



Physical characteristics and photoluminescence properties of phosphorous-implanted ZnO thin films

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Abstract

ZnO films were implanted with phosphorus in the range from 5×10^{12} to 5×10^{15} cm⁻². Effect of phosphorus concentration on structural characteristics and photoelectric behavior of phosphorus-implanted ZnO films under different atmosphere and annealing treatment was investigated. It has been demonstrated that below solubility (1.5×10^{18} ions/cm³), the defect formation will be dominated by annealing atmosphere and more defects can be formed in oxygen ambient than in nitrogen atmosphere as revealed from PL spectra. However, excess phosphorus doping, above solubility (1.5×10^{18} ions/cm³), will induce the formation of the phosphide compounds in ZnO films and seriously deteriorate the crystallinity and optical property of the films. However, a high-resistive but not p-type ZnO film is obtained by phosphorus doping.

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1. Introduction

ZnO is a wide bandgap semiconductor, which has many optoelectronic applications such as laser diodes (LDs), light emission diodes (LEDs), invisible field effect transistors, and phosphorescent display [1,2]. It has been recognized to grow high-quality both p- and n-type ZnO thin films for the development of ZnO-based optoelectronic devices. However, p-type ZnO is very difficult to develop because of problems such as self-compensating process on doping and low solubility of the dopants [3]. Recently, several research groups proposed the formation of p-type ZnO by

various dopants and doping method [4,5]. Joesph et al. have demonstrated that p-type ZnO films can be fabricated by co-doping Ga and N into ZnO. Moreover, Kim et al. mentioned that p-type ZnO can be also developed by phosphorus doping via thermal activation process [6]. Even though it was reported that p-type ZnO has been developed, no detailed studies were made to investigate the effect of phosphorus doping on the structural change and photoluminescence properties of ZnO films. Therefore, in this work, the effect of various phosphorus concentrations and different annealing conditions on structure and photoluminescence properties of phosphorus-implanted ZnO films will be focused and discussed.

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2. Experimental

The ZnO thin films (~ 150 nm) were deposited on 4 in. diameter Si substrates by rf magnetron sputtering, using 99.99% ZnO as a target at a substrate temperature of 50°C , rf power of 50 W, sputtering pressure of 10 mTorr. The phosphorus ions with the fluence ranging from 5×10^{12} to 5×10^{15} cm^{-2} were implanted into the as-grown ZnO films. After ion implantation, the specimens were annealed at 850 and 1000°C for 20 min in pure oxygen and nitrogen atmospheres. The crystal structure was determined by X-ray diffractometer using Cu K α radiation. Photoluminescence measurement was performed by the excitation from 325 nm He–Cd laser at room temperature. The depth profile of the implanted ions was measured by secondary ion mass spectrometry (CAMECA IMS-SF). The surface and cross-sectional morphologies of the ZnO:P films was analyzed by scanning electron microscopy (FE-SEM, S-4100) and transmission electron microscopy (TEM Philips TECNAI 20). The electrical properties of the doped ZnO films were investigated by van der Pauw method room-temperature Hall measurements with non-sintered indium contacts and magnetic field of 0.315 T.

3. Results and discussion

Fig. 1 shows the XRD patterns of the P-implanted (fluence of 5×10^{12} , 1×10^{14} , and 5×10^{15} cm^{-2}) and non-implanted ZnO thin films annealed at 850°C in nitrogen atmospheres. With an increase of phosphorus concentration, the (002)-peak intensity decreased obviously and a weak diffraction peak was observed at the fluence of 5×10^{15} cm^{-2} for the P-implanted ZnO films annealed at 850°C in nitrogen. Similar behavior was also observed in the case of oxygen atmosphere. It was believed that the phenomenon is strongly dependent on the solubility limit of the implanted phosphorus in ZnO films. In addition, the (002) diffraction peak of the ZnO films was shifted towards the direction of smaller 2θ angle with the increase of fluence from 5×10^{12} to 5×10^{15} cm^{-2} . According to Bragg Law, the shift toward smaller 2θ direction indicates an increase of the lattice constant that was considered due to the

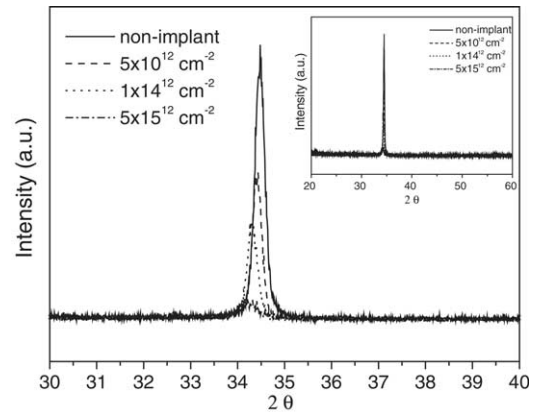


Fig. 1. XRD patterns of ZnO films implanted with different phosphorus fluences and annealed at 850°C in nitrogen.

incorporation of the phosphorus into ZnO matrix to form antisite P_{Zn} or phosphide (PO_4^-) compound. Fig. 2 shows the depth profile of phosphorus-implanted ZnO films with various fluences. As it

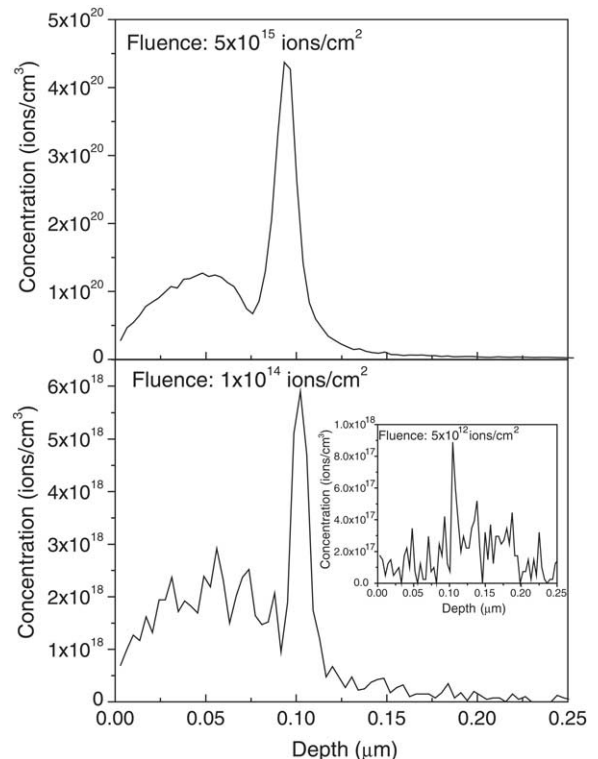


Fig. 2. SIMS depth profile of ZnO films implanted with different phosphorus fluences after annealing at 850°C in nitrogen atmospheres.

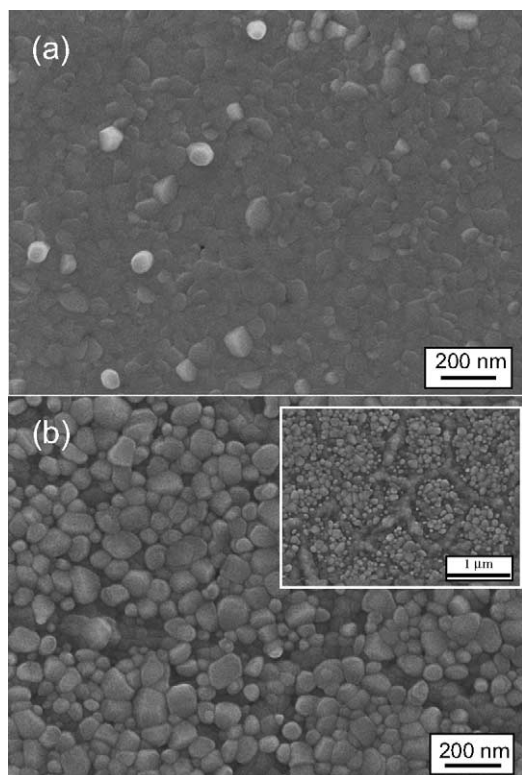


Fig. 3. SEM images of ZnO films doped with phosphorus at fluences of (a) 5×10^{12} and (b) 5×10^{15} ions/cm² and then annealed at 850 °C in nitrogen atmosphere.

can be seen, the secondary ion counts of phosphorus abruptly increase near the side of Si substrate regions. It was believed due to the original implanted phosphorus and incomplete diffusion in annealing process. This concentration corresponds to the solubility [7] of phosphorus in ZnO film that is determined as 2.5×10^{17} , 1.5×10^{18} , and 8.5×10^{19} ions/cm³ for the fluence of 5×10^{12} , 1×10^{14} , and 5×10^{15} ions/cm², respectively.

Fig. 3 shows the SEM images of ZnO films doped with phosphorus and then annealed at 850 °C in nitrogen atmosphere. As shown in Fig. 3(a), both ZnO films with non-implanted and implanted with 5×10^{12} ions/cm² exhibit similar surface morphology (r.m.s.: ~ 2.5 nm). Above that concentration, i.e. 5×10^{15} ions/cm², Fig. 3(b) illustrates that several ridge regions are formed in ZnO films (r.m.s.: ~ 5.4 nm). It was postulated that the formation of

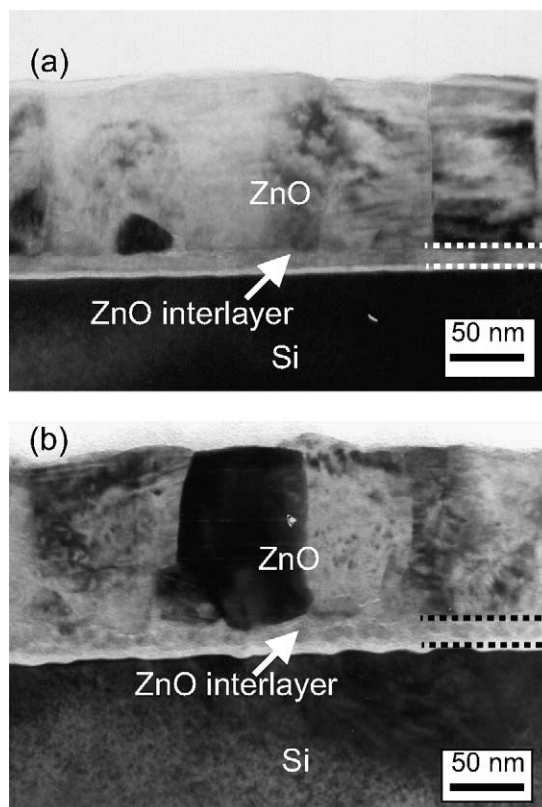


Fig. 4. Cross-sectional TEM images of ZnO films annealed at 850 °C in nitrogen atmosphere: (a) without phosphorus-implanted; (b) with phosphorus-implanted (fluence: 1×10^{14} ions/cm²).

the glass-like ridge structure may be related to the excess doping of phosphorus.

In order to investigate the phosphorus doping effect on the crystalline ZnO films, TEM analysis were performed. As shown in Fig. 4 for ZnO films annealed at 850 °C in nitrogen atmosphere, it was found that the cross-sectional microstructure was clearly divided into two regions: crystalline (columnar shape) and interlayer (flat-belt) structure. The interlayer could be considered as a buffer layer to reduce the stress due to lattice mismatch between ZnO and Si. However, for ZnO films with 1×10^{14} ions/cm² implanted, several small clusters were observed in the ZnO interlayer in Fig. 4(b) as marked with arrows. According to energy-dispersive spectrometry (EDS) measurement, those clusters were primarily composed of phosphorus, zinc and oxygen elements that may be related to the formation of glass-like ridge structure.

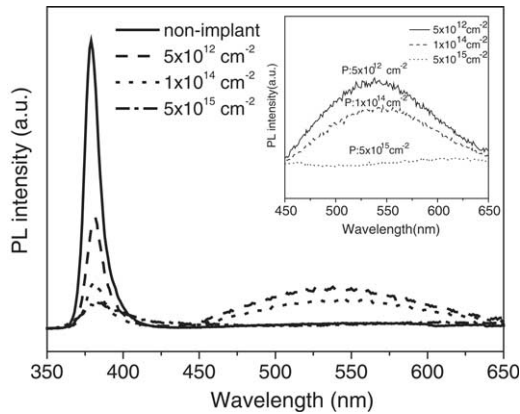


Fig. 5. Dependence of fluence conditions on room-temperature PL spectra for the phosphorus-implanted ZnO films annealed at 850 °C in nitrogen atmospheres. The inset is the deep-level emission of ZnO films implanted with various fluences of phosphorus.

Fig. 5 shows the room-temperature PL spectra of non-implanted and phosphorus-implanted ZnO films annealed at 850 °C in nitrogen atmosphere. The PL behavior for deep-level emission of ZnO films implanted with various fluences of phosphorus is also illustrated in the inset of Fig. 5 for comparison. The inset is the deep-level emission of ZnO films implanted with various fluences. It was observed that the peak intensity of the UV emission varies with the concentration of fluence. A very stronger UV peak (378 nm) and a relatively low deep-level emission (545 nm) were obtained for the non-implanted sample. However, as the ZnO films were implanted with different phosphorus fluences and annealed in nitrogen atmosphere, the UV emission peak of the ZnO films becomes weaker and presents slightly red shift as compared to the non-implanted one. This PL result along with the XRD analysis and surface morphology implies that there should be a solubility limit for phosphorus incorporated into ZnO films. If the implanted concentration is close to the solubility limit, both crystal structure and NBE emission would be strongly influenced and become poor.

On the other hand, as the phosphorus-implanted ZnO films were annealed in O₂ atmosphere (not shown here), the UV peak intensity was remarkably decreased compared to that annealed in N₂ atmosphere. In addition, with increasing phosphorus-implanted concentration up to 1×10^{14} fluence, a

weaker UV peak accompanied with a stronger deep-level emission around 545 nm was detected in O₂ atmosphere than that in N₂ atmosphere. It implies that more defects were probably induced in ZnO film annealed in oxygen atmosphere than that annealed in nitrogen atmosphere. Therefore, according to above discussion, it was believed that the property deterioration in the phosphorus-implanted ZnO films is correlated closely with the formation of defects and some glassy phase (MPO₄⁻) as evidenced from Fig. 4(b) of TEM.

In addition, the resistivity and carrier type of non-implanted and phosphorus-implanted ZnO films were further investigated by Hall measurement. The non-implanted ZnO film has the resistivity of 52 Ω cm and exhibits n-type ($-1.65 \times 10^{16} \text{ cm}^{-3}$) characteristics. However, with phosphorus-implanted fluence of $5 \times 10^{12} \text{ ions/cm}^{-2}$, the resistivity of phosphorus-doping ZnO films increases up to 256 Ω cm but the carrier concentration approaches to $1.65 \times 10^{15} \text{ cm}^{-3}$. Thus, the conversion of carrier type was never observed that is probably attributed to the formation of phosphide even though the phosphorus element was successfully incorporated into ZnO films.

4. Conclusion

As evidenced from TEM results, the implanted phosphorus in ZnO films tends to react with zinc and oxygen elements to form the clusters and this would induce defects as revealed from PL spectra. Furthermore, it has been demonstrated that below solubility ($1.5 \times 10^{18} \text{ ions/cm}^3$), the defect formation is mainly dominated by annealing atmosphere. Above that, both the crystalline quality and optical property will be deteriorated due to the formation of phosphide compounds. Therefore, in this condition, high resistive but not p-type ZnO film is obtained by phosphorus doping.

Acknowledgements

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