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RESEARCH ARTICLE

Growth of phosphorus-doped p-type ZnO thin films by MOCVD

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Abstract Phosphorus-doped p-type ZnO thin films are prepared on glass substrates by metalorganic chemical vapor deposition (MOCVD). DEZn, O_2, and P_2O_5 powders are used as reactant and dopant sources. The p-type ZnO films are grown at a temperature between 673 K and 723 K. The best p-type sample has a low resistivity of 4.64 Ω·cm, a hole concentration of 1.61×10^{18} cm^{-3}, and a Hall mobility of 0.838 $cm^2 \cdot (V \cdot s)^{-1}$ at room temperature. A strong emission peak at 3.354 eV corresponding to neutral acceptor bound excitons is observed at 77 K in the photoluminescence spectra, which further verifies the p-type characteristics of the films.

Keywords p-type ZnO, metalorganic chemical vapor deposition (MOCVD), phosphorus-doping

1 Introduction

II–VI compound semiconductor ZnO with a wide band gap of 3.37 eV, large exciton binding energy of 60 meV at room temperature and a high optical gain of 300 cm^{-1}, has attracted much interest due to its potential applications in ultraviolet optoelectronic devices, such as light emitting diodes and laser diodes [1,2]. Due to the asymmetric doping limitation, n-type ZnO with excellent properties can be obtained by Al, Ga, or In doping. However, high-quality p-type ZnO with low resistivity and high mobility is still hard to achieved. On one hand, it is due to the formation of native donor defects, such as O vacancies and Zn interstitials [3,4]; on the other hand, it is due to the low solubility of dopants and the deep-acceptor levels.

The most widely investigated acceptor dopants for p-type ZnO are group-V elements (N, P, As and Sb). Several research groups have reported the realization of p-type ZnO using nitrogen as acceptor dopants by various growth methods [5–8]. However, the obtained p-type ZnO films are commonly unstable and unreproducible [9–11]. Meanwhile, several research groups have recently reported p-type conductivity in ZnO with exceptionally large-size-mismatched dopants such as P [12–14], As [15], and Sb [16]. Interestingly, phosphorus-doped p-type ZnO films showed excellent stability and reproducibility.

By far, the most reported phosphorus-doped ZnO films are deposited by frequency sputtering [13,14], and the p-type conduction can only be achieved after an annealing treatment. However, there are few reports about the fabrication of phosphorus-doped p-type ZnO films by metalorganic chemical vapor deposition (MOCVD) method, which has special advantages such as large scaling and reproduction. In this study, as-prepared phosphorus-doped p-type ZnO films were investigated by varying the substrate temperature and flow rate of Zn source via MOCVD. O_2 and P_2O_5 were used as oxidant and P source respectively.

2 Experiments

Phosphorus-doped ZnO thin films were grown using low-pressure MOCVD on glass substrates. Diethylzinc (DEZn) (99.999% purity) was used as the zinc precursor and N_2 (99.999% purity) gas was used as the carrier gas. P_2O_5 powder (99.999% purity) was used as both oxidizing and doping sources. P_2O_5 was thermally evaporated at a temperature in the range of 873–1173 K. The chamber pressure was 133 Pa. The growth temperature was in the range of 623–773 K. The film thickness was about 0.2–0.6 μm.

The crystal structures of ZnO thin films were examined by X-ray diffraction (XRD) using a Bede D1 system with Cu K_α radiation ($\lambda = 0.1542$ nm). The electrical properties were measured by Hall analysis in the van der Pauw configuration at room temperature by using a magnetic field of 0.5 T and a current automatically set by a Hall system (BIO-RADHL5500PC). The P content was investigated by energy-dispersive spectrometry (EDS).

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The transmission spectra were measured by a Varian Cary-300 spectrophotometer. Photoluminescence (PL) spectra were obtained by using a RAMALOG6 spectrometer with an excitation wavelength of 325 nm.

3 Results and discussion

3.1 Structural properties

Figure 1 shows the typical XRD profiles for the undoped ZnO and P-doped thin films grown at 693 K. It can be seen that both films exhibit a dominant peak corresponding to the (002) plane of ZnO, which indicates the *c*-axis orientation of the films. For the phosphorus doped p-type ZnO film, the diffraction intensity of the ZnO (002) peak is lower than that of the undoped ZnO film, and other weak diffraction peaks ((100) and (101)) also appear, which indicates some degradation of the crystallinity resulting from P doping. No secondary phase is observed in the pattern, indicating that P is doped into ZnO films successfully. EDS measurements further verify this result (P content: 0.64%–0.81%). Additionally, it is found that the (002) peak position shifts slightly to the low angle side, which indicates an increase of plane distance and the resulting tensile strain. The biaxial stress in the films can be calculated from [17]

$$\sigma = -453.6 \times 10^9 [(c - c_0)/c_0] \quad \text{N/m}, \tag{1}$$

where c_0 is the strain-free lattice parameter measured from a ZnO powder sample, and c is the lattice parameter of the film samples. According to this expression, it can be inferred that the lattices are distorted and the *c*-axis tensile stress exists, which is closely related to the P substitution and the lattice defects such as Zn interstitials, and O vacancies in the films [18].

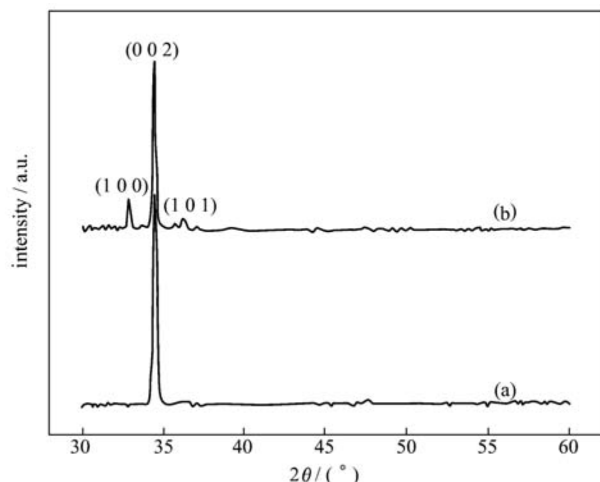

Fig. 1 XRD spectra of undoped (a) and phosphorus-doped (b) ZnO thin films grown at 693 K

3.2 Electrical properties

The electrical properties of ZnO films growing at different temperatures with Zn flow rate of 25 sccm and O_2 of 40 sccm are investigated, and the results are listed in Table 1. As shown in the table, p-type conduction is obtained in the films deposited at the substrate temperature of 673–723 K. At the growth temperature of 693 K the best p-type ZnO film is obtained with a hole carrier concentration of 1.61×10^{18} cm^{-3}, a resistivity of 4.64 Ω·cm, and a carrier mobility of 0.838 $cm^2 \cdot (V \cdot s)^{-1}$. The electrical measurements are performed again after 6 months, and it was found that the film kept the p-type conduction without any obvious degradation, indicating an excellent reliability and stability.

As shown in Table 1, when the substrate temperature is below 713 K or above 723 K, the ZnO films show an n-type conduction. P-type ZnO films can only be obtained in a certain temperature range. These results could be understood as follows. When the substrate temperature is lower than 673 K phosphorus atoms do not have enough energy to diffuse into the lattice site, so no p-type conductivity is obtained. However, when the substrate temperature is higher than 723 K, the P atoms doped into ZnO films evaporate, and ZnO films turn into n-type. Thus, substrate temperature plays a significant role in phosphorus doping of ZnO films, and only at an appropriate temperature can low resistivity p-type ZnO thin films with high hole concentration be achieved, which is in the range of 673–723 K in this work.

The realization of p-ZnO suggests that P is incorporated into the films as acceptor dopant. The previous studies on group-V elements (N, P, As and Sb) proposed that the doped P atom tended to occupy the O lattice sites acting as an acceptor. However, the formation energy of the substitutional defects (P_O) is very high, and the calculated acceptor level is rather deep (960 meV above the valence band maximum) [19], which is difficult to ionize at room temperature, thus the p-ZnO films are difficult to prepare by P doping. However, recent experimental results showed ZnO could be doped p-type using P as dopant with a hole concentration higher than 10^{18} cm^{-3}. Park et al. suggest that P_{Zn}^{3+} is likely to form to relieve the local stress arising from the size misfit between O and P in oxygen-rich ambient [19]. Using first-principles calculations, Limpijumnong et al. presented a theory for large-size-mismatched impurities [20]. Guided by strain relief and Coulomb interaction, they found that among the complexes a P_{Zn}-$2V_{Zn}$ complex represents a new class of low energy defects with shallow acceptor levels. In this complex, the core P occupies the Zn antisite, which is energetic enough to spontaneously induce two Zn vacancies at the same time. So the resulting P_{Zn}-$2V_{Zn}$ complex is an acceptor with both low formation energy and low ionization energy especially under an oxygen-rich growth or annealing conditions.

Table 1 Electrical properties of ZnO thin films deposited at different growth temperatures

sample	T_s/K	P content/%	resistivity/Ω·cm	Hall mobility/ $cm^2 \cdot (V \cdot s)^{-1}$	carrier concentration/ cm^{-3}	type
un-doped	693	0.000	85.400	3.540	2.060×10^{17}	n
1	623	1.420	0.182	2.120	4.970×10^{19}	n
2	673	0.810	63.400	0.488	2.010×10^{17}	p
3	693	0.640	4.640	0.838	1.610×10^{18}	p
4	723	0.660	10.800	0.189	1.060×10^{18}	p
5	773	0.380	0.068	1.520	4.470×10^{19}	n

This finding explains the puzzling experimental observations.

3.3 Optical properties

Figure 2 shows the typical room-temperature transmission spectra of n-type (1#), p-type (3#) and undoped ZnO films. It is found that both phosphorus-doped and undoped ZnO films show a high transmittance (about 90%) in visible regions and a sharp fundamental absorption edge. The fundamental absorption, which corresponds to the excitation from valence band to conduction band, is usually used to determine the optical band gap (E_g). As a direct band gap semiconductor, ZnO has an absorption coefficient (α) obeying the following relation [21]:

$$\sigma^2 = A\left(hv - E_g\right), \quad (2)$$

$$T = (1-R)^2 \exp(-\alpha d). \quad (3)$$

Here, A is a constant; v is the photon frequency; T is the transmittance of ZnO films; R is the reflectivity; d is the film thickness. Figure 3 shows the plot of σ versus hv derived from transmittance spectra. The E_g values, which can be determined by extrapolating the straight line portion of the spectrum to $\alpha^2 = 0$, are found to be about 3.34, 3.26 and 3.28 eV for n-type, p-type and undoped ZnO films, respectively.

The optical band gap of n-type ZnO films shows a blueshift due to the Burstein-Moss effect, which is an energy band widening effect resulting from the increase of the Fermi level in the conduction band of degenerate semiconductors. However, the optical band gap of p-type ZnO films shows a redshift, which is related to phosphorus doping. Since P atoms are incorporated into the ZnO matrix, they would introduce strain in the films, which may cause the band gap to be narrowed. On the other hand, P-related defects, such as shallow acceptor P_{Zn}-$2V_{Zn}$ complex, deep acceptor P_O, deep donor P_{Zn}, amphoteric P_i etc, could form, which would make the defect-related energy level and sub-band generated, causing the redshift of intrinsic absorption.

In order to further investigate the optical properties and confirm the p-type conductive behavior of P-doped ZnO films (3#), room-temperature (RT) and low-temperature (77 K) photoluminescence (PL) measurements are carried out. As shown in Fig. 4, p-type ZnO films have an excellent optical performance. At room-temperature, a near-band-edge (NBE) emission peak at 3.28 eV corresponding to the UV emission, is dominant with a full width at half maximum (FWHM) of 124 meV, which can be attributed to the recombination of free

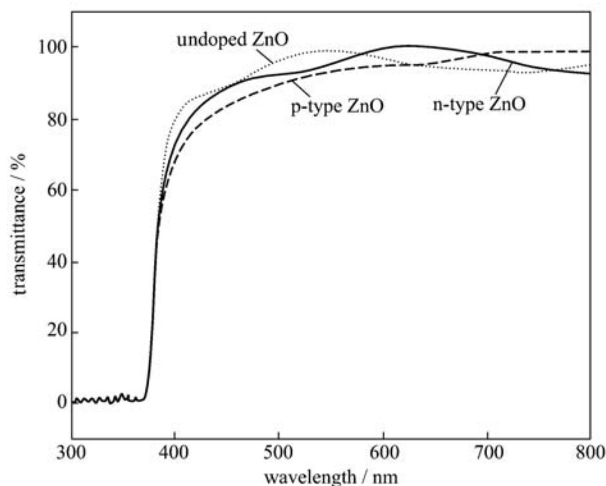

Fig. 2 Transmission spectra of n-type, p-type, and undoped-ZnO thin films

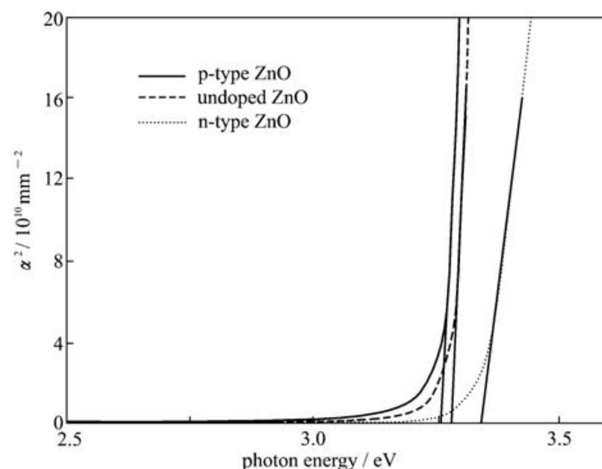

Fig. 3 Plot of σ versus hv derived from transmittance spectra

excitons. At low-temperature, a peak at 3.354 eV with FWHM of 53 meV is dominant, which may be associated with the neutral-acceptor bound exciton emissions. Combined with the results of Hall-effect measurements, it is reasonable to attribute the emission located at 3.354 eV for neutral-acceptor bound exciton. This result agrees well with the reported value [13]. We note that nearly no emission is in the visible region, which is related to the defects at either room or low temperature. It indicates that the as-grown p-type films exhibits a good optical performance, and is a good candidate for the preparation of semiconductor optoelectronic devices.

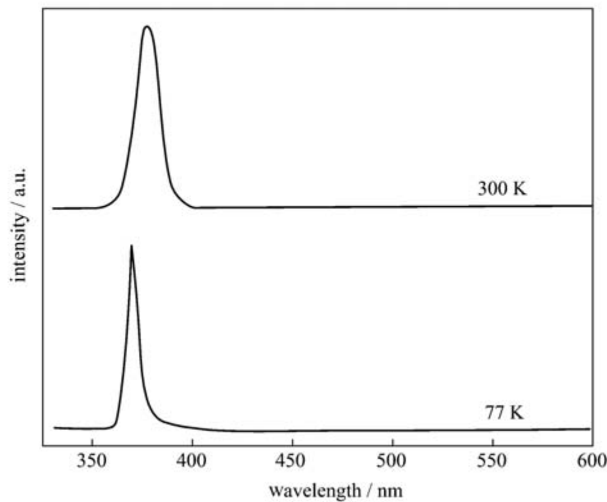

Fig. 4 Room temperature (300 K) and low temperature (77 K) photoluminescence (PL) spectra for p-type ZnO thin film

4 Conclusions

Phosphorus-doped, p-type ZnO thin films have been realized on a glass substrate via MOCVD. An optimized result with a resistivity of 4.64 Ω·cm, Hall mobility of $0.838\ cm^2 \cdot (V \cdot s)^{-1}$, and hole concentration of $1.61 \times 10^{18}\ cm^{-3}$ are achieved at the growth temperature of 693 K. The as-grown films show a preferential orientation of *c*-axis and a high transmittance (about 90%) in visible regions. A neutral-acceptor bound exciton emission at 3.354 eV is also observed in low-temperature photoluminescence measurements.

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