

Photoluminescence relevant to intrinsic defects of ZnO crystal by Zn doping

WEIYING ZHANG*, JIANGUO ZHAO, ZHAOJUN LIU, LIJIE SUN^a, ZHUXI FU^a

College of Physics and Electronic information, Luoyang Normal College, Henan Luoyang, 471022, PR China

^aDepartment of Physics, University of Science and Technology of China, Anhui Hefei, 230026, PR China

ZnO single crystal wafers were treated by thermal diffusion Zn doping to study the intrinsic defects in ZnO, optical properties of samples which were obtained under different diffusion time and cooling mode were investigated by photoluminescence (PL) spectra. It can be seen that the UV intensity enhanced clearly by Zn doping, and when prolonging diffusion time, the visible band also appeared. According to the analysis of the thermal diffusion mechanism, it can be concluded that Zn_i formed in the first stage of diffusion, and then Zn_o generated later. Based on the energy levels of these defects, the visible peak at 510nm is probably from Zn_o. Low temperature (LT) PL spectrum of ZnO sample with the strongest UV peak was measured and investigated. At 10K, the neutral donor-bound excitons dominate in the PL spectrum. Two electron satellite (TES) transitions of the donor-bound excitons appeared in the chart allow us to determine the donor binding energy around 52meV, which is consisted with Zn_i defect. Therefore, the Zn_i is an important shallow defect contributing to the conductance of ZnO at room temperature.

(Received February 11, 2014; accepted July 10, 2014)

Keywords: ZnO crystal, Zn doping, Intrinsic defect, Photoluminescence

1. Introduction

Zinc Oxide is a wide-band-gap semiconductor with numerous applications as an ultraviolet emitting material [1], a buffer layer for GaN-based devices [2], a transparent conductor in solar cells [3], and a transparent transistor [4]. Specially, recent progress in crystal growth has also opened up prospects for optoelectronic devices based on n and p-type ZnO. High quality n-type ZnO can be easily obtained by Al, Ga and In doping. However, for the p-type doping, in spite of ten years effort the reliability and reproducibility of it are serious issues. The most fundamental reason is that some of the basic properties of ZnO still remain unclear, such as the dominant native defects in ZnO [5-8] and the origin of the defect-related emission [9-12]. Understanding the property of native defects is an important issue to get great progress in optoelectronic applications. We can modulate the concentration and type of native defects through high-temperature diffusion doping Zn or O.

As we know, high-temperature diffusion doping is an important method to get n or p type semiconductors that has been successfully used in Si and Ge. In this process, the doping atom goes into the lattice through diffusion at high temperature from 800°C to 1300°C, the microscopic mechanism of doping atom diffusion mainly includes vacancy diffusion (the exchange of vacancy and doping atom), the interstitial atom diffusion, exchange of interstitial atom and substitutional atom. The unexpected

results can get using the technology in ZnO, up to now, few works has been done on it. In this paper, the single crystal ZnO was treated in Zn ambient at 800 °C under different conditions, the optical and electrical properties have been investigated detailed.

2. Experiment details

Bulk ZnO single crystals bought from KMT Corporation of USA were used in our experiments. The crystal ZnO wafers were treated in Zn ambient according to the process as follows. First, place ZnO crystal with certain Zn powder in a sealed quartz ampoule, and then sealed it in an autoclave with nitrogen as a protecting gas. In this experiment, high temperature and high pressure are the key factor, the sealed autoclave ensure the experimental conditions. In order to investigate the effect of diffusion time and cooling mode on the optical property of ZnO, the samples were treated in muffle furnace according to three different courses. The first one denoted as A was treated at 800 °C for 60min and natural cooling in autoclave; the second one denoted B was treated at 800°C for 10min and natural cooling in autoclave; the third one denoted C was treated at 800 °C for 10min and rapid cooling in air. The ZnO crystals as received are denoted as-grown.

The optical properties of these samples were characterized by PL at low temperature of 10K and room

temperature (RT) using a 325nm line of a He-Cd laser. The electrical properties were examined by the Hall measurement in the Vander Pauw configuration.

3. Results and discussion

3.1 Effect of diffusion time

Fig. 1 shows the PL spectra of sample A, B and as-grown ZnO crystals at RT. It can be seen that all the curves show two peaks, one is the near-band-energy (NBE) emission at around 380nm; the other is the intrinsic deep level (DL) emission at around 510nm. Furthermore, it was found that the UV and visible peak became more intense as the diffusion time went on, and the UV peak shifted to longer wavelength. The energy positions in PL spectra were clearly shown in Table 1. Xu et al [13] have reported that the UV intensity of ZnO crystal enhanced by Zn treated which is resulting from the formation of Zn_i , and they deduced that the existence of Zn_i may elevate the transition rate of FX and result in the enhancement of UV emission. Naturally, the concentration of Zn_i in samples greatly depends on the diffusion parameter including diffusion temperature, time and atmosphere etc. For diffusion time, it not only affects the diffusion depth, but also affects the type and concentration of defects. In certain condition, it is possible to formation two types and more defects. Thus, different defects will generate with diffusion time because of the defects with different formation energy. For example, at high temperature, the Zn atoms can effectively diffuse into ZnO lattice, and the in-diffusion Zn atoms may pile up at the interstitial position forming Zinc interstitial (Zn_i) or occupy the oxygen vacancies forming Zn antisite (Zn_O). As reported by Anderson Janotti [14], the formation energy of Zn_O is much higher than Zn_i . Therefore, it can be deduced that the in-diffusion Zn atoms can generate Zn_i defects at the initial diffusion stage, and as the diffusion time went on, when the concentration of Zn_i reached a certain value, the Zn_O defect generates. Note that the PL spectra of the three sample, in Fig. 1, the UV intensity of sample A with 60min diffusion time is much stronger than sample B with 10min, according to above analysis, it is because of the concentration of Zn_i increase with inducing the strong emission. For the visible peak, it is absent in as-grown ZnO crystal, and clearly showing in sample A and B, it resulted from the change of Zn_O concentration. The concentration of Zn_O increased from B to A.

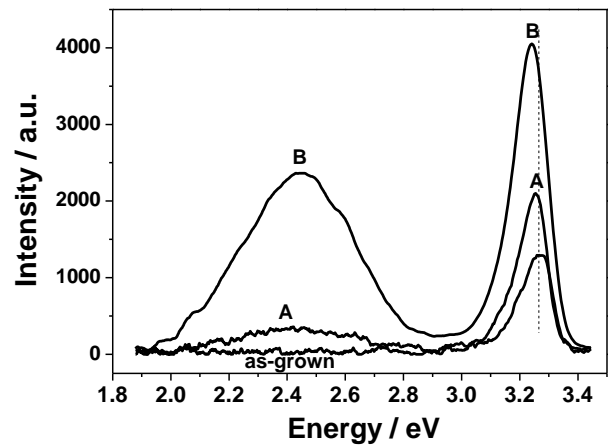


Fig. 1. PL spectra of sample A, B and as-grown sample at room temperature.

Table 1. Energy positions in PL spectra of sample A, B and as-grown ZnO crystal.

sample	UV peak(eV)	Visble peak(eV)
A	3.24	2.44
B	3.25	2.43
As-grown	3.26	—

3.2 Effect of cooling mode

Fig. 2 shows the PL spectra of sample B, C and as-grown ZnO crystal. It can be seen that UV peak enhanced in Zn doping samples than as-grown one, which was shown above. And the intensity of UV peak at around 380nm of sample C is much stronger than that of B. Conversely, the visible band at 510nm appeared in B suppressed in C. In the experiment, sample C had the same diffusion time with B, but the cooling mode was different. Sample B is cooled down naturally in the furnace, and the sample C is quickly cooled by removing from furnace. Thus, the latter process makes the Zn powder which isn't diffused into ZnO crystal adhered to the inner walls of muffle furnace, not on the surface of ZnO crystal. Moreover, it makes the generated Zn_i defects in ZnO remaining when decreasing the temperature of muffle furnace quickly. For the naturally cooling process, in a sense, it prolongs the diffusion time than the quickly cooling. So, based on the analysis of diffusion time, the concentration of Zn_i in sample B increased than that in C, and also, there is Zn_O defects formation when the Zn_i reach a certain value. Therefore, the UV peak in C enhanced than that in B because of the more Zn_i defect, and the visible band from Zn_O defect appeared in sample B. Conversely, Zn_i is the dominant defect in C, and few Zn_O , So, the visible peak suppressed in it. Above all, UV peak in ZnO at around 380nm related to Zn_i , and the visible

peak at about 510nm resulted from ZnO .

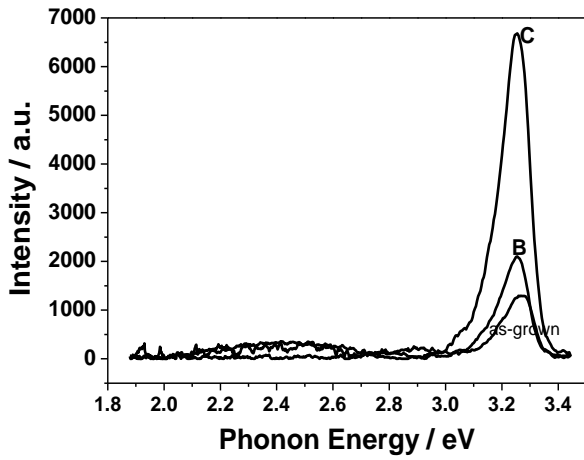


Fig. 2. PL spectra of sample B, C and as-grown sample at room temperature.

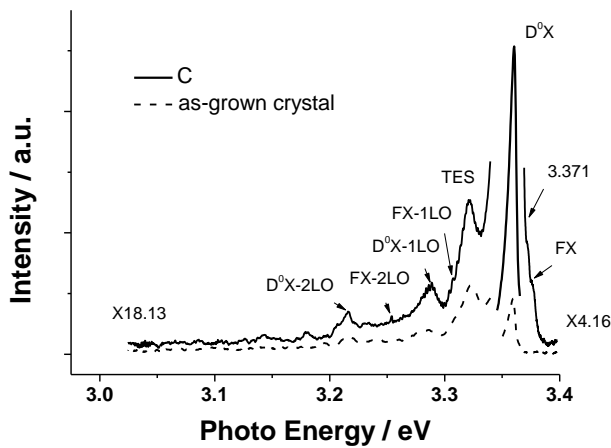


Fig. 3. PL spectra of sample C and as-grown ZnO crystal at 10K.

3.3 Low temperature PL

To understand the UV enhancement of the Zn-treated ZnO, low-temperature PL measurements of sample C and as-grown sample were carried out at 10 K, as shown in Fig. 3. Several emission lines are observed in both samples in the energy range 3.20–3.40 eV. These emission lines are peaked at 3.376 (FX), 3.371, 3.360 (D^0X), 3.321 (TES), 3.307 (FX-1LO), 3.289 (D^0X -1LO), 3.254 (FX-2LO) and 3.216 eV (D^0X -2LO). Note that the exciton emission bound to a neutral donor dominated in the low temperature of ZnO, and the intensity enhanced clearly by Zn doping. The source of D^0X was classified as emission related to hydrogen donor by many researchers [15,16], and their

study demonstrated that the hydrogen impurities can be easily removed after annealing at 600 °C. In our experiments, the sample was treated at 800°C by Zn doping, and D^0X line has not been eliminated, on the contrary, the integral intensity enhanced many times. Therefore, we believe that D^0X not come from hydrogen donor. In the LT photoluminescence, the determination of the donor binding energies was based on the observation of two electron satellite lines (3.321eV). During the recombination of an exciton bound to a neutral donor, the donor final state can be the 1S state(normal D^0X) or the 2S, 2P state (TES line), the energy separation between $n = 1$ and $n = 2$ states would be equal to $3/4$ of the donor binding energy $E_D = \frac{4}{3}(D^0X - TES) = 52\text{meV}$. This is consistent to ionization energy of Zn_i reported by [17,18], Applying the Haynes rule with the parameters as given in [19], $E_{loc} = 0.365E_D - 3.8\text{meV}$, the localization energy of the bound exciton is about 15.2 meV, which is consistent with the spacing energy of 16 meV between the FX recombination at 3.376 eV and D^0X at 3.360 eV. This further confirms the assigning of 3.321 eV to TES of D^0X . It is suggested that the enhancement of D^0X and TES is related to this shallow donor Zn_i . Moreover, a new emission at 3.371 was observed after Zn treated in the Fig. 3. Many opinions were reported about this peak, Sann etc. studies [20] have shown that the peak at 3.371 eV was related to Zn interstitial. Fig. 3 shows the sample after diffusion through Zn in PL, 3.371 eV and ZnO in the emergence of increasing the concentration of Zn interstitial related.

3.4 Hall measurement

The electrical properties of sample C and as-grown sample were investigated by hall measurement, which shown in Table 2. Both of them show n type conductivity; their electron concentrations are $2.4 \times 10^{15} \text{ cm}^{-3}$ and $2.6 \times 10^{16} \text{ cm}^{-3}$, respectively. The electron concentration of sample C increased by three orders of magnitude. Theoretically there are three kinds of n-type defects in ZnO; they are Zn_i , Zn_o and V_o .

Table 2. Hall data of sample C and as-grown ZnO crystal.

Sample	$\rho(\Omega \cdot m)$	$n(cm^{-3})$	$\mu(cm^2 / v \cdot s)$
As-grown	1282.3	2.4×10^{13}	202
C	1.28	2.6×10^{16}	186

However, V_o is a deep donor locating 0.7–1.0 eV below the conduction band [21] and Zn_o which determines the 2.43 eV visible band should also be a deep donor, neither can account for residual n-type conductivity. So the n-type conductivity is supposed to come from the shallow donor Zn_i with ionization energy of 52meV. According to the PL analysis above, the increase of electron concentration results from the formation of low donor Zn_i in sample C.

4. Conclusion

In summary, photoluminescence relevant to intrinsic defects of ZnO crystal by Zn doping has been studied. In the course of diffusion, both diffusion time and cooling mode influence the photoluminescence by changing the intrinsic defects in ZnO. According to the analysis of diffusion mechanism, combining the result of photoluminescence, it can be concluded that the visible peak at 510nm is probably from Zn_o , the ultraviolet peak is relative to intrinsic defects Zn_i .

Acknowledgments

The work is supported by Joint Funds of the National Natural Science Foundation of China under Grant No. U1204109, also is supported by program for innovative research team (in science and technology) in University of Henan Province under grant Nos. 13IRTSTHN020.

References

- [1] M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, E. Weber, R. Russo, P. D. Yang, *Science* **292**, 1897 (2001).
- [2] T. Detchprohm, H. Amano, K. Hiramatsu, I. Akasaki, *Journal of Crystal Growth* **128**, 384 (1993).
- [3] Akhlesh Gupta, Alvin D. Compaan, *Applied Physics Letters* **85**, 684 (2004).
- [4] R. L. Hoffman, B. J. Norris, J. F. Wager, *Applied Physics Letters* **82**, 733 (2003).
- [5] D. C. Look, J. W. Hemsky, *Physics Review Letters* **82**, 2552 (1999).
- [6] A. F. Kohan, G. Ceder, D. Morgan, Chris G. Van de Walle, *Physics Review B* **61**, 5019 (2001).
- [7] L. S. Vlasenko, G. D. Watkins, *Physics Review B* **72**, 035203 (2005).
- [8] F. Tuomisto, V. Ranki, K. Saarinen D. C. Look, *Physics Review Letters* **91**, 205502-1 (2003).
- [9] T. Moe Børseth, B. G. Svensson, A. Yu. Kuznetsov P. Klason, Q. X. Zhao, M. Willander, *Applied Physics Letters* **89**, 262112 (2006).
- [10] A. Allenic, X. Q. Pan, Y. Che, Z. D. Hu, B. Liu, *Applied Physics Letters* **92**, 022107 (2008).
- [11] Bixia Lin, Zhuxi Fu, Yunbo Jia, *Applied Physics Letters* **79**, 943 (2001).
- [12] K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, J. A. Voigt, *Applied Physics Letters* **68**, 403 (1996).
- [13] X. Q. Xu, B. X. Lin, L. J. Sun, Z. X. Fu, *Journal of Physics D: Appl. Phys.* **42**, 085102 (2009).
- [14] Anderson Janotti, Chris G. Van de Walle, *Physics Review B* **76**, 165202 (2007).
- [15] A. F. Kohan, G. Ceder, D. Morgan, C. G. Van de Walle, *Physics Review B* **61**, 15019 (2000).
- [16] E. C. Lee, K. Chang, *Physics Review B* **70**, 115210 (2004).
- [17] S. B. Zhang, S. H. Wei, A. Zunger, *Physics Review B* **63**, 075205 (2001).
- [18] D. C. Look, J. W. Hemsky, J. R. Sizelove, *Physics Review Letters* **82**, 2552 (1999).
- [19] Y. Zhang, B. X. Lin, X. K. Sun, Z. X. Fu, *Applied Physics Letters* **86**, 131910 (2005).
- [20] J. Sann, J. Stehr, A. Hofstaetter, D. M. Hofmann, A. Neumann, M. Lerch *Physics Review B*, **76**, 195203 (2007).
- [21] F. A. Selim, M. H. Weber, D. Solodovnikov, K. G. Lynn, *Physics Review Letters* **99**, 085502 (2007).

*Corresponding author: zhangwy0379@gmail.com