The influence of Ar/O2 gas on phosphorus-doped ZnO (ZnO:P) thin films deposited by radio frequency magnetron sputtering was studied. As the partial pressure of O2 increased in the Ar/O2 sputtering gas, the structure of ZnO:P changed from nanorods to a smooth thin film. The electron concentration of the thin film was also decreased due to the reduction in oxygen vacancies that act as donors. Photoluminescence spectra of ZnO:P thin films also showed a reduction in the intensity of the deep level emission peaks, due to the reduction in native defects related to the oxygen vacancies as the O2 partial pressure was increased. The ZnO:P thin films grown under an Ar/O2 gas ratio of 1:3 showed p-type characteristics after a rapid thermal annealing (RTA) activation process. The p-type ZnO:P showed a resistivity of 0.05 Ω cm, a mobility of 4.19 cm²/V s, with a hole concentration of 1.7 × 10¹⁴ cm⁻³.

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ZnO is a very attractive II-VI wide-bandgap semiconductor with a direct bandgap of 3.37 eV and a hexagonal wurtzite structure. ZnO has great potential for use in short-wavelength devices, such as ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes (LDs) because it has certain advantages over GaN which include a large exciton binding energy of 60 meV, the availability of a large ZnO substrate, and relatively low material costs. However, it is very difficult to control the conductivity of ZnO thin films, especially p-type ZnO films which are very essential in the manufacture of ZnO-based devices. There are several reasons for the difficulty in obtaining p-type ZnO, for example, self-compensation by a large background electron concentration, the low solubility of dopants, and deep acceptor levels. The difficulty in achieving p-type ZnO layer is the most significant obstacle for realizing ZnO-based optoelectronic devices. Considerable efforts have been made to date to obtain p-type ZnO films. Although their preparation is not straightforward, there are successful reports on the preparation of ZnO ultraviolet light-emitting diodes (LEDs) by growing a p-type ZnO layer. Kim et al. recently reported that phosphorus-doped p-type ZnO (p-type ZnO:P) thin films can be grown reproducibly on an Al2O3(0001) substrate by radio frequency (rf) magnetron sputtering using phosphorus oxide as a p-type dopant, followed by a rapid thermal annealing (RTA). They reported that phosphorus can be used as a p-type dopant and the post-thermal annealing of ZnO:P is essential for obtaining p-type ZnO:P. In this study, we report an investigation of the influence of the Ar/O2 sputtering gas ratio on the properties of ZnO:P thin films to give p-type ZnO:P, because it is well known that the Ar/O2 sputtering ratio has considerable influence on the structural, electrical, and optical properties of deposited films.

**Experimental**

An undoped ZnO film with a thickness of 1 μm was used as a buffer layer for the growth of a ZnO:P epilayer on an Al2O3(0001) substrate by rf magnetron sputtering. The ZnO:P thin films were grown at a substrate temperature of 700°C on the undoped ZnO buffer layer using a 2 wt % P₂O₅ doped ZnO target. The plasma source was operated at 30 W of rf power and the working pressure in the growth chamber was 1 mTorr. The mixture of Ar and O2 sputtering gas was varied from pure Ar to pure O2 during the growth of the ZnO:P films, in order to examine the effect of sputtering gas on the properties of the film. The RTA process under a nitrogen ambient at 900°C for 1 min was employed to convert the as-grown n-type ZnO:P films with a low carrier concentration into p-type ZnO:P films. Hall-effect measurements were carried out in the van der Pauw configuration using a commercial system (BIO-RAD HL5500PC). A scanning electron microscope (SEM) was used to observe the surface morphologies and cross-sectional structures of the thin films. The optical properties of the films were examined by photoluminescence (PL) spectroscopy using a He-Cd laser (λ = 325 nm) as an excitation source.

**Results and Discussion**

Figure 1 shows cross-sectional SEM images of ZnO:P thin films grown using various ratios of Ar/O2 gas ranging from pure Ar to pure O2. They clearly show that film structure and surface morphol-

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Figure 1. SEM images of ZnO:P thin films grown under various Ar/O2 gas ratios: (a) pure Ar; (b) Ar/O2 = 3/1; (c) Ar/O2 = 1/1; (d) Ar/O2 = 1/3; (e) pure O2.
ogy are significantly dependent on the Ar/O_2 sputtering gas ratio. As shown in Fig. 1a, a ZnO:P thin film grown in a pure Ar plasma has a honeycomb-shaped nanostructure with a highly preferred c-axis orientation. When the O_2 content of the sputtering gas was increased, the ZnO:P layer with honeycomb-shaped tube structure (Fig. 1a) changed to a film with a pine-tree-shaped structure (Fig. 1b) and these structure became more dense as shown in Fig. 1c. When the O_2 content in the sputtering gas was further increased, the ZnO:P thin film showed a smooth and flat film structure as shown in Fig. 1d and e. These results are consistent with a previous study reporting that the nucleation of ZnO depends on the amount of active oxygen on the ZnO buffer layer. When the growth ambient is changed from Ar rich to O_2 rich, the density of the nucleus and lateral growth rate are increased, resulting in smooth, dense ZnO:P thin films. Therefore, it would be expected that structural defects or native defects would also be reduced in ZnO:P films grown under O_2-rich conditions.

The electrical properties of thin films, grown at different Ar/O_2 gas ratios and annealed at 900°C for 1 min under a N_2 ambient, are shown in Fig. 2. Figure 2 shows that the resistivity of the films is increased with increasing partial pressure of O_2. The increase in resistivity with increasing O_2 content in the growth ambient can be attributed to a reduction in native defects such as oxygen vacancies which act as donors and show n-type characteristics in ZnO films. Figure 2 also shows that the electron concentration of n-type ZnO:P film is decreased with increasing O_2 content in the Ar/O_2 sputtering gas. Thin films grown at an Ar/O_2 gas ratio of 1/3, which showed a good surface morphology and semi-insulating properties, showed a p-type conductivity after a thermal activation process at 900°C under a N_2 ambient. In-Zn metal alloy was used as a contact material for Hall-effect measurements and annealed for 1 min in an Ar ambient. The sample size was 5 x 5 mm. The p-type ZnO:P showed a resistivity of 0.05 Ω cm, a mobility of 4.19 cm²/V s, and a hole concentration of 1.7 x 10¹⁸ cm⁻³. However, ZnO:P films grown under an Ar/O_2 gas ratio from pure Ar to a ratio of 1/1 showed n-type characteristics, even after a post-thermal activation, due to the large number of native defects in the films. ZnO:P films grown under a pure O_2 ambient also showed an n-type conductivity after the annealing process. This n-type conductivity can be attributed to the formation of complex defects involving a split-interstitial-O complex that acts as double donors because the excess oxygen atoms create oxygen interstitials and O_2-induced defects, which can compensate for the hole carriers generated by phosphorus dopants.

To study the influence of the ratio of sputtering gas on deep level PL emission, we also investigated the PL properties of ZnO:P thin films. Figure 3 shows room-temperature PL spectra of the deep level emission for ZnO:P deposited using various Ar/O_2 gas ratios. The ZnO:P films grown under a pure Ar ambient did not show any deep level emission due to the poor crystal quality of the resulting ZnO:P film. ZnO:P films deposited under an Ar/O_2 gas ratio of 3/1, however, showed a very strong deep level emission peak. The deep level emission gradually decreased when the O_2 content of the sputtering
gas was increased, as shown in Fig. 3. Deep level emission is known to be related to a variety of defects such as donor defect Zn interstitial (Zn$_i$). O vacancies (V$_{O2}$), acceptor defect Zn vacancies (V$_{Zn}$), and antisite defect O substitutional Zn (O$_{Zn}$) (Ref. 24) due to the poor stoichiometry of ZnO. The decrease in deep level emission from p-type ZnO:P grown in an Ar/O$_2$ plasma with increasing O$_2$ content can be attributed to a reduction in oxygen vacancies and (or) zinc interstitials. Figure 4 shows the secondary ion mass spectroscopy (SIMS) profiles of P atoms before and after an RTA process. The SIMS profiles of P atoms show that the P atoms are uniformly distributed in the ZnO film and the concentrations of P atoms are not changed before and after an RTA process.

Conclusion

The structures and electrical properties of ZnO:P thin films were greatly dependent on the Ar/O$_2$ sputtering gas ratio. The nanorod structures of ZnO:P films became more dense and the electron density decreased with increasing O$_2$ content in the sputtering gas. The n-type ZnO:P thin films grown at an Ar/O$_2$ gas ratio of 1/3 showed a smooth surface and the electrical type of the films was converted to p-type after a thermal activation process. The deep level PL emission was decreased with increasing O$_2$ content of the sputtering gas, indicating that the origin of the deep level emission is defects that are closely related to oxygen vacancies in the ZnO:P film.

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