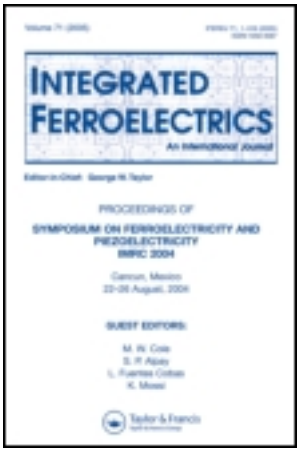

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Xuan Fang [a b], Xiaohua Wang [a b], Shuangshuang Pu [a], Jinhua Li [a b], Zhipeng Wei [a], Fang Fang [a b], Shuang Li [a b], Fei Wang [a] & Dongxu Zhao [c]

[a] School of Science, Changchun University of Science and Technology, Changchun, 130022, China

[b] International Joint Research Center for Nanophotonics and Biophotonics, Changchun University of Science and Technology, Changchun, 130022, China

[c] Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, 130022, China

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P-doped ZnO Nanoparticals Synthesized by Thermal Decomposition

XUAN FANG,[1,2] XIAOHUA WANG,[1,2,*] SHUANGSHUANG PU,[1] JINHUA LI,[1,2] ZHIPENG WEI,[1] FANG FANG,[1,2] SHUANG LI,[1,2] FEI WANG,[1] AND DONGXU ZHAO[3]

[1]School of Science, Changchun University of Science and Technology, Changchun 130022, China
[2]International Joint Research Center for Nanophotonics and Biophotonics, Changchun University of Science and Technology, Changchun 130022, China
[3]Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130022, China

Phosphorus doped ZnO nanoparticles have been synthesized by simple thermal decomposition. By adjusting the concentration of reaction sources, different doping concentrations nanoparticals were obtained and kept wurtzite structure. The EDX and XPS results confirmed P incorporated in ZnO lattice and formed P_{Zn}-$2V_{Zn}$ complex acceptor. In low temperature PL spectra and temperature dependent PL spectra, the emission peak located at 3.350 eV, 3.310 eV and 3.241 eV could be observed which were attributed to A^0X, FA and DAP. Then, the increasing of P-doping concentrations would cause the energy of acceptor bound exciton became lower, and enhance the intensity of FA emission.

Keywords P-doped ZnO; nanoparticles; thermal decomposition and photoluminescence

1. Introduction

Due to large bandgap energy and high excition binding energy, low dimensional ZnO nanostructures have many applications on photodetectors [1–3], nanolasers [4, 5], solar cells [6, 7] and nanogenerator have been investigated extensively [8, 9]. However, in the research process of ZnO realm, obtainment of p-type ZnO is still a major challenge becaused of self-compensation effect, low doping efficiensy [10, 11]. At present, III-V group elements, especially for Phosphorus has been considered as the excellent dopant for p-type doping in ZnO, owing to the shallow acceptor level in ZnO [12, 13]. Many research works about synthesizing P-doped ZnO nanostructures by CVD, PLD and other methods have reported. Solid P_2O_5 and Zn_3P_2 or Zinc Oxide were usually used as reaction sources [11, 14, 15]. In our previous work, P-doped ZnO nanorods had been synthesized by hytrothermal method and homojunctions had been realized [16]. In addition, Yu also

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*Corresponding author. E-mail: biewang2001@126.com

reported stable P-doped ZnO nanwires synthesized in this way [13]. A stable p-type ZnO can be obtained.

In this paper, different doping concentrations ZnO nanoparticals were synthesized. The morphologies and structures were measured by SEM, XRD. And low temperature PL and temperature dependent PL were used to characterize the relationship between doping concentrations and optical property. The formation mechanism of this nanoparticles was discussed.

2. Experiments

0.01M zinc acetate, HMT and required amount $NH_4H_2PO_4$ were dissolved in aqueous solution. The white products were isolated by centrifugation and cleaned by water. At last, the samples were annealed at 850°C for 1h under Ar_2 ambient.

The samples were investigated by field-emission scanning electron microscopy (FESEM, Hitachis-4800), energy-dispersive X-ray spectroscopy (EDS, GENE SIS 2000 XMS 60S, EDAX, Inc.) attached to the SEM, and a D/max-RA X-ray spectrometer (Rigaku). Photoluminescence (PL) measurements were performed using a He–Cd laser line of 325 nm as the excitation source.

3. Results and Discussion

SEM images of as-grown samples were shown in Fig. 1. Figure 1a shows doping concentration about 5% P-doped ZnO nanoparticles, the diameter of the particle was about 500 nm and some particles formed larger nanocluster. From the insert of Fig. 1a, we could see that these particles were also composed of smaller particles. Figure 1b shows 10% P-doped ZnO nanoparticles, the morphology and size of particle didn't change a lot. The composition analysis of as-grown nanoparticles is shown in Fig. 1c. The peaks from Zn, O and P can be observed in the EDX spectrum, the intensity ratios among the Zn, O and P peaks suggest that the P content in the nanoparticles was approximately 5 atom%, revealing the possibility of incorporation of P entering into the ZnO nanoparticles. However, because of the limit of EDX analysis, only the surface layer elements of as-grown nanoparticles could be detected. The chemical composition of the P-doped ZnO nanoparticles were further analyzed to prove P doped into the ZnO nanoparticles by the XPS. Figure 1d shows the samples before and after annealing XPS spectrum. The peaks located at 531.8 eV, 1021.8 eV and 1044.7 eV were corresponding to the binding energies of O (1s) and Zn (2p3/2) and (2p1/2), respectively in ZnO nanoparticles (shown in Fig. S1). And the peak located at 133.5 eV was originated from the P (2p), which was not observed in unannealing samples. this result indicates that as-samples contains P which agrees with the previous reports [13, 15, 17]. The XPS result clearly show that the doped ZnO nanoparticles contain P.

Figure 2 shows the XRD pattern of as-grown samples. For each sample, all the observed diffraction peaks can be indexed to a ZnO wurtzite structure. The ZnO (002) diffraction peak is dominance demonstrates that the samples had a preferred orientation along the c-axis direction. For comparison, a typical XRD pattern of undoped ZnO was also shown, compared to undoped ZnO, the (002) diffraction peak of 5% P-doped ZnO nanoparticles shifted to large-angle. For 10% P-doped ZnO nanoparticles, the (002) diffraction peak shifted larger. XRD results confirmed P diffused into the ZnO lattice and formed P_{Zn}-$2V_{Zn}$ complex acceptor [11, 16].

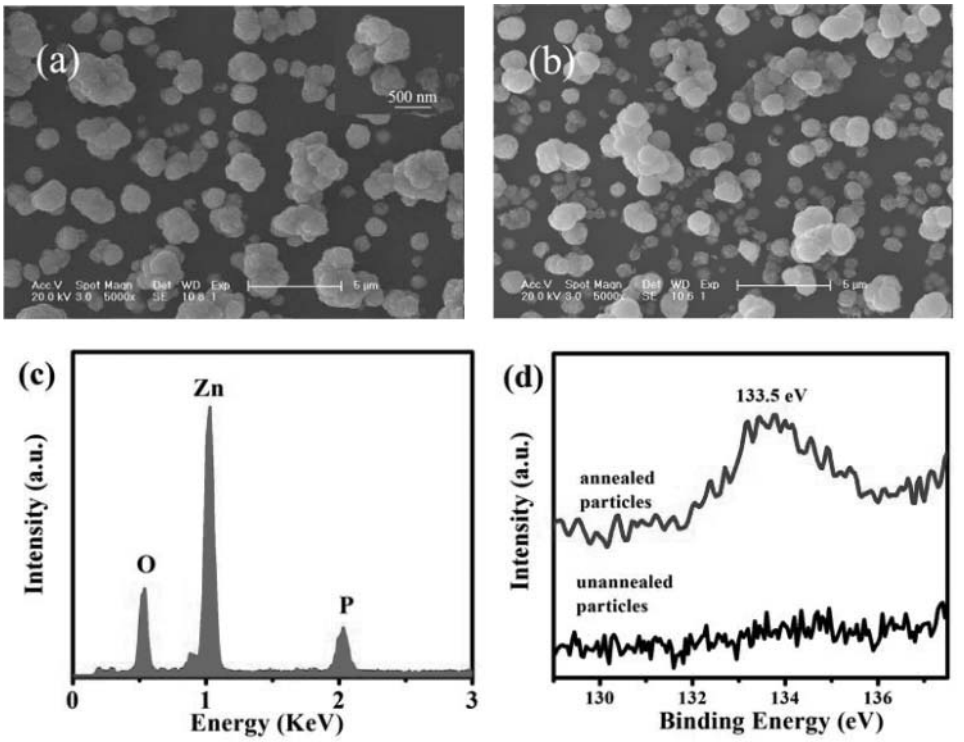

Figure 1. (a), (b) SEM images of 5% P-doped ZnO and 10% P-doped ZnO nanoparticles, respectively; (c) EDX spectrum of annealed P-doped ZnO; (d) XPS spectrum of annealed P-doped ZnO and unannealed samples.

According to above results and our previous work, [16] the P doping occurred during $Zn_3(PO_4)_2$ thermal decomposition process. The synthesizing of $Zn_3(PO_4)_2$ were as follows:

$$NH_4H_2PO_4 + H_2O - NH_3 + 3H^+ + [PO_3]^{3-}$$

$$2[PO_3]^{3-} + 3Zn^{2+} - Zn_3(PO_4)_2 \downarrow$$

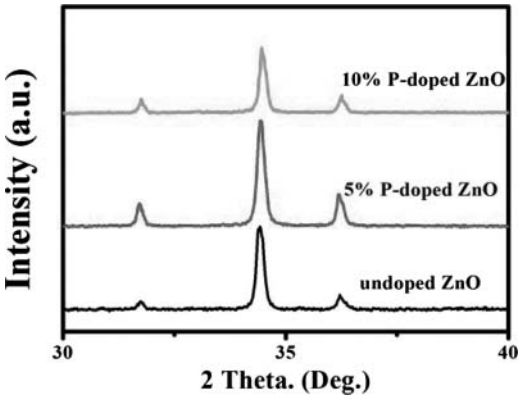

Figure 2. XRD pattern of 5% P-doped ZnO, 10% P-doped ZnO nanoparticles and undoped ZnO.

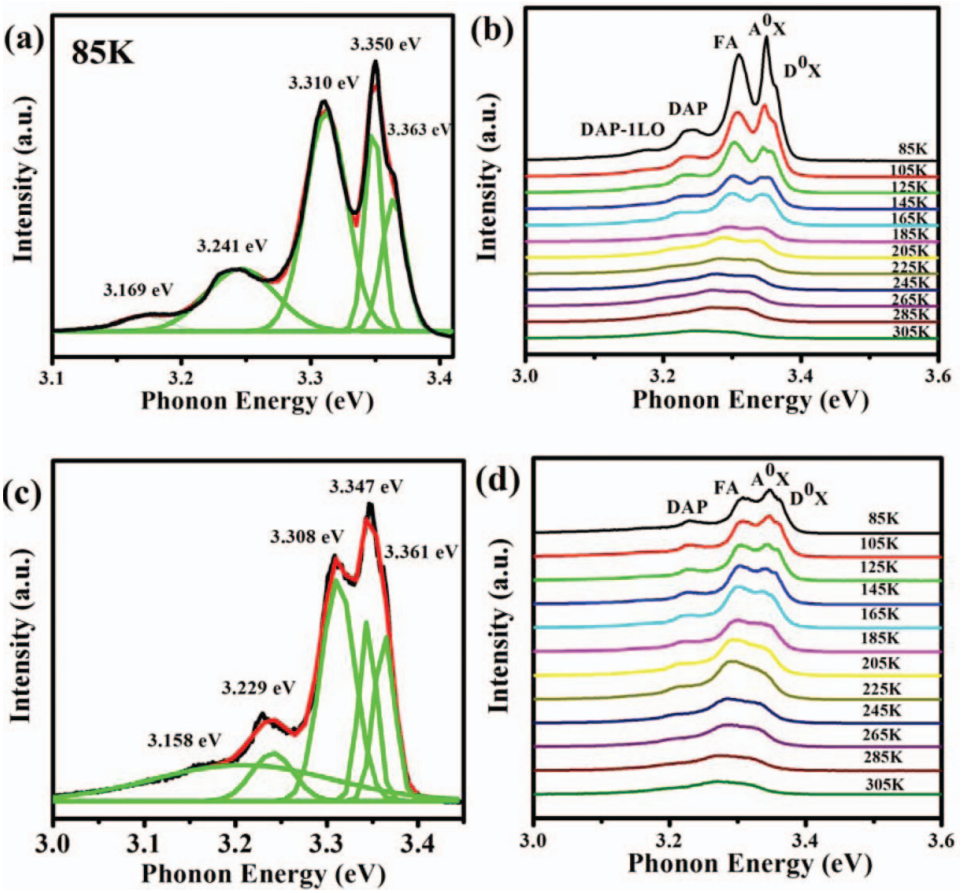

Figure 3. (a) Low-temperature PL spectra of 5% P-doped ZnO, (b) temperature-dependent PL spectra of 5% P-doped ZnO, (c) Low-temperature PL spectra of 10% P-doped ZnO, (d) temperature-dependent PL spectra of 10% P-doped ZnO.

$NH_4H_2PO_4$ dissolved in aqueous solution and released $[PO_3]^{3-}$. Then $Zn_3(PO_4)_2$ precipitate would formed. The $Zn_3(PO_4)_2$ thermal decomposition would cause P atoms diffused into the ZnO crystal lattice and formed accepter dopants.

Figure 3 shows the low temperature PL spectra and temperature dependent PL spectra of different doping concentration P-doped ZnO nanoparticles. The low temperature PL spectra of 5% P-doped ZnO nanoparticles could be well fitted by five Gaussian peaks, which were located at 3.363, 3.350, 3.310, 3.241 and 3.169 eV, respectively (shown in Fig. 3a). And the dominant peak located at 3.350 eV could be assigned to acceptor bound exciton (A^0X), which was usually observed in P-dope ZnO nanostructures [15, 18] the peak located at 3.363 eV was attributed to a donor bound exciton (D^0X) [19]. Because of the intensity of A^0X was stronger than D^0X which indicated that after P doping, the acceptor level was formed in ZnO[20]. In addition, from the temperature dependent PL spectra (shown in Fig. 3b), these two peaks located at 3.3310 eV and 3.241 eV can also be observed at room temperature. According to previous reports [18, 20, 16], these peaks were considered to assigned to free electron to the acceptor transition (FA) and the donor-acceptor pair transition (DAP). The peak located at 3.169 eV was

assigned to DAP phonon replica (DAP -1LO) because the energy difference with DAP was 72 meV [16, 18].

For the 10% P-doped ZnO, Fig. 3c shows the low temperature PL spectra at 85 K, which could also be well fitted by five Gaussian peaks, which were located at 3.361, 3.347, 3.308, 3.229 and 3.158 eV, respectively. Due to the P doping concentration increased, the dominant peak located at 3.347 eV could also be assigned to A^0X [15, 18], its peak position redshifted slightly. It was noted that there appeared a shoulder peak located at 3.361 eV (D^0X) [19], becaused the acceptor concentration increased, the intensity of D^0X became lower. Correspondingly, FA and DAP located at 3.308 eV and 3.229 eV, the peaks position redshifted slightly. And the peak located at 3.158 eV was attributed DAP-1LO [16, 18]. Furthermore, the ability of free electrons to acceptor bound holes transition (FA) was enhanced. The emission of FA would be enhanced too. With increasing temperature, the intensity of FA emission was still stronger (shown in Figure 3d). This phenomenon futher proved the formation of acceptor level related to P doping.

4. Conclusions

In conclusion, different doping concentrations P-doped ZnO nanoparticals were synthesized by thermal decomposition. The SEM images and XRD pattern showed the P-doped ZnO nanoparticles consisted of smaller particles and had a c-axis direction orientation. The incorporation of P was further confirmed by EDX and XPS. The A^0X peak at 3.350 eV and P related peaks at 3.310 and 3.241 eV (FA and DAP) was observed that indicated the acceptor level related to P was formed and as-grown P-doped ZnO had a p-type conductivity. With increasing of doping concentration, the peak of A^0X shifted slightly (3.347 eV) and the ability of free electrons to acceptor bound holes transition was enhanced, then the emission of FA enhanced too.

Acknowledgments

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References

1. K. Hannes, Y. Haoquan, M. Benjamin, *et al.*, Nanowire ultraviolet photodetectors and optical switches. *Adv. Mater.* **14**, 158–160 (2002).
2. S. Ke, J. Yi, P. Namseok, *et al.*, Solution synthesis of large-scale, high-sensitivity ZnO/Si hierarchical nanoheterostructure photodetectors. *J. Am. Chem. Soc.* **132**, 15465–15467 (2010).
3. C. K. Dong, O. J. Byung, L. Ju Ho, *et al.*, Dramatically enhanced ultraviolet photosensing mechanism in a n-ZnO nanowires/i-MgO/n-Si structure with highly dense nanowires and ultrathin MgO layers. *Nanotechnology*. **22**, 265506 (2011).
4. G. Zhen, Z. Dongxu, L. Yichun, *et al.*, Electrically pumped single-mode lasing emission of self-assembled n-ZnO microcrystalline film/p-GaN heterojunction diode. *J. Phys. Chem. C*, **114**, 15499–15503 (2010).
5. C. Sheng, O. Mario, Y. Zheng, *et al.*, Electrically pumped ultraviolet ZnO diode lasers on Si. *Appl. Phys. Lett.* **93**, 181106 (2008).

6. H. K. Seung, L. Daeho, W. K. Hyun, *et al.*, Nanoforest of Hydrothermally Grown Hierarchical ZnO Nanowires for a High Efficiency Dye-Sensitized Solar Cell. *Nano Lett.*, **11**, 666–671 (2011).
7. L. D. Wang, D. X. Zhao, Z. S. Su, *et al.*, Enhanced efficiency of polymer/ZnO nanorods hybrid solar cell sensitized by CdS quantum dots. *J. Electrochem. Soc.* **158**, H804–H807 (2011).
8. Y. Hu, Y. Zhang, C. Xu, *et al.*, High-output nanogenerator by rational unipolar assembly of conical nanowires and its application for driving a small liquid crystal display. *Nano Lett.* **10**, 5025–5031 (2010).
9. X. Sheng, Q. Yong, X. Chen, *et al.*, Self-powered nanowire devices, *Nature nanotechnology*, **5**, 366–373 (2010).
10. C. H. Park, S. B. Zhang, and S. H. Wei, Origin of p-type doping difficulty in ZnO: The impurity perspective. *Phys. Rev. B*. **66**, 073202 (2002).
11. B. Xiang, P. W. Wang, X. Z. Zhang, *et al.*, Rational synthesis of p-type zinc oxide nanowire arrays using simple chemical vapor deposition. *Nano Lett.* **7**, 323–328 (2007).
12. Y. W. Heo, Y. W. Kwon, Y. Li, *et al.*, p-type behavior in phosphorus-doped (Zn,Mg)O device structures. *Appl. Phys. Lett.* **84**, 3474 (2004).
13. J. Gao, Q. Zhao, Y. Sun, *et al.*, A novel way for synthesizing phosphorus-doped zno nanowires. *Nanoscale. Res. Lett.* **6**, 45 (2011).
14. B. Q. Cao, M. Lorenz, A. Rahm,, et al., Phosphorus acceptor doped ZnO nanowires prepared by pulsed-laser deposition, *Nanotechnology*, **18**, 455707 (2007).
15. V. Vaithianathan, B. T. Lee, S. S. Kim, et. al., Pulsed-laser-deposited p-type ZnO films with phosphorus doping, *J. Appl. Phys.* **98**, 043519 (2005).
16. F. Xuan, L. Jinhua, Z. Dongxu, *et al.* Phosphorus-doped p-type ZnO nanorods and ZnO nanorod p−n homojunction LED fabricated by hydrothermal method. *J. Phys. Chem. C.* **113**, 21208 (2009).
17. X. H. Pan, J. Jiang, Y. J. Zeng, *et al.*, Electrical and optical properties of phosphorus-doped p-type ZnO films grown by metal organic chemical vapor deposition. *J. Appl. Phys.* **103**, 023708 (2008).
18. C. X. Shan, Z. Liu, and S. K. Hark, Temperature dependent photoluminescence study on phosphorus doped ZnO nanowires. *Appl. Phys. Lett.* **92**, 073103 (2008).
19. F. X. Xiu, Z. Yang, L. J. Mandalapu, *et al.*, p-type ZnO films with solid-source phosphorus doping by molecular-beam epitaxy. *Appl. Phys. Lett.* **88**, 052106 (2006).
20. D. K. Hwang, H. S. Kim, J. H. Lim, *et al.*, Effect of annealing temperature and ambient gas on phosphorus doped p-type ZnO. *Appl. Phys. Lett.* **86**, 151917 (2005).

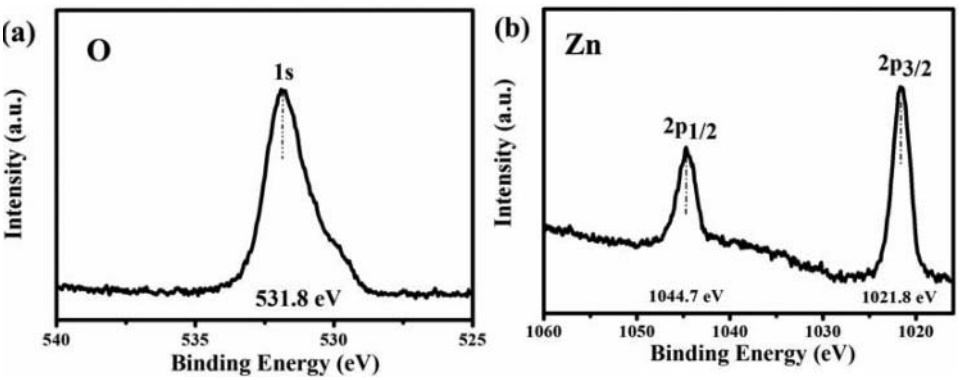

Figure S1. XPS spectrum of P-doped ZnO nanoparticles, (a) O spectrum, (b) Zn spectrum.