

Characterization of Phosphorus Diffused ZnO Bulk Single Crystals*

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Abstract: Phosphorus was diffused into CVT grown undoped ZnO bulk single crystals at 550 and 800°C in a closed quartz tube. The P-diffused ZnO single crystals were characterized by the Hall effect, X-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy (PL), and Raman scattering. The P-diffused ZnO single crystals are n-type and have higher free electron concentration than undoped ZnO, especially for the sample diffused at 800°C. The PL measurement reveals defect related visible broad emissions in the range of 420~550nm in the P-diffused ZnO samples. The XPS result suggests that most of the P atoms substitute in the Zn site after they diffuse into the ZnO single crystal at 550°C, while the P atom seems to occupy the O site in the ZnO samples diffused at 800°C. A high concentration of shallow donor defect forms in the P-diffused ZnO, resulting in an apparent increase of free electron concentration.

Key words: diffusion; defect; ZnO; phosphorus

PACC: 8160C; 7155H **EEACC:** 2520D

CLC number: TN304.2⁺5 **Document code:** A **Article ID:** 0253-4177(2008)09-1674-05

1 Introduction

ZnO is a II-VI compound semiconductor with a wide band gap (3.37eV) and large exciton binding energy (60meV) at room temperature. In recent years, it has attracted interest due to its potential application in short wavelength devices. While natural ZnO exhibits n-type conductivity, there exist several problems in developing p-type ZnO like the self-compensation effect caused by the nature defects oxygen vacancies, Zn interstitials^[1], and the low doping solubility of acceptor impurity^[2]. Until now, Group I and Group V elements have both been considered candidates for acceptor impurities, while the studies show that the Group V elements are more appropriate^[3,4]. Notably, many experiments used phosphorus as their dopant and p-type conduction was obtained. However, most of the research has been carried out on ZnO epitaxial film grown at low temperature. After high temperature annealing, the P-doped ZnO film becomes n-type^[5~7]. The reason for the conduction type conversion remains unclear and further research is necessary. Compared to thin film ZnO material, it is an advantage to study P-doping and the related defect using bulk ZnO single crystal. In contrast, P-doped bulk ZnO single crystal is rarely reported. In this work, electrical and optical properties of phosphorus diffused ZnO bulk single crystals are studied. Results of deep level defects induced by P-diffusion and their

influence on the properties of ZnO are presented. We find that a high concentration of shallow donor defect is generated after P-diffusion in ZnO single crystals.

2 Experiment

ZnO single crystals with diameters of 30~50mm were grown by the chemical vapor transport (CVT) method in a closed ampoule at about 1000°C in our laboratory^[8]. The as-grown ZnO single crystals were annealed at 1100°C for 5h in flowing oxygen to remove oxygen vacancies and Zn interstitial defects that formed during the growth process. (0001) and (10 $\bar{1}0$) oriented, 5mm×5mm ZnO single crystal wafers were sliced from the crystal ingot and used for the experiment. Phosphorus was diffused into the ZnO single crystals at 550 and 800°C for about 100h in a closed quartz tube that was chemically cleaned in advance. Red phosphorus with 6N's purity was used as the diffusion source. After diffusion, the samples were lapped and polished, and a surface layer thickness of about 40μm was removed. Some of the samples were annealed at 850°C in flowing oxygen for 3h. A conventional Hall effect measurement was used to examine the electrical properties of the ZnO samples. Raman scattering and low temperature photoluminescence (PL) were used to study defects in the samples. X-ray photoelectron spectroscopy (XPS) was used to determine the existence and chemical bonds of phosphorus in the ZnO samples.

* Project supported by the National Natural Science Foundation of China (No. 60736032)

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Received 13 April 2008, revised manuscript received 27 May 2008

Table 1 Room temperature electrical properties of undoped and P-diffused ZnO samples

Sample No.	Orientation	Diffusion condition	Carrier density / cm^{-3}	Resistivity / $(\Omega \cdot \text{cm})$	Mobility / $(\text{cm}^2/(\text{V} \cdot \text{s}))$
P1	(0001)	Before	4.469×10^{16}	6.510×10^{-1}	215
		800°C /100h	3.626×10^{17}	1.118×10^{-1}	151
P2	(10 $\bar{1}0$)	Before	1.189×10^{17}	4.316×10^{-1}	122
		800°C /100h	1.662×10^{17}	4.107×10^{-1}	92
P5	(0001)	Before	6.978×10^{17}	6.657×10^{-2}	135
		550°C /100h	7.175×10^{17}	6.371×10^{-2}	137
P6	(10 $\bar{1}0$)	Before	2.435×10^{17}	2.059×10^{-1}	125
		550°C /100h	3.115×10^{17}	1.648×10^{-1}	122
P0	(0001)	As-grown	2.031×10^{17}	1.563×10^{-1}	198
		annealed	2.433×10^{17}	1.563×10^{-1}	165

3 Results and discussion

Hall effect measurement results of undoped, P-diffused, and annealed ZnO single crystals are given in Table 1. Both the undoped and the P-diffused ZnO samples are n-type. After the P-diffusion, free electron concentrations of the ZnO samples increase significantly, especially for the sample P1 in which phosphorus is diffused at 800°C. This result suggests that a shallow donor defect is formed after the P-diffusion in ZnO. It indicates that the shallow donor concentration increases as temperature and the concentration of the diffused P in the ZnO samples increases. This finding implies that the in-diffused P atom substitutes for Zn and acts as a shallow donor in ZnO. Since the atomic size mismatch is large between P (110pm) and O (66pm) and small between P and Zn (125pm), P is expected to be energetically favorable to occupy Zn sites rather than O sites, which is an atomic size dependent site selection phenomenon of impurity in ZnO, as evidenced experimentally in recent publications^[9,10]. On the other hand, the recent theoretical calculation and experimental study suggest that a complex defect $\text{P}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ is formed under specific conditions in P-doped ZnO^[11,12]. This defect is a shallow acceptor, which accounts for the p-type conduction observed in P-doped ZnO. It seems that the present diffusion condition (temperature, stoichiometry) does not assist the formation of the acceptor defect complex in ZnO. The following PL result gives evidence of shallow donor formation in the P-diffused ZnO samples.

Furthermore, there is a slight decrease of the carrier concentration of the P-diffused ZnO after annealing, implying an increase of electrical compensation. In contrast, the free electron concentration of as-grown undoped n-type ZnO increases after annealing under similar conditions, which can be seen from a typical result of the sample P0 in Table 1. The electri-

cal compensation of the n-type P-diffused ZnO increases and the formation of a quantity of acceptor defect such as $\text{P}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ in the P-diffused ZnO is most likely in the annealing process since the annealing is completed in oxygen rich ambient at high temperature. Thus, the annealing induced $\text{P}_{\text{Zn}}-2\text{V}_{\text{Zn}}$ is a possibly responsible for the compensation. The results in Table 1 also indicate that the (0001) ZnO wafer has a higher donor concentration than (10 $\bar{1}0$) ZnO wafer after diffusion under the same conditions. This difference may be related with the influence of the polarity of the (0001) face on impurity doping and substitution. XPS spectra of two typical P-diffused ZnO samples are shown in Fig. 1. In addition to the peaks of C, O, and Zn, a P—O bond related XPS peak at

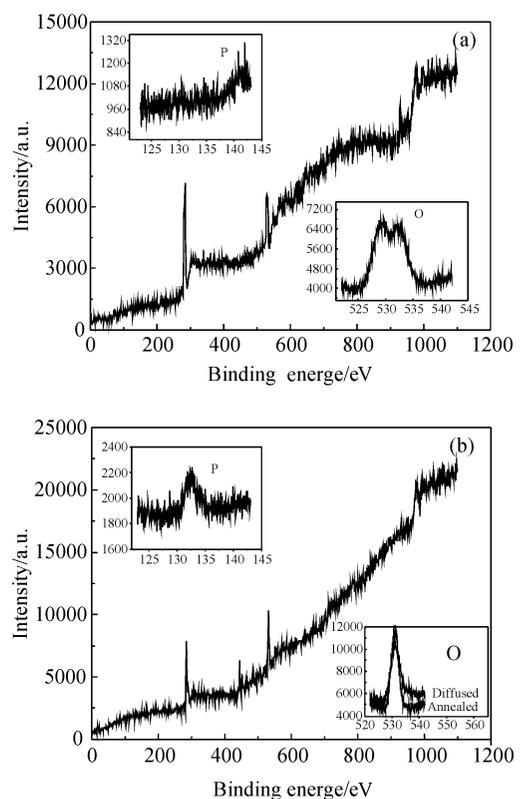


Fig.1 XPS survey spectra of ZnO:P-diffused at 800°C (a) and 550°C (b)

133.2 eV^[13] appears in Fig. 1 (b). Thus, the existence of phosphorus in the ZnO single crystals is confirmed, suggesting that P atoms occupy the Zn site rather than the O site in the P-diffused ZnO samples. As shown in the insets of Fig. 1, the P—O bond related XPS peak of sample P6 is apparently stronger, while it is nearly absent in sample P1. An XPS peak at about 141 eV is observed in samples P1 and P2, and the spectrum of P1 is shown in Fig. 1 (a). This peak is close to the Zn—P bond XPS binding energy^[13]. These results imply that the in-diffused P atoms in ZnO occupy the Zn site at low diffusion temperature, while they tend to occupy the O site at high diffusion temperature. As further evidence, we found that undoped ZnO single crystal samples easily turn into grey power Zn₃P₂ after P-diffusion at 900°C. This fact also limits our annealing temperature to below 900°C. Therefore, the phosphorus-oxygen bond is formed at low temperature and the zinc-phosphorus bond is formed at high temperature in ZnO. Our findings agree with the result of Heo *et al.*^[14] in which phosphorus dopant ions in ZnO films occupy multiple sites.

The insets in Fig. 1 present the relative XPS intensity of O_{1s} from the diffused and annealed sample P6. The peak of the annealed sample is more symmetrical and intense. Since the condition of the ZnO single crystal CVT growth is zinc-rich, production of V_O defect is favored. The O_{1s} peak center shifts from 531.3 to 531.1 eV, which means the oxygen deficient regions^[15] have recovered slightly because the annealing occurs in oxygen ambient. Thus, the intensity change of this region may associate with the decrease of V_O concentration^[15,16].

The origin of the visible PL emission peaks in ZnO has been studied extensively^[17~20]. In general, they are related with defects in ZnO single crystals although the exact nature of the defect remains unclear. Figure 2 (a) shows the PL spectra of the samples P1, P6, and an as-grown ZnO sample at room temperature. The broad peaks centered at 490 nm are the dominant emission peaks and the study is focused on the samples P1 and P6, which have a relatively high defect concentration reflected by the spectra. Figure 2 (b) is the low temperature PL spectra of P1, P6, and undoped ZnO after annealing. A bluish peak centered at 478 nm can be observed in sample P1, which may associate with a higher concentration of defects formed in the diffusion process compared to P6 and the undoped sample. Blue luminescence has been observed in ZnO thin film grown by various methods, such as PLD^[18,19] and sputtering^[20]. Electronic transition from zinc interstitial Zn_i to Zn va-

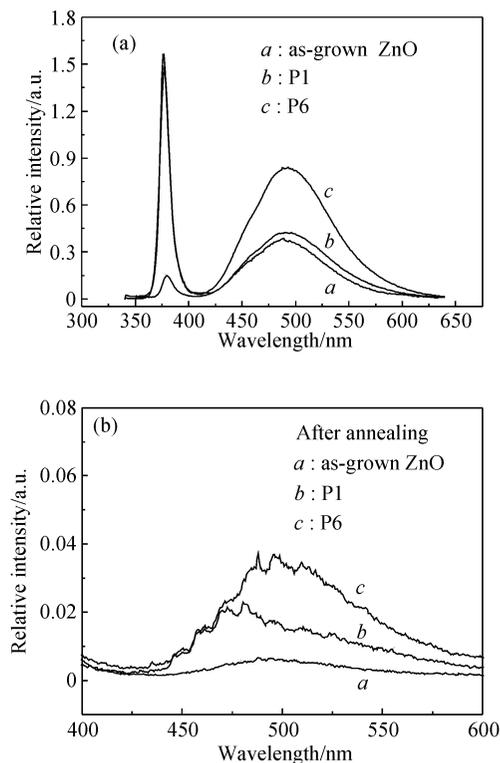


Fig. 2 PL spectra of P1, P6 and as-grown ZnO at room temperature (a) and 6K (b)

cancy V_{Zn} is attributed to the emission since the emission intensity is anti-correlated with oxygen pressure in the ZnO film preparation process. Formation of Zn_i and oxygen vacancy V_O are expected since the P-diffusion of our ZnO samples was completed in an oxygen deficient vacuum condition. On the other hand, the in-diffused P might generate more Zn_i by a diffusion process named kick-out substitution of Zn in ZnO. Thus, it is reasonable that sample P1 has a higher concentration of Zn_i because its P-diffusion temperature is high.

The Hall effect results give further evidence of donor defects affecting the visible blue luminescence. Compared to the undoped ZnO, the P-diffused ZnO has an increase of free electron concentration and appearance of the blue luminescence, suggesting a shallow donor defect is involved in the blue luminescence. This is more clearly reflected by sample P1, which has a much higher donor concentration and obvious blue luminescence after P diffusing at 800°C. The broad luminescence peak from 425 to 600 nm can also be seen from the PL spectra of all the samples. This can be explained by the existence of native defects in as-grown ZnO^[21,22]. However, the concentration of the native defects in as-grown ZnO is low. Since the broad luminescence peak in ZnO is believed to be a combined contribution of native defect related transitions^[17,23~25], the appearance of an apparent blue peak

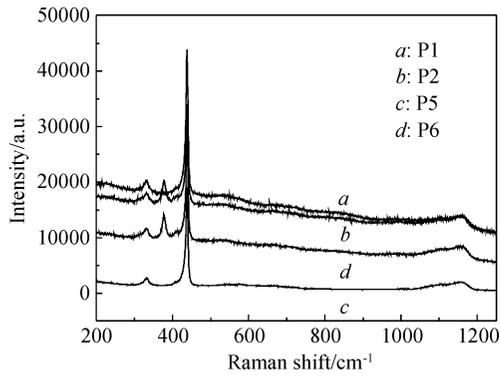


Fig.3 Raman scattering spectra of the diffused samples P1, P2, P5, P6

in the P-diffused ZnO sample indicates that a dominant single shallow donor defect is formed through the diffusion.

According to Fig. 3, Raman scattering spectra of the P-diffused ZnO samples indicate non-existence of a 580cm^{-1} shift, which is generally considered to be V_{O} related^[26~28]. Thus, V_{O} can be excluded as the candidate of the donor defect formed after P-diffusion in the ZnO samples. In this case, Zn_{i} seems to be the most likely donor defect formed in the diffusion process and contributes to the strong blue emission of the ZnO samples. The result presented here also supplies further evidence that stable p-type ZnO is difficult to obtain by P-doping due to the formation of a high concentration of shallow donor defects at high temperature.

In particular, Meyer *et al.*^[29] introduced nitrogen into ZnO by three different techniques at temperatures similar to those in our experiment. They proposed that nitrogen on an oxygen site works as the acceptor. But the samples still exhibit n-type conductivity. Both results indicate that the realization of p-type ZnO relies on the weakening of the influence of compensation. In addition, it has been confirmed that acceptor levels such as P, As, and Sb on O sites are quite deep (around 200meV)^[7,30] and the electrical activation ratio of the acceptors is as low as 10^{-3} in ZnO. A very high doping concentration of the group V elements is required to realize p-type ZnO. Thus, a reasonable approach to obtain p-type ZnO is to form the shallower acceptor defect $P_{\text{Zn}}-2V_{\text{Zn}}$ by controlling the stoichiometry and temperature of the doping process of ZnO single crystal. More research is needed to study the effect of the ZnO growth condition on the p-type doping efficiency.

4 Conclusion

P atoms substitute at the Zn site and O site in ZnO single crystals at low and high diffusion temper-

ature, respectively. A shallow donor defect with high concentration is formed in the P-diffused ZnO single crystal. The donor defects correlate with the blue luminescence of the ZnO sample. It is necessary to study the influence of stoichiometry and temperature on the P-doping or diffusion in ZnO.

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磷扩散氧化锌单晶的性质*

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摘要: 分别在 550 和 800℃ 对 CVT 方法生长的非掺 ZnO 单晶进行闭管磷扩散. 通过 Hall 测试、X 射线光电子谱(XPS)、光致发光(PL)以及喇曼散射对扩散后的样品进行测试分析. 发现扩散掺杂后的 ZnO 单晶仍显示 n 型导电性, 自由电子浓度比非掺样品增高, 在 800℃ 扩散后尤为明显. PL 测试结果表明, 掺杂样品在 420~550nm 范围的可见光发射与缺陷有关. XPS 测试表明: 在 550℃ 掺杂, P 原子更易代替 Zn 位; 在 800℃ 扩散时, P 未占据 Zn 位, 而似乎占据了 O 位. 最终在磷扩散后的 ZnO 单晶中形成了高浓度的浅施主缺陷, 造成了自由电子的显著增加.

关键词: 扩散; 缺陷; ZnO; 红磷

PACC: 8160C; 7155H **EEACC:** 2520D

中图分类号: TN304.2⁺5 **文献标识码:** A **文章编号:** 0253-4177(2008)09-1674-05

* 国家自然科学基金资助项目(批准号:60736032)

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2008-04-13 收到, 2008-05-27 定稿