Effect of annealing temperature on the electrical characteristics of P-doped ZnO thin films

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Abstract

In order to realize effective p-type doping in ZnO thin films, ZnO films were deposited on P-doped Si layers by RF-magnetron sputter deposition technique and annealed at various temperatures. The result indicated that ZnO film annealed at 700℃ showed p-type conduction with a high carrier concentration in the order of 10^{19} cm^{-3}.

1. Introduction

ZnO has attracted enormous attention because of its direct wide band gap (~3.37 eV) and large exciton binding energy (~60 meV) which is about 2.5 times higher than that of GaN at room temperature, and the availability of large area ZnO substrates, etc.[1]. Moreover, ZnO is very attractive for the application of active matrix future display. For realizing such ZnO-based devices, a crucial step is needed the fabrication of high quality, stable and reproducible *p*-type ZnO thin film. However, it is difficult to obtain *p*-type ZnO due to self-compensation from native donor defects such as zinc interstitials (Zn_i) and oxygen vacancies (V_O) or hydrogen as unintentional extrinsic donor [2,3].

Various dopants (N, P, As, and Sb) and fabrication techniques have been studied to obtain *p*-type ZnO. Some research groups have fabricated *p*-type ZnO film by co-doping method where N and group-Ⅲ elements such as Ga and Al are used as dopants to fabricate *p*-type ZnO[4]. Although theoretical calculations indicated that the acceptor level of N is deep in the band gap[5], N has been used as a popular *p*-type dopant among group-Ⅴ elements due to the smallest atomic size and lowest p-orbital energy[6]. However, there is still high demand for improvements on reproducibility and stability of electrical properties of doped ZnO.

In this work, ZnO film was deposited on P-doped Si layer and annealed to realize effective *p*-type doping by having P diffuse into ZnO layer. The electrical properties of P-doped ZnO films were investigated with respect to the annealing temperature.

2. Experimental

P-doped Si film was deposited on 100nm SiO_2-coated Si substrates using atmospheric pressure chemical vapor deposition (APCVD) technique. The P concentration in the APCVD-Si layer was approximately $3x10^{20}$atoms/cm^3. Then, 150 nm–thick ZnO thin films were deposited on P-doped Si layer at 200℃ using RF- magnetron sputter deposition technique. For the deposition process, undoped ZnO target (99.99%) was used. The samples were annealed at temperatures ranging from 600 to 900℃ in an oxygen ambient for 1hr on a resistive heater. The pressure of annealing chamber was 70mtorr. The crystallinity of ZnO thin films were analyzed by x-ray diffraction (XRD). Hall measurements were carried out to estimate the carrier type, concentration, and mobility in the van der Pauw configuration at room temperature. Secondary-ion mass spectrometry (SIMS) was used to verify the distribution of P and the ZnO film thickness before and after annealing.

3. Results and discussion

Figure 1 showed the XRD data of ZnO films before and after annealing process. The XRD data showed that as-deposited ZnO thin films had the strong preferential orientation of (002) plane and the relative intensity of ZnO (002) diffraction peak was decreased with increasing annealing temperature. This result implicates that the P content in ZnO layer increased, and the crystallinity of ZnO was degraded with increasing temperature. The reduction of ZnO layer with annealing temperature could be one of the reasons for the decrease of XRD peak, as shown in Fig. 2.

Figure 1 also showed that ZnO (002) diffraction peak was considerably decreased by annealing at 800℃, and disappeared after annealing at 900℃. The disappearance of ZnO diffraction peak can be explained by the reduction of ZnO layer and the intermixing of ZnO and underlying Si layer, which is supported by the SIMS depth profile of ZnO sample annealed at 900℃ (the data not shown here).

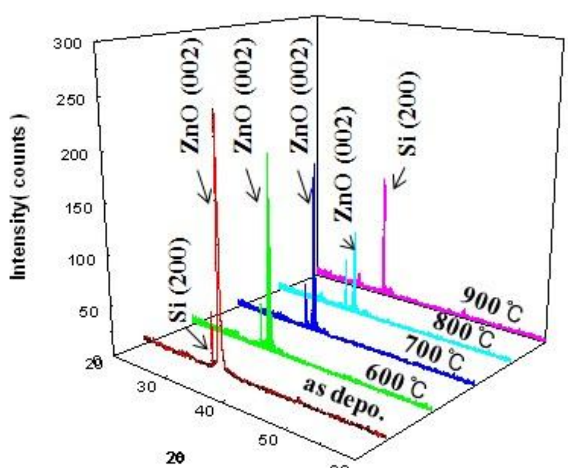

Figure 1. XRD data of ZnO thin films as-deposited and annealed at 600, 700, 800, and 900℃

The depth profiles of the elements in as-deposited ZnO film and 700 ℃- and 800 ℃-annealed ZnO films were shown in Fig. 2. The SIMS profile of 700 ℃-annealed sample illustrates that P and Si diffused out up to half the ZnO thickness. It is evident in the SIMS profiles that P had been diffused into ZnO layer

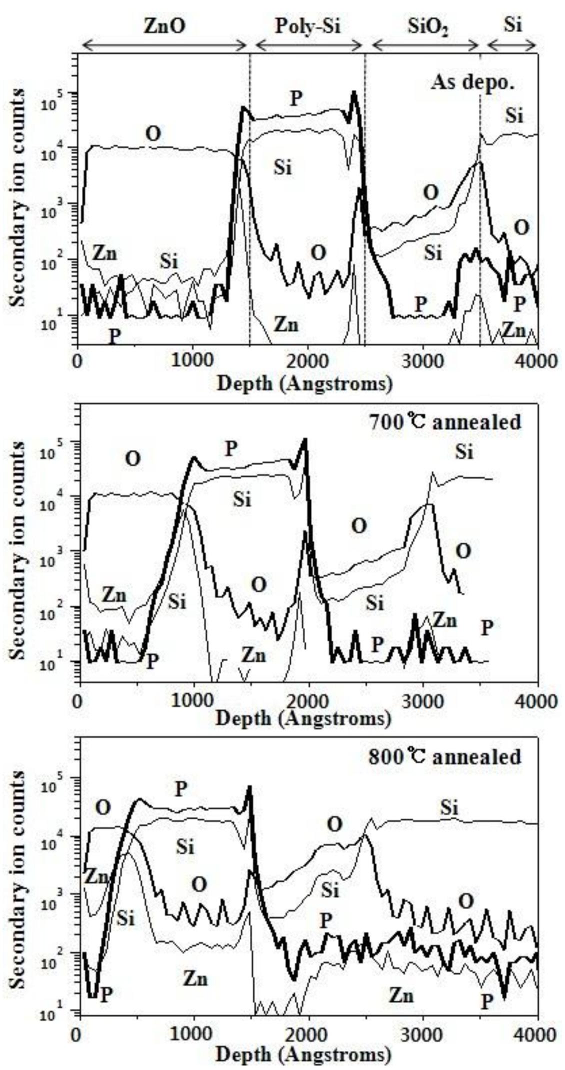

Figure 2. SIMS depth profile of as-deposited and 700℃- and 800℃-annealed ZnO films on P-doped Si/SiO_2/Si substrate

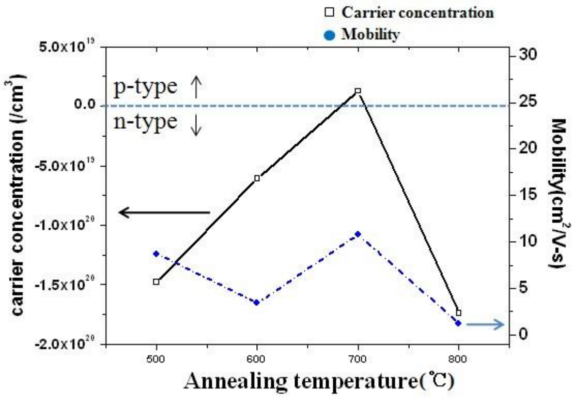

Figure 3. Dependence of carrier concentration and carrier mobility on annealing temperature

by post-annealing process. However, the annealing at a temperature of 700℃ or higher results in a severe reduction of ZnO layer. The thickness of ZnO layer was considerably reduced with increasing the annealing temperature. Furthermore, the SIMS profile of 800℃-annealed sample showed the intermixing of ZnO and underlying layer.

The reduction of the ZnO film thickness might be explained by the following reasons. One reason is possibly the densification of ZnO film. The secondary ion counts of Zn atoms in 700 ℃-annealed ZnO film are higher than those of as-deposited ZnO film. Another reason is the intermixing of ZnO and P-doped Si layer. In addition, the evaporation of Zn dissociated from O at a temperature much higher than 450℃ can not be excluded under the annealing conditions used in this work (oxygen ambient, 70mtorr). These results suggest that the post annealing of ZnO layer is to be done at a temperature of 700℃ or lower.

Figure 3 showed the dependence of carrier concentration and carrier mobility on the annealing temperature. As shown in this figure, the film annealed at 700℃ showed *p*-type conductivity with a hole concentration of 1.28×10^{19} cm^{-3} and a mobility of 10.8 cm^2/Vs.

4. Summary

In the present work, ZnO thin films were deposited on P-doped Si layers by RF magnetron sputter deposition technique. Then the samples were annealed at temperatures ranging from 600 to 900℃ to realize *p*-type doping by having P diffuse into ZnO layer. The ZnO layer annealed at 700℃ revealed *p*-type conduction. The *p*-type ZnO film revealed a hole concentration of 1.28×10^{19} cm^{-3} and a hole mobility of 10.8 cm^2/Vs. The results indicated that P-doping into ZnO layer from P-doped under-layer is effective to obtain *p*-type ZnO film. Further study is required to clarify the mechanism of *p*-type conduction in P-doped ZnO.

5. References

[1]. S. J. Pearton, D. P. Norton, K. Ip, and Y. W. Heo, J. Vac. Sci. Technol. B 22, 932 (2004).

[2]. S. B. Zhang, S. H. Wei, and A. Zunger, Phys. Rev. B 63, 075205 (2001).

[3]. C. G. Van de Walle, Phys. Rev. Lett. 85, 1012 (2000).

[4]. T. Yamamoto and H. Yoshida, Jpn. J. Appl. Phys., Part 2 38, L166 (1999) and references therein.

[5]. C. H. Park, S. B. Zhang, S.-H. Wei, Phys. Rev. B 66, 073202 (2002).

[6]. A. V. Singh, R. M. Mehra, A. Wakahara, A. Yoshida, J. Appl. Phys., 93, 396 (2002).