Electrical and optical properties of phosphorus-doped *p*-type ZnO films grown by metalorganic chemical vapor deposition

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P-doped *p*-type ZnO thin films have been grown by metalorganic chemical vapor deposition. By modulating the *P* evaporating temperature, *p*-type conductivity can be controlled due to the different *P* content incorporated into the ZnO films. The *P*-doped *p*-type ZnO thin films are of high optical quality, as indicated by low-temperature photoluminescence. *P*-related acceptor state with an energy level of 163 meV is identified from free-to-neutral-acceptor transitions. In addition, x-ray photoelectron spectroscopy confirms that only one chemical bonding state of *P* exists in the *P*-doped ZnO thin films. © 2008 American Institute of Physics. [DOI: 10.1063/1.2828017]

I. INTRODUCTION

ZnO has gained considerable attention as a promising material for short-wavelength optoelectronic devices, such as photodetectors, light emitting diodes, and laser diodes, due to its wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature.^{1,2} An important issue is the growth of both high quality *p*- and *n*-type ZnO. However, nominally undoped ZnO typically exhibits *n*-type conductivity. The realization of *p*-type ZnO has proven difficult due to the self-compensating effect from native defects and interstitial hydrogen.^{3,4} Fortunately, thanks to the considerable worldwide efforts, investigations on *p*-type ZnO have proceeded at a rapid pace and various elements have been used as *p*-type dopants, including group-V (Ref. 5–8) and group-I (Ref. 9) elements. Among them, N appears promising considering its size and energy level.¹⁰ However, the obtained *p*-type ZnO:N films are usually unstable.¹¹ The lack of stable *p*-type materials is still the key issue which hinders the development of ZnO-based optoelectronic devices. Recently, a theory for large-sized-mismatched group-V dopants based on first-principles calculations has been presented.¹² Also, several groups have reported *p*-type conductivity in ZnO by doping with large-sized-mismatched impurities, such as P,¹³ As,¹⁴ and Sb.¹⁵ In spite of this progress, the improvement of *p*-type behavior and a better understanding of the doping mechanism in *p*-type ZnO are strongly demanded for the device development.

Based on our previous study, we develop an effective and reproducible route to prepare *P*-doped ZnO by metalorganic chemical vapor deposition (MOCVD), which has many advantages over other growth methods, such as the feasibility of large-area growth and potential industrial application. On the other hand, there are few reports on *P*-doped *p*-type ZnO films grown by MOCVD. In this paper, we in-

vestigate *p*-type behavior in *P*-doped ZnO thin films grown by MOCVD with a special thermal evaporator. The electrical and optical properties of the films are readily presented.

II. EXPERIMENTAL DETAILS

P-doped ZnO thin films were grown on quartz and *n*-type Si (100) substrates using a low-pressure MOCVD system. Diethylzinc was used as the zinc source and N₂ was used as the carrier gas. High-purity O₂ (99.999%) and P₂O₅ powder (99.999%) were used as the oxygen source and *P*-dopant source, respectively. A special thermal evaporator was used to evaporate P₂O₅. The detailed growth procedures were described elsewhere.¹⁶ Room-temperature Hall-effect measurements were carried out in the van der Pauw configuration (BIO-RAD HL5500PC). Energy-dispersive spectrometry (EDS) was used to examine the *P* content in ZnO films. Temperature-dependent photoluminescence (PL) measurements were performed on a Fluorolog-3-Tau fluorescence spectrometer, using a 320-nm xenon lamp as the excitation light source. The chemical bonding state of *P* was analyzed by x-ray photoelectron spectroscopy (XPS) (Thermo ESCALAB 250, Al *Kα* radiation source $h\nu=1486.6$ eV).

III. RESULTS AND DISCUSSION

Figure 1 shows the resistivity, Hall mobility, and carrier concentration of *P*-doped ZnO thin films grown on quartz substrates as a function of *P* evaporating temperature ranging from 350 to 550 °C. All the films exhibit definitive *p*-type conductivity. Hall measurements have revealed that the optimal result on the insulating quartz is realized at the evaporating temperature of 450 °C, with a resistivity of 14.9 Ω cm, a Hall mobility of 0.227 cm² V⁻¹ s⁻¹, and a hole concentration of 1.84 × 10¹⁸ cm⁻³. Note that the *p*-type behavior is very reproducible, since these results could be consistently repeated. Dependence of electrical properties on the *P* evaporating temperature illustrated here may be under-

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FIG. 1. Dependence of electrical properties of P-doped ZnO thin films grown on quartz substrates on the P evaporating temperature.

stood as follows. From EDS analysis, the contents of P in the ZnO thin films were calculated to be 0.54%, 0.91%, 1.43%, 1.21%, and 1.04%, respectively, corresponding to the P evaporating temperature ranging from 350 to 550 °C. In this regard, the difference of *p*-type conductivity in P-doped ZnO films may be ascribed to the different P contents. When the evaporating temperature is low (350 °C), only a part of P₂O₅ undergo an evaporation. Thus, the content of P atoms incorporated in the ZnO films is relatively low, which is responsible for the relatively high resistivity and low carrier concentration (as shown in Fig. 1). With the evaporating temperature increasing, more P₂O₅ evaporate and dissociate, supplying activated P atoms. As a result, more P atoms are incorporated into the ZnO thin films and *p*-type conduction is enhanced gradually. An optimal result is achieved at the evaporating temperature of 450 °C. When the evaporating temperature further increases, especially to 550 °C, P₂O₅ evaporation is very fast, resulting in high concentration of P existing in the interface of gas and the film. Because of the slow bulk diffusion coefficient, some gaseous P may flow away with the O₂ flowing instead of being incorporated into the ZnO thin films. Thus, it is reasonable to infer that the P content decreasing is responsible for the degradation of *p*-type conduction at the high evaporating temperature. A better understanding of this origin is in progress.

To further confirm the *p*-type conduction in P-doped ZnO thin films, ZnO-based *p-n* homojunction was fabricated by deposition of a Al-doped *n*-type ZnO layer on a P-doped *p*-type ZnO layer grown at the evaporating temperature of 450 °C on quartz substrate, as illustrated in the inset in Fig. 2. In-Zn alloy was used as both *n*- and *p*-side electrodes, showing linear current-voltage (*I-V*) characteristics indicative of good ohmic contacts (date not shown). Figure 2 shows the *I-V* characteristics of the ZnO homojunction. The rectification of *I-V* characteristics, which is very reproducible for repeated measurements, suggests that the fabricated P-doped ZnO thin film is truly *p* type.

Hall-effect measurements were performed again 90 days later to investigate the stability of the *p*-type conductivity. It is found that the P-doped *p*-type ZnO thin films still keep the *p*-type conductivity without any obvious degradation.

To evaluate the acceptor states of P in ZnO, low-temperature PL measurements were performed. Figure 3

FIG. 2. (Color online) *I-V* characteristics of Al-doped ZnO/P-doped ZnO *n-p* homojunction measured at room temperature. The inset shows the schematic of the homojunction.

shows the PL spectrum at 8 K for the P-doped ZnO thin film grown at the evaporating temperature of 450 °C on the *n*-type Si (100) substrate. A strong emission peak at 3.337 eV is dominant in the spectrum, which is labeled as A. On the higher energy side, an obvious peak at 3.373 eV is attributed to a free exciton (FX) emission. The evidence of the FX emission suggests a high optical quality. In addition, a peak at 3.271 eV labeled as B with two shoulder peaks at 3.199 and 3.127 eV is also observed. From these peak positions, we tentatively assign band A to a neutral acceptor-bound exciton emission (*A*⁰X), band B to a free-to-neutral-acceptor (*e*,*A*⁰) transition and the others to its longitudinal optical-phonon replicas.

To gain more information of the origin of the observed emissions, temperature-dependent PL measurements were performed, as shown in Fig. 4. For the FX emission, an obvious temperature-dependent redshift from 3.373 eV at 8 K to 3.300 eV at 250 K is observed. While for band A, a temperature-dependent blueshift from 3.337 eV at 8 K to 3.341 eV at 70 K is observed. We believe that this blueshift

FIG. 3. PL spectrum at 8 K for the P-doped ZnO thin film grown at the evaporating temperature of 450 °C on the *n*-type Si (100) substrate.

FIG. 4. (Color online) Temperature-dependent PL spectra of the P-doped *p*-type ZnO thin film grown at the evaporating temperature of 450 °C on the *n*-type Si (100) substrate. The dotted lines show the shifts of the A^0X , FX emission and (e, A^0) transitions.

is a result of a transition from bound exciton emission to free exciton FX emission mainly due to the thermal dissociation of the A^0X at a higher temperature. A similar transition from A^0X to FX emissions has also been observed in GaN, with the transition temperature at 70 K.¹⁷ As the temperature further increases, the A^0X emission is buried by FX emission. This clearly suggests that the A^0X emission gives way to FX emission at the elevated temperatures due to the thermal effect.

Furthermore, temperature-dependent peak positions of the FX are plotted in Fig. 5. The temperature-dependent band gap is described according to Ref. 18 as

$$E_g(T) = E_g(0) - k/[\exp(\theta/T) - 1], \quad (1)$$

where $E_g(0)$ is the band gap energy at 0 K. Also, k is a constant and θ represents the Einstein temperature. A fitting curve of $E_g(T) - 60$ meV, as shown in Fig. 5, confirms its typical FX characteristics.

FIG. 5. (Color online) Temperature-dependent peak positions and their fitting curves for FX and band B.

FIG. 6. (Color online) XPS narrow scan spectrum of $P 2p_{3/2}$ for the P-doped *p*-type ZnO thin film grown at the evaporating temperature of 450 °C on the *n*-type Si (100) substrate.

For (e, A^0) emission, the temperature dependence of the peak position can be well described according to Ref. 19 as

$$E_{eA} = E_g(T) - E_A + k_B T/2, \quad (2)$$

where E_A is the acceptor energy level and k_B is the Boltzmann constant. The fitting to the data gives an acceptor level of 163 meV, as shown in Fig. 5. This value agrees fairly well with that reported for P-doped ZnO, such as 180 meV reported by Xiu²⁰ and 127 meV reported by Hwang.²¹ A perfect match between the experimental values and the fitting curves confirms our assignment of the (e, A^0) transitions.

In addition to the earlier mentioned PL measurements, the chemical bonding state of P in ZnO thin films was examined by XPS. Figure 6 illustrates the $P 2p_{3/2}$ narrow scan spectrum for the P-doped *p*-type ZnO thin film grown at the evaporating temperature of 450 °C on the *n*-type Si (100) substrate. The peak of the $P 2p_{3/2}$ core level can be fitted into one Gaussian peak on deducting the base line, which indicates that only one chemical bonding state of P exists in the P-doped ZnO thin film. $P 2p_{3/2}$ peak centered at 135.2 eV is generally attributed to P-O bonding.²² Therefore, it is concluded that P incorporated in the film should exist as P_{Zn} rather than P_O . However, isolated P_{Zn} behaves as a donor rather than an acceptor, which will not result in *p*-type conductivity. Thus, it is reasonable to infer that another P-related acceptor state exists in the P-doped ZnO thin film. Recently, based on first-principles calculations, a model for large-size-mismatched group-V dopants in ZnO has been proposed,¹² in which a $P_{Zn}-2V_{Zn}$ complex has been considered to be the most likely defect to form a shallow acceptor level. In addition, the P-related acceptor state, with a shallow acceptor level of 163 meV, is identified by the previous temperature-dependent PL. With these considerations, the clear *p*-type behavior in the P-doped ZnO thin film is most likely attributed to the $P_{Zn}-2V_{Zn}$ complex in the present case.

Recently, theoretical calculations give different sentiment toward the outlook of P-doped ZnO. Yu²³ *et al.* suggested that a possible acceptor P_O could be formed with an

energy level of 0.49 eV above the valence band maximum. On the other side, Limpijumrong¹² proposed a model for large-size-mismatched group-V dopants in ZnO, in which a $P_{Zn}-2V_{Zn}$ complex has been suggested to be the most likely defect to form a shallow acceptor level. Experimentally, the acceptor activation energy of P-doped ZnO films is shown to be much smaller than 0.49 eV, in the range of 127–180 meV. Our experimental results including XPS analysis and PL spectra are in agreement with $P_{Zn}-2V_{Zn}$ acceptor state.

IV. CONCLUSIONS

In summary, we have demonstrated the reproducible growth of P-doped *p*-type ZnO thin films by MOCVD using P_2O_5 as the dopant source. PL spectra reveal that the *p*-type ZnO films are of high optical quality. A shallow acceptor level of 163 meV is identified from free-to-neutral-acceptor transitions. Guided by XPS, PL, and a model for large-sized-mismatched group-V dopant in ZnO, a $P_{Zn}-2V_{Zn}$ complex is believed to be the most possible acceptor in the P-doped *p*-type ZnO thin films.

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