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Mechanism of p-type conductivity for phosphorus-doped ZnO thin film

B Yao[1,2], Y P Xie[1], C X Cong[1], H J Zhao[1], Y R Sui[1], T Yang[1] and Q He[1]

[1] Department of Physics, Jilin University, Changchun 130023, People's Republic of China
[2] Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, People's Republic of China

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Abstract
A p-type phosphorus-doped ZnO film (ZnO : P) was grown on a quartz substrate by sputtering a ZnO target mixed with 2 wt% P_2O_5 using a mixture of Ar and O_2 and then annealed rapidly at 750 °C for 5 min in air ambient. The lattice constant of the *c*-axis was 0.5176 nm, smaller than the value of 0.5211 nm of pure ZnO, implying substitutional P at a Zn antisite (P_{Zn}). The binding energy of $P_{2p1/3}$ is 133.5 eV, which is different from that of the P–O bond in P_2O_5 and of the P–Zn bond in Zn_3P_2, but close to that of P–O–P and P–O–Zn bonds in zinc phosphate glass mainly composed of ZnO and P_2O_5. The 80 K photoluminescence spectrum shows neutral acceptor bound exciton emission at 3.34 eV. Based on the above experimental results, it is suggested that P substitutes for a Zn antisite in the ZnO : P and forms an acceptor complex with two Zn vacancies, and the acceptor complex is responsible for p-type conductivity of ZnO : P.

1. Introduction

Due to a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, ZnO is considered as a promising semiconductor for fabrication of ultraviolet light-emitting diodes and laser diodes and has been investigated extensively in recent years. However, ZnO has suffered from one major disadvantage: the lack of stable and reproducible p-type ZnO with low resistivity, high carrier concentration and high mobility. Many efforts have been made to fabricate p-type ZnO by doping of group-I (Li, Na) and group-V (N, P, As, Sb) elements, but many problems are still unsolved. Recently, some research groups have fabricated p-type phosphorus (P)-doped ZnO (ZnO : P) by using P_2O_5, Zn_3P_2, GaP and PH_3 as the P source [1–5] and usually attribute the p-type conductivity of the ZnO : P to an acceptor formed by substitutional P at an O site (P_O) [6–8]. However, according to the first-principle calculation based on the density functional theory, P_O is an acceptor with a deep level of 600–900 meV [9, 10], and hence it may not make P-doped ZnO conductive in p-type. In fact, similar problems are also found in As and Sb doped ZnO. In order to understand this problem, Limpijumnong *et al* [11] proposed a model for large-size-mismatched group-V dopants (As and Sb) based on first-principle pseudopotential calculation, indicating that the dopants do not occupy the O sites, but rather the Zn sites, and each forms a complex with two spontaneously induced Zn vacancies, denoted as As_{Zn}–$2V_{Zn}$ (or Sb_{Zn}–$2V_{Zn}$). Moreover, the complex has lower formation energy than any of the parent defects. Lee *et al* suggested [12] that there also exists a P_{Zn}–$2V_{Zn}$ acceptor complex with a shallow level in ZnO : P, which consists of a substitutional P at a Zn antisite (P_{Zn}) and two Zn vacancies (V_{Zn}), and this kind of acceptor may be responsible for p-type conductivity of P-doped ZnO. However, no experimental evidence has demonstrated the presence of this acceptor complex up to now. Therefore, the origin of p-type conduction is still unclear for P-doped ZnO.

In this work, a p-type P-doped ZnO film was fabricated by sputtering, using P_2O_5 as the P source, and the mechanism of p-type conductivity was discussed for P-doped ZnO.

2. Experimental procedures

ZnO : P thin film was grown on the quartz substrate by the radio-frequency (rf) magnetron sputtering technique and then annealed rapidly at 750 °C in air ambient for 5 min or isothermally at 600 °C under vacuum for 30 min. A P-doped ZnO target was prepared by sintering a mixture of 99.99% pure ZnO and 2 wt% 99.99% pure P_2O_5 powders at 1000 °C for 10 h in air ambient. Prior to deposition, the quartz substrate was cleaned with acetone, alcohol and de-ionized water in an ultrasonic bath. The growth chamber was pumped to a base

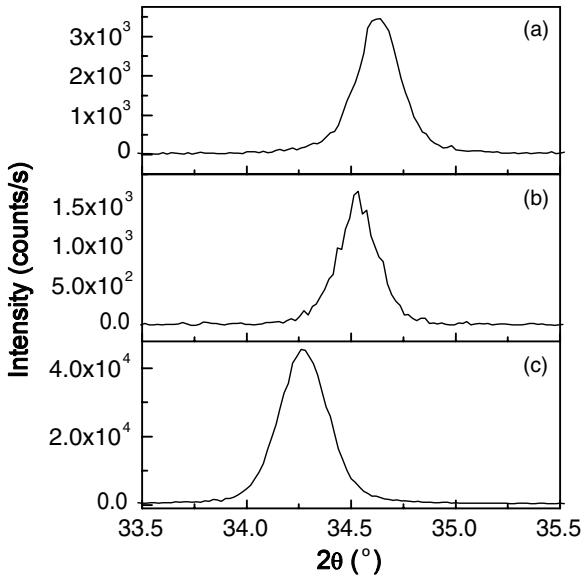

Figure 1. XRD patterns of (*a*) ZnO : P annealed rapidly at 750 °C for 5 min in air ambient, (*b*) annealed isothermally at 600 °C for 30 min under vacuum and (*c*) undoped ZnO annealed isothermally at 600 °C for 60 min under vacuum.

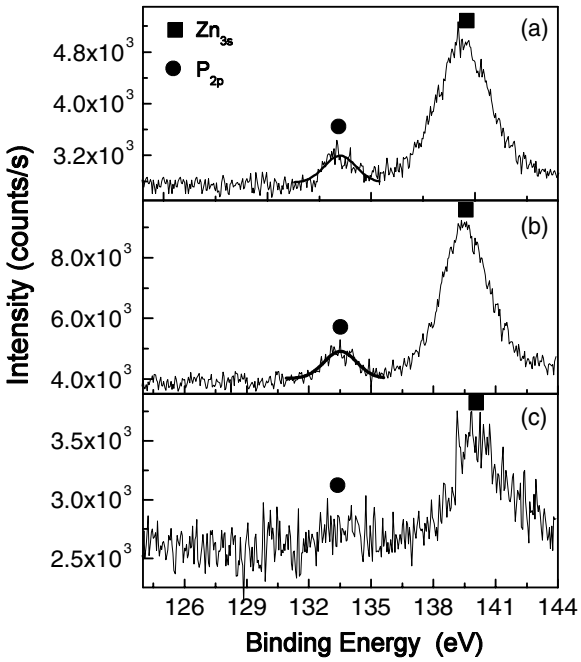

Figure 2. $P_{2p1/3}$ XPS spectra of (*a*) as-grown ZnO : P, (*b*) ZnO : P annealed rapidly at 750 °C for 5 min in air ambient and (*c*) annealed isothermally at 600 °C for 30 min under vacuum.

pressure of 5×10^{-4} Pa and then filled up to 0.5 Pa with a high pure Ar and O_2 mixture with the mass ratio of Ar to O_2 of 1 to 0.05. The film was deposited at 500 °C for 60 min with an rf power of 100 W.

The crystal structure of the film was identified by a rotation anode x-ray diffractometer (XRD) (Rigaku D/Max-RA) with Cu Kα_1 radiation ($\lambda = 0.154\,06$ nm), the scan step size used is 0.02° and the error is within ±0.0003 nm for the lattice constant measurement. Energy dispersive x-ray (EDX) (Genesis 2000 XMS 60S, Edax Inc.) and x-ray photoelectron spectroscopy (XPS) (Escalab Mark II, VG Inc.) excited by Al K_α x-rays were used to characterize the composition and chemical state of P in the ZnO : P film. The operating voltage of the EDX is 15 kV. The energy step size is 0.1 eV and the intrinsic error is within ±0.5 eV for the XPS measurement. The XPS peak shift due to the electrostatic charging of the surface layer was corrected considering the increment registered on the surface C–C/C–H peak position, with respect to the literature value of 284.6 eV. The electrical properties were investigated by the Hall measurement system (Lakeshore 7707) at room temperature using the van der Pauw configuration. Low temperature (80 K) photoluminescence (PL) measurement was performed using the LabRam Infinity UV–VIS–NIR Integrated and Automated Raman System (Jobin Yvon Inc.) excited by a He–Cd laser with a wavelength of 325 nm; the intrinsic error is in an order of magnitude of meV.

3. Experimental results and discussion

The XRD measurement shows that both as-grown and annealed P-doped ZnO are of hexagonal structure with (0 0 2) preferential orientation. Figures 1(*a*) and 1(*b*) show the (0 0 2) diffraction peak of the ZnO : P annealed rapidly in air ambient (denote as r-ZnO : P) and isothermally under vacuum (denoted as v-ZnO : P), respectively, from which the full-width at half maximum (FWHM) is calculated to be 0.22° for the r-ZnO : P and 0.20° for the v-ZnO : P, indicating that both films have good crystallinity. Using the data of figures 1(*a*) and (*b*), the lattice constant of the *c*-axis is measured to be 0.5176 nm for the r-ZnO : P and 0.5191 nm for the v-ZnO : P. Figure 1(*c*) reveals the (0 0 2) diffraction peak of the undoped ZnO film annealed for 60 min at 600 °C under vacuum, from which the lattice constant of the *c*-axis is calculated to be 0.5211 nm, which is within the lattice constant of the *c*-axis (0.5206–0.5219 nm) of pure ZnO reported previously and larger than the lattice constant of both the annealed ZnO : P. It is known that the radii of trivalent P and bivalent Zn cations are 0.44 nm and 0.88 nm, respectively, and that the radii of trivalent P and bivalent O anion are 1.86 nm and 1.35 nm, respectively. If P occupies an O site, the lattice constant should increase, not in agreement with the results of figures 1(*a*) and (*b*). However, if P substitutes for a Zn antisite, the lattice constant should decrease, consistent with the result of figures 1(*a*) and (*b*). Therefore, it is deduced that the decrease in the lattice constant of the ZnO : P is attributed to substitutional P at a Zn antisite, and the lattice constant of the *c*-axis decreases with increasing P concentration. In comparison with lattice constants between r-ZnO : P and v-ZnO : P, it is concluded that the P concentration in the r-ZnO : P is larger than that in the v-ZnO : P.

In order to confirm the deduction, the XPS measurement was performed for the as-grown and annealed ZnO : P films. Figure 2(*a*) shows the $P_{2p1/3}$ and Zn_{3s} XPS spectrum of as-grown ZnO : P, indicating that the binding energy of $P_{2p1/3}$ is 133.5 eV, which is different from the binding energy of 135.5 eV observed in pure P_2O_5. This implies that no P_2O_5 clusters exist in ZnO : P and the P of P_2O_5 is incorporated

Table 1. The electrical properties of as-grown, r- and v-ZnO : P thin films.

Sample	Resistivity (Ω cm)	Type	Concentration (cm^{-3})	Mobility ($cm^2\,V^{-1}\,s^{-1}$)
As-grown ZnO : P	high	—	—	—
r-ZnO : P	59.8–59.9	p	$(2.11–3.16) \times 10^{17}$	0.349–0.471
v-ZnO : P	0.237–0.239	n	$(3.30–3.33) \times 10^{19}$	0.789–0.797

into ZnO films during the growth process to form P-doped ZnO, consistent with the XRD results mentioned above. It was reported that the binding energy of $P_{2p1/3}$ is 128.3 eV in Zn_3P_2 and 129.8 eV in ZnP_2, smaller than the value in ZnO : P, implying that no Zn–P bond is formed in the ZnO : P film, that is, P does not substitute for O. Onyiriuka [13] investigated XPS of zinc phosphate glass composed of mainly ZnO and P_2O_5 and found that the binding energy of $P_{2p1/3}$ in P–O–P and P–O–Zn bonds is between 133.3 and 133.8 eV, which is close to the binding energy of $P_{2p1/3}$ in the as-grown ZnO : P. Taking the ZnO structure as well as the XPS and XRD results into account, it is deduced that P does not substitute for the O site but a Zn antisite in the as-grown ZnO : P film.

The $P_{2p1/3}$ XPS spectrum of the r-ZnO : P is the same as that of the as-grown ZnO : P, as shown in figure 2(*b*). So the P also substitutes for a Zn antisite in the r-ZnO : P, in agreement with the deduction obtained from the XRD result of figure 1(*a*). However, as figure 2(*c*) shows, the $P_{2p1/3}$ XPS peak almost disappears in the XPS spectrum of the v-ZnO : P, implying that most of the P atoms escape from the ZnO : P during the annealing process and few P atoms exist in it. Obviously, the P concentration is larger in the r-ZnO : P than in the v-ZnO : P, which is consistent with the deduction obtained from the XRD measurement.

Table 1 shows Hall measurement results of the as-grown, r- and v-ZnO : P, indicating that the as-grown ZnO : P is of high resistance, while the r-ZnO : P and v-ZnO : P is p-type and n-type conduction, respectively. The high resistance, which is usually attributed to poor crystal quality, is a common feature of the as-grown ZnO film prepared by the magnetron sputtering technique. The conductivity of the annealed ZnO : P seems to be related to P-doping, combining with XPS results of figures 2(*b*) and (*c*). Based on XPS results mentioned above, P substitutes for a Zn antisite in the r-ZnO : P, which should form a donor defect P_{Zn} and result in n-type conduction. However, the r-ZnO : P behaves with p-type conductivity, implying that the p-type conductivity comes from other forms of acceptor.

Lee *et al* investigated the electron structure of various P-related defects in ZnO using first-principle pseudopotential calculation, indicating that substitutional P at an O site can form a deep acceptor P_O with a level of 620–900 meV, which cannot be responsible for p-type conduction of P-doped ZnO [12]. So, he proposed that P occupied the Zn antisite and formed a acceptor complex with two Zn vacancies V_{Zn} (denoted as P_{Zn}–$2V_{Zn}$) under O-rich condition. The complex has a shallow acceptor level, can effectively compensate native donor defects, such as O vacancies and Zn interstitials, and is responsible for p-type conductivity of the P-doped ZnO. In this

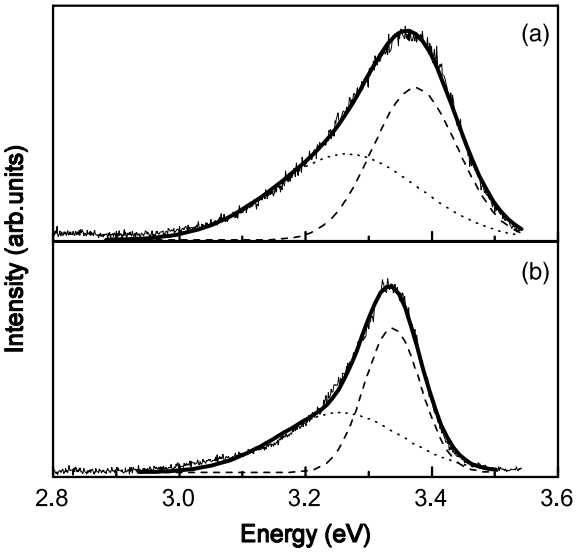

Figure 3. 80 K PL spectra of ZnO : P (*a*) annealed isothermally at 600 °C for 30 min under vacuum and (*b*) annealed rapidly at 750 °C for 5 min in air ambient.

work, the EDX measurement indicates that the composition percent of O, Zn and P in the r-ZnO : P is 52.2 at%, 46.1 at% and 1.7 at%, respectively, implying that the r-ZnO : P is O-rich, consistent with the result of XPS measurements. Both XPS and EDX results imply the existence of many V_{Zn} in the r-ZnO : P. Due to substitution of P for the Zn antisite and the existence of many V_{Zn} as mentioned above, we deduce that the p-type conductivity of the r-ZnO : P comes from the contribution of the P_{Zn}–$2V_{Zn}$ acceptor complex.

However, for the v-ZnO : P, since few P exist in it and not enough P_{Zn}–$2V_{Zn}$ acceptor complexes can be formed to compensate native donors, it conducts in n-type.

Figures 3(*a*) and (*b*) show 80 K PL spectra of the v- and r-ZnO : P, respectively. By using the Gaussian fitting method, both figures 3(*a*) and (*b*) can be fitted well with two sub-PL spectra. For figure 3(*a*), the two sub-PL spectra are located at 3.37 eV and 3.26 eV, respectively, as shown in figure 3(*a*). The former is assigned as neutral donor-bound exciton emission D^0X [3, 14], and the latter is due to donor–acceptor pair (DAP) emission. This implies that the major carriers are electrons in the v-ZnO : P, in agreement with Hall measurement results of table 1. For figure 3(*b*), the sub-PL spectra are located at 3.34 eV and 3.25 eV, respectively, as shown in figure 3(*b*). The sub-PL peak located at 3.34 eV is due to neutral acceptor bound exciton emission A^0X [3, 14] and the acceptor should be the P_{Zn}–$2V_{Zn}$ complex. The 3.25 eV sub-PL peak is attributed to DAP emission. The PL results of figure 3(*b*) imply that the major carriers are holes in the r-ZnO : P, consistent with the Hall measurement results.

4. Conclusions

A p-type ZnO : P with (0 0 2) preferential orientation was grown on a quartz substrate by sputtering the ZnO target mixed with 2 wt% P_2O_5 using a mixture of Ar and O_2 and sequentially annealing rapidly at 750 °C for 5 min in air ambient. The lattice

constant of the *c*-axis was 0.5176 nm, smaller than the value of 0.5211 nm of pure ZnO. The binding energy of $P_{2p1/3}$ is 133.5 eV, which is different from that of the P–O bond in P_2O_5 and of the P–Zn bond in Zn_3P_2, but close to that of P–O–P and P–O–Zn bonds in zinc phosphate glass composed of mainly ZnO and P_2O_5. The XRD and XPS measurements demonstrate that P substitutes for Zn in the r-ZnO : P. The 80 K PL spectrum shows a neutral acceptor bound exciton emission peak at 3.34 eV, demonstrating the existence of a lot of acceptors. Based on XRD, XPS and PL results, it is deduced that most of P do not substitute for O site but rather a Zn antisite in the r-ZnO : P and forms a P_{Zn}–$2V_{Zn}$ acceptor complex with a shallow level with two V_{Zn}. The P_{Zn}–$2V_{Zn}$ acceptor complex should be responsible for p-type conductivity of the r-ZnO : P.

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