Electrical and Optical Properties of p-type ZnO:P Fabricated by Ampoule-tube Vapor-state Diffusion

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ZnO has intensively attracted interest for the next generation of short wavelength LEDs and semiconductor lasers. However, for the development and application of the devices based on this material, the fabrication of p-type ZnO thin films is pivotal. Generally, the process of preparation of ZnO is unavoidably accompanied by the natural donor ions such as interstitial Zn ions and oxygen vacancy ions that show n-type electrical property and make fabrication of p-type ZnO to be a hard problem. On this study, to realize stable high-quality p-type ZnO thin films, the undoped ZnO thin films were diffused with P in vapor state. The ZnO:P thin films showed high-quality p-type properties electrically and optically.

Keywords : ZnO thin films, RF sputtering, Ampoule-tube, Diffusion

1. INTRODUCTION

ZnO is II-VI compound semiconductor that is direct transition type. It not only has wide band gap of about 3.37 eV at room temperature but also possesses similar structural and optical properties as GaN, which is widely used in LEDs and LDs of current short wavelengths fields, thus has been receiving enormous attention as materials for optical devices[1]. Especially, the exciton binding energy of ZnO is 60 meV, which is about 2.5 times higher than that of GaN, thus optical devices with high efficiency can be expected if ZnO optical device is materialized[2,3].

In general, ZnO displays n-type conductive properties due to the existence of natural donor ion such as interstitial Zn ion (Zn_i^{2+}) or oxygen vacancy ion (V_O^{2+}). High quality ZnO bulks which can be used as base materials to be doped are available and n-type ZnO thin films[4,5] with high electron concentration are easily achieved experimentally which are essential for making p-n junctions of LEDs. Nevertheless, it is hard to fabricate p-type ZnO thin films which are also imperative for p-n junctions of LEDs. To get p-type ZnO thin films, many methods and dopant species have been used[6-10].

To realize ZnO LED, requisite p-type ZnO thin films were fabrication. First Undoped ZnO films were grown on substrates by an RF sputtering system. Then the grown films were diffused with P by ampoule tube method for the conversion of films to p-type. The diffused ZnO:P thin films were confirmed to be with high quality p-type conductivity properties ifn electrical and optical analyses.

2. EXPERIMENTAL

In this study, the undoped ZnO thin film used in the diffusion of P was deposited in the thickness of about 2.1 μm using ZnO 5N target as the RF sputtering method. The substrate used in the depositing was n-type $GaAs_{0.6}P_{0.4}$/GaP 2-inch wafer. As for the deposit conditions, base pressure and work pressure were set at 2.2×10^{-6} Torr and 5.2 mTorr respectively and nitrogen and oxygen were set at 17 sccm and 3 sccm respectively as ambient gases. RF sputtering conditions for undoped ZnO thin film deposit are summarized in Table 1.

The undoped ZnO film/$GaAs_{0.6}P_{0.4}$/GaP wafer deposited by RF sputtering was inserted into the ampoule with 3.5 g of P powder whose purity was 5N. In previous study[11],

Table 1. RF Sputtering conditions to deposit undoped ZnO thin film.

Parameters	Process conditions
Substrate	n-type GaAsP/GaP
Target	ZnO 5 N
Base pressure	2.2×10^{-6} Torr
Work pressure	5.2 mTorr
RF Power	360 W
Pre-sputtering time	5 min
Deposition time	2 hr
Substrate temperature	300 °C
Target distance	178 mm

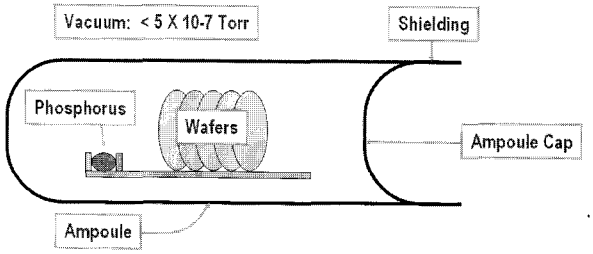
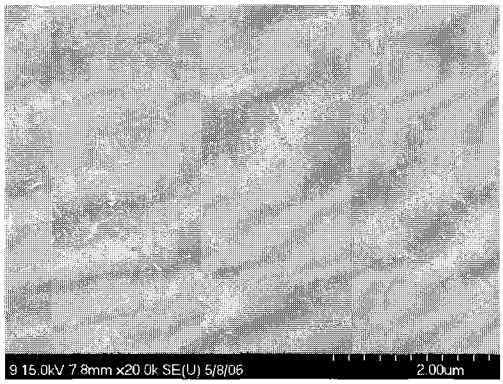


Fig. 1. Constitution of ampoule to diffusion P into undoped ZnO thin film.

diffusion sources were Zn_3P_2 and $ZnAs_2$ and P and As (arsenic) as well as zinc were diffused into undoped ZnO thin films. To diffuse the vapor-state P, the ampoule was sealed using extra pure oxygen and hydrogen gases while maintaining the vacuum within the ampoule below 5×10^{-7} Torr. Figure 1 shows the constitution of wafer, diffusion source and ampoule prepared for the diffusion. The sealed ampoule shown in Fig. 1 was diffused for 3 hr at 630 °C.

SEM (Scanning Electron Microscopy) was used for the analysis on the thickness and microstructure of undoped ZnO thin film acquired from RF sputtering and undoped ZnO thin film from diffusion process. HR-XRD (High Resolution XRD) carried out the changes in crystal quality resulting from the diffusion conditions and the Hall effect measurement for the analysis of carrier's behavior was measured at room temperature using HL5500PC system of van der Pauw method. The ohmic contacts for electrical measurement were made of indium at four corners of square sample which were about 5 mm × 5 mm. Moreover, the optical properties of doped ZnO thin film were accomplished through PL (Photoluminescence) measurement at 30 K and the elemental behavior of diffused P was analyzed by SIMS (Secondary Ion Mass Spectroscopy) with ZnO:P thin film diffused at 630 °C.

(a)



(b)

Fig. 2. Microstructures of (a) undoped ZnO thin film and (b) doped ZnO:P thin film diffused in ampoule-tube at 630 °C for 3 hr.

3. RESULTS AND DISCUSSION

Figure 2 is the SEM analysis on the surfaces of undoped ZnO thin film that was sputtered without diffusion process and ZnO:P thin films diffused in ampoule tube at 630 °C for 3 hr. Figure 2(a) indicated that long shaped big grain and small grain coexisted in undoped ZnO thin film. Diffused ZnO:P had a different surface from undoped ZnO thin film. In previous study, ZnO thin film diffused at 700 °C had not only thermal decomposition and evaporation but also re-crystallization due to the very high diffusion temperature[11]. However, in this study the thickness of ZnO films remained unchanged in thermal diffusion process at 630 °C and the microstructure was thought to be re-crystallized without thermal decomposition and evaporation.

Figure 3 shows the XRD patterns of undoped ZnO thin film and doped ZnO:P thin films diffused at 630 °C for 3 hr. All of the ZnO thin films showed a typical (0002) ZnO peak of about 34.4 °. Compared to the undoped ZnO thin film, the intensity was remarkably increased and the FWHM (Full-Width Half-Maximum) was decreased for (0002) peak of doped ZnO:P diffused

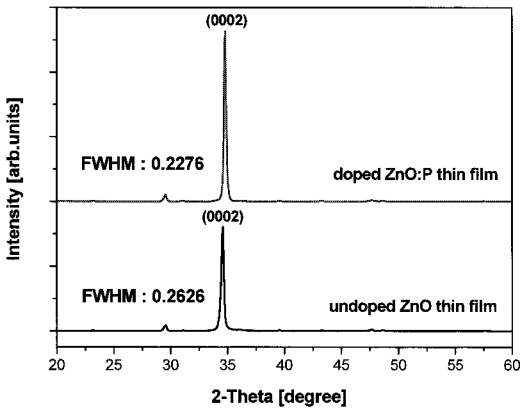


Fig. 3. XRD patterns of undoped ZnO thin film and doped ZnO:P thin films diffused at 630 °C for 3 hr.

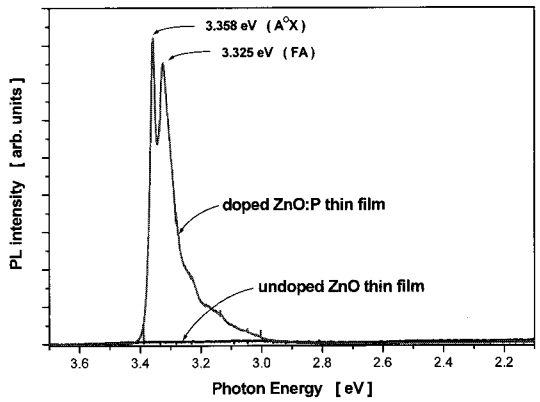


Fig. 4. PL spectra measured at 30 K for undoped ZnO thin film and doped ZnO:P thin films diffused at 630 °C for 3 hr.

Table 2. Results of Hall effect measurements for doped ZnO:P thin film diffused at 630 °C for 3 hr.

Diffusion Temp. [°C]	Resistivity (Ω cm)	Mobility (cm^2/V s)	Carrier Concentration (cm^{-3})	Type
630	6.45×10^{-3}	532	1.52×10^{18}	P

at 630 °C. This means that ZnO thin films were re-crystallized by diffusion temperature of 630 °C during diffusion process, which was reported that the crystallinity of films is affected by post-annealing[11].

The undoped ZnO thin film without diffusion process had too high of resistivity that it deviated from the Hall effect measurement range. Such condition seemed to have resulted from the shortage of majority carriers that could contribute to the electrical conductivity in pure ZnO thin films and the absence of process that activates such carriers. Table 2 shows the results of Hall effect measured at doped ZnO:P diffused at 630 °C for 3 hr. The electrical property of the doped ZnO:P thin film diffused at 630 °C for 3 hr showed p-type conductivity. The carrier concentration of our ZnO:P thin film were about $1.52\times10^{18}/cm^3$, which is clearly higher than the previous recorded level (about $4\times10^{17}/cm^3$)[3], and resistivity showed a very low value of 6.45×10^{-3} Ωcm in this study where as showed 2 ~ 13 Ωcm in other previous studies[12,13]. Also, the mobility of hole was a high value of 532 cm^2/Vs. The phenomenon is ezplained that after diffusion process P instituted O site in undoped ZnO thin films and the P ion acted as accepter ion.

Figure 4 shows the PL spectra measured at 30 K to analyze optical property for undoped ZnO and doped ZnO:P thin films. As shown in Fig. 4, PL intensity for undoped ZnO thin films was so small that any peak wasn't appeared in the range from 3.7 to 2.1 eV.

However, doped ZnO:P thin films showed two peaks which were located at 3.358 and 3.325 eV. Ryu et al. were reported that the peak located at 3.359 and 3.325 eV is identified as arising from acceptor-bound excitons (A^OX), and recombination between free electrons and acceptor holes respectively[12]. Therefore, we are considering that our doped ZnO:P thin films fabricated by ampoule-tube vapor-state diffusion indicate p-type property because the peaks of 3.58 eV and 3.325 respectively are A^OX and FA. Also, we are thinking that diffusion temperature affected the crystality of ZnO thin films because the microstructures were changed at SEM analysis and PL peaks appeared after diffusion process.

SIMS measurements were performed to help determining the response for p-type doping behavior on P in ZnO thin films. Figure 5 shows the results of SIMS analysis of ZnO:P thin film diffused at 630 °C for 3 hrs. Ion sputtering time, up to 1,600 seconds, belongs to ZnO thin film area whose thickness is about 2.1 μm. P shows Gaussian Distribution Form as sputtering time goes up to 250 seconds. 250-second is about 0.33 μm deep and this means P has been diffused that deep. The distribution of Zn and O for this deep is higher than the 250-second area

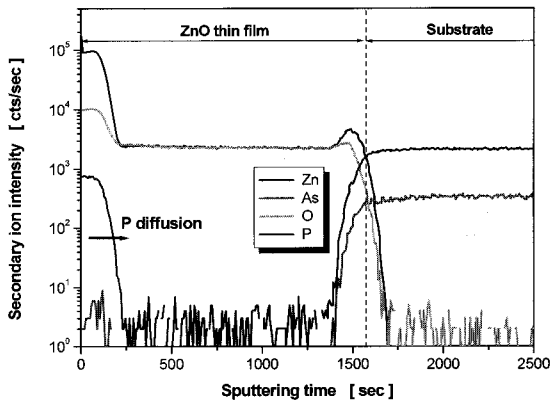


Fig. 5. SIMS results of the doped ZnO:P thin films diffused at 630 °C for 3 hr.

which P is not distributed. The reason would be the change of sputtering amount of diffused ZnO film of P for steady energy of ion sputtering.

4. CONCLUSION

In this study, P was diffused into the undoped ZnO thin films using the ampoule-tube method for the production of p-type ZnO thin films. Undoped ZnO thin films was deposited on 2-inch wafer of n-type $GaAs_{0.6}P_{0.4}$/GaP by RF sputtering system and its thickness is about 2.1 μm. After diffusion process, we confirmed that the crystality of ZnO thin film was changed on the analyses using by XRD, SEM, PL and SIMS. Especially, the doped ZnO:P thin film diffused at 630 °C for 3 hr had good p-type conductivity whose carrier concentration was above $10^{18}/cm^3$ and resistivity was below 10^{-2} Ωcm. Also, the doped ZnO:P thin film showed strong peaks which were located at 3.358 and 3.325 eV which are respectively A^OX and FA at PL analysis. In SIMS Analysis, P was detected until about 0.3μm of ZnO film, which means P has been diffused to ZnO film.

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