$  and  $E_{loc}$  is 29 and 28 meV. Considering the corresponding  $E_A$  of 113 and 112 meV, we can deduce almost the same Haynes factor of 0.25. Therefore, the quenching processes include the thermal ionization of acceptor besides the above dissociation in undoped and N-In codoped films.

The reported visible emission in ZnO was attributed to different types of electron transitions in various defects involving oxygen vacancy ( $V_O$ ),  $V_{Zn}$ , zinc interstitial ( $Zn_i$ )



**Figure 4.** Temperature dependence of deep-level emission energy in undoped ZnO. The inset shows the integrated intensity as a function of temperature. The solid curves are the fitting results.

and  $O_{Zn}$  [1]. To clarify its origin, we have calculated the temperature-dependent peak energies of the deep-level emission in undoped ZnO (figure 4) from the good single-Gaussian fittings of the experimental spectra. Since the deep-level emission follows the shrinkage of the band gap with increasing temperature (solid curve by Varshni fitting), we exclude the possibility of the transition within localized defects. The obtained  $E(0)$  of 2.57 eV clearly indicates that this deep-level emission is caused by the electron transition from the  $V_O$  donor level to the valance band [23]. The inset of figure 4 presents the corresponding integrated intensity as a function of temperature. The yielded  $E_a$  through fitting to the thermal quenching equation (solid curve) is 30 meV, which is close to the reported value [24] and may attribute to the process  $V_O^x \rightarrow V_O^\bullet + e$ . Furthermore, as interpreted above, fewer and fewer free electrons can be thermally activated in N-doped and N-In codoped ZnO, i.e. weaker and weaker deep-level emissions in figure 1, confirming again the electron transition for the ZnO deep-level emission.

In summary, we have performed the multi-Gaussian fittings to the experimental NBE spectra of undoped, N-doped and N-In codoped p-type ZnO in the temperature range from 83 to 303 K. With the assignments of FX,  $A^0X$  and  $eA^0$  transitions, the temperature dependences of UV peak energy, width and intensity have been analysed in detail. The obtained  $E_A$  of 113 meV, 140 meV and 112 meV with  $E_D$  of 56 meV, 82 meV and 112 meV for undoped, N-doped and N-In codoped ZnO, respectively, exhibits good correlations with the different carrier recombination processes. The broadening of acceptor levels has been observed in N-doped and N-In codoped ZnO. In addition, we have confirmed that the deep-level visible emission in ZnO originates from the electron transition from the  $V_O$  donor level to the valance band.

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## References

- [1] Özgür Ü, Alivov Ya I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S-J and Morkoc H 2005 *J. Appl. Phys.* **98** 041301
- [2] Yamamoto T and Yoshida H K 2001 *Physica B* **302–303** 155
- [3] Zeng Y J, Ye Z Z, Xu W Z, Lu J G, He H P, Zhu L P, Zhao B H, Che Y and Zhang S B 2006 *Appl. Phys. Lett.* **88** 262103
- [4] Zeng Y J, Ye Z Z, Xu W Z, Li D Y, Lu J G, Zhu L P and Zhao B H 2006 *Appl. Phys. Lett.* **88** 062107
- [5] Wang L and Giles N C 2004 *Appl. Phys. Lett.* **84** 3049
- [6] Look D C, Reynolds D C, Litton C W, Jones R L, Eason D B and Cantwell G 2002 *Appl. Phys. Lett.* **81** 1830
- [7] Xiu F X, Yang Z, Mandalapu L J, Liu J L and Beyerermann W P 2006 *Appl. Phys. Lett.* **88** 052106
- [8] Ryu Y R, Lee T S and White H W 2003 *Appl. Phys. Lett.* **83** 87
- [9] Look D C, Renlund G M, Burgener R H II and Szelove J R 2004 *Appl. Phys. Lett.* **85** 5269
- [10] Xiu F X, Yang Z, Mandalapu L J, Zhao D T and Liu J L 2005 *Appl. Phys. Lett.* **87** 252102
- [11] Bian J M, Li X M, Gao X D, Yu W D and Chen L D 2004 *Appl. Phys. Lett.* **84** 541
- [12] Lu J G, Ye Z Z, Zhuge F, Zeng Y J, Zhao B H and Zhu L P 2004 *Appl. Phys. Lett.* **85** 3134
- [13] Ye J D, Gu S L, Li F, Zhu S M, Zhang R, Shi Y, Zheng Y D, Sun X W, Lo G Q and Kwong D L 2007 *Appl. Phys. Lett.* **90** 152108
- [14] Kong J F, Chen H, Ye H B, Shen W Z, Zhao J L and Li X M 2007 *Appl. Phys. Lett.* **90** 041907
- [15] Ye H B, Kong J F, Shen W Z, Zhao J L and Li X M 2007 *Appl. Phys. Lett.* **90** 102115
- [16] Varshni Y P 1967 *Physica* **34** 149
- [17] Hutson A R 1959 *J. Phys. Chem. Solids* **8** 467
- [18] Ko H J, Chen Y F, Zhu Z, Yao T, Kobayashi I and Uchiki H 2000 *Appl. Phys. Lett.* **76** 1905
- [19] Reynolds D C, Look D C, Jogai B, Litton C W, Collins T C, Harsch W C and Cantwell G 1998 *Phys. Rev. B* **57** 12151
- [20] Yamamoto T 2003 *Japan. J. Appl. Phys. Part 2* **42** L514
- [21] Makino T, Chia C H, Tuan N T, Segawa Y, Kawasaki M, Ohtomo A, Tamura K and Koinuma H 2000 *Appl. Phys. Lett.* **76** 3549
- [22] Shen W Z and Shen S C 1996 *J. Appl. Phys.* **80** 5941
- [23] Kang H S, Kang J S, Kim J W and Lee S Y 2004 *J. Appl. Phys.* **95** 1246
- [24] Liu Z S, Jing X P, Wang L X and Li Y 2006 *J. Electrochem. Soc.* **153** G1035