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p-Type conduction in phosphorus-doped ZnO thin films by MOCVD and thermal activation of the dopant

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Abstract

Phosphorus-doped p-type ZnO thin films have been realized by metalorganic chemical vapor deposition (MOCVD). The conduction type of ZnO films is greatly dependent on the growth temperature. ZnO films have the lowest resistivity of 11.3 Ωcm and the highest hole concentration of 8.84×10^{18} cm^{-3} at 420 °C. When the growth temperature is higher than 440 °C, p-type ZnO films cannot be achieved. All the films exhibited p-type conduction after annealing, and the electrical properties were improved comparing with the as-grown samples. Secondary ion mass spectroscopy (SIMS) test proved that phosphorus (P) has been incorporated into ZnO.

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Keywords: p-Type conduction; Doping; Metalorganic chemical vapor deposition; Zinc compounds; Semiconducting II–VI materials

1. Introduction

Zinc oxide (ZnO) is a direct-bandgap (3.3 eV) semiconductor that has been used extensively in various optoelectronic devices. In particular, it has been considered as a prime candidate for ultraviolet light emitting diodes and lasers due to the larger exciton binding energy (60 meV, versus 25 meV for GaN), and this property should translate to an even brighter light emission than that obtained with GaN photonics [1–4]. In order to develop such optical devices, one important issue that should be resolved is the fabrication of reproducible p-type ZnO with low resistivity [5–8]. ZnO, however, has proved to be difficult to dope as p-type due to zinc interstitials (Zn_i) and oxygen vacancies (V_O) or hydrogen [9–12]. Nitrogen has long been considered as a possible dopant for p-type ZnO [13]. While Several groups have claimed achievements of p-type ZnO by molecular beam epitaxy (MBE) [4], pulsed laser deposition (PLD) [14], metalorganic chemical vapor deposition (MOCVD) [15], and radio-frequency (RF) sputtering [16] by doping with the acceptor N_O, there is still lack of reliable and reproducible p-type doping. These ZnO films indicate the presence of high concentrations with an unrealistically high hole mobility. Also, some have reported that p-type material changes back to n-type over time [4,17]. To further pursue p-type ZnO, other group-V dopants have been tried. Several research groups have recently reported p-type conductivity in ZnO with large-size-mismatched dopants such as P [18], As [19], and Sb [20]. Interestingly, ZnO:P thin films showed good stability and reproducibility [18]. More recently, a theory for large-size-mismatched impurities by first-principles calculations has been presented, which can successfully explain this interesting phenomenon [21]. The dopants (such as P, As, Sb) prefer to occupy the Zn sites than the O sites as widely perceived, and the resulting As_{Zn}–$2V_{Zn}$ complex is an acceptor with both low formation energy and low ionization energy.

Phosphorus-doped ZnO films were deposited by RF sputtering [18], and the p-type conductivity has been realized only by a thermal annealing treatment as the thermal activation. MOCVD is a technique suitable for industrial mass production and is frequently employed for the growth of ZnO films [1,22–25]. However, so far there is no report about the fabrication of phosphorus-doped p-type ZnO films by MOCVD. In a

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MOCVD system, especially when operated at low temperatures, the characteristic of ZnO films are generally affected by preparation conditions such as the working pressure, substrate temperature, and the substrate type. Among these factors, the substrate temperature is crucial [26].

In this work, reproducible phosphorus-doped p-type ZnO films were prepared by MOCVD. The effect of substrate temperature on electrical, structural, and optical properties of ZnO films has been examined. Annealing of the films was performed to activate the dopants after growth.

2. Experimental procedure

Phosphorus-doped ZnO thin films were grown using low-pressure MOCVD on glass substrates. Diethylzinc (DEZn) was used as the zinc precursor with the flow rate of 20 μmol/min and N_2 (99.999% purity) gas was used as the carrier gas with the flow rate of 60 sccm. O_2 gas (99.999% purity) and P_2O_5 powder (99.999% purity) were used as the oxidizing and doping sources, respectively. O_2 gas flow rate was set at 40 sccm. P_2O_5 was evaporated with the temperature maintained at about 500 °C. The chamber pressure was 1 Torr. The growth temperature was in the range of 360–460 °C. After growth, annealing of the films was performed at 550 °C for 20 min under air ambient. Other growth parameters have been described elsewhere [27].

The crystal structures of ZnO thin films were examined by X-ray diffraction (XRD) using a Bede D1 system with Cu Kα radiation ($\lambda = 0.1541$ nm). The electrical properties were measured by Hall analysis in the van der Pauw configuration at room temperature by using a magnetic field of 5 kG and a current automatically set by a Hall system (BIO-RAD HL5500PC). The transmission through the film was investigated in the wavelength range from 300 to 600 nm by a Varian Cary-300 spectrophotometer. Photoluminescence (PL) spectra were obtained from 80 to 300 K by using a RAMALOG6 spectrometer with an excitation wavelength of 325 nm. The depth profile of the films was measured with secondary ion mass spectroscopy (SIMS, IMS 6F, CAMECA, Courberoie, France).

3. Results and discussion

3.1. Electrical properties

The electrical properties of ZnO films grown at different temperatures were measured, and the results are listed in Table 1 and Fig. 1, respectively. The films deposited at the substrate temperatures in the range of 360–420 °C showed p-type conduction. The resistivity is high (>100 Ω cm) at low temperatures and continuously decreases with the increase of substrate temperature. The p-type ZnO thin film grown at 420 °C has the lowest resistivity of 11.3 Ω cm and the highest hole concentration of 8.84×10^{18} cm^{-3}. When the substrate temperature increases to 440 °C, the carrier type flips from p-type to n-type. These observations may be understood as follows:

Table 1
Electrical properties of as-grown ZnO thin films prepared at different substrate temperatures (T_s)

S. no.	T_s (°C)	Resistivity (Ω cm)	Hall mobility (cm^2/Vs)	Carrier concentration (cm^{-3})	Type
1	360	6440	2.15	4.50×10^{14}	p
2	380	1470	1.26	3.38×10^{15}	p
3	400	226	0.704	3.92×10^{16}	p
4	420	11.3	0.0623	8.84×10^{18}	p
5	440	122	0.211	2.42×10^{17}	n
6	460	1.17	0.0875	6.11×10^{19}	n

(a) When the substrate temperature is low, it is difficult for the acceptor (P_{Zn}–$2V_{Zn}$, or V_{Zn}) to diffuse to an appropriate lattice site due to a low energy. So, the amount of the acceptors doped into ZnO thin films is small, inducing a low hole density and high resistivity.

(b) When the substrate temperature is higher than 420 °C, the concentration of native defects such as oxygen vacancies (V_O) or Zn interstitials (Zn_i) was more than that of active acceptors. Hence, n-type conduction was observed.

(c) Only at an appropriate temperature could low resistivity p-type ZnO thin films with high hole concentration be achieved. It is 420 °C in this work.

Therefore, substrate temperature is crucial to prepare low-resistivity p-type ZnO film.

Fig. 2 exhibits the SIMS profiles of the as-grown p-type ZnO thin film (sample 1). The film thickness is about 500 nm. It is clear from the phosphorus depth concentration profile that phosphorus was incorporated homogeneously, as intended. Meanwhile, hydrogen (H) is present in the film. There appears to be a large P and H segregation at the surface and the substrate/film interface, with the indication that SIMS measurements sometimes are subject to artifacts at surfaces and interfaces.

Hydrogen, which is present in the Zn growth precursor, could easily be incorporated into ZnO during its growth. Hydrogen is known to be amphoteric in most semiconductor, but it is always a shallow donor in ZnO and can passivate acceptors [2,28]. For phosphorus-doped ZnO, it was reported that activation of acceptors occurred by a thermal treatment [29]. Table 2 shows that all the films in our work exhibited p-type conduction after annealing as expected, and the

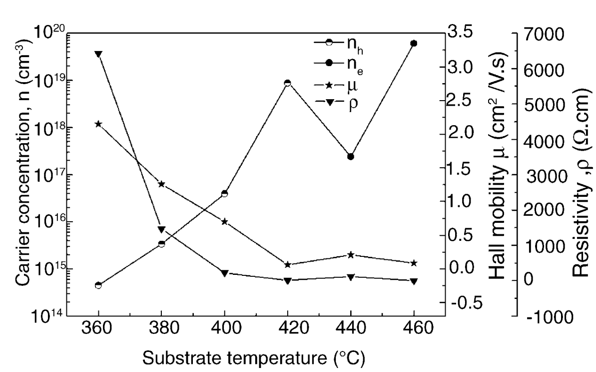

Fig. 1. Effect of substrate temperature on conduction type, carrier concentration, Hall mobility, and resistivity of ZnO thin films.