Characteristics of ZnO/Si prepared by Zn\textsubscript{3}P\textsubscript{2} diffusion

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Abstract

p-ZnO thin film formation on Si substrate is investigated using rf magnetron sputtering followed by Zn\textsubscript{3}P\textsubscript{2} diffusion process. In order to form p-ZnO thin film, n-ZnO thin film is initially deposited on Si substrate using rf magnetron sputtering. Then, Zn\textsubscript{3}P\textsubscript{2} source diffusion by closed ampoule technique is performed on ZnO/Si test structure. The electrical and optical characteristics of the ZnO thin films are investigated and the effect of Zn\textsubscript{3}P\textsubscript{2} diffusion on the properties of ZnO thin films are examined. From the analysis results, it is verified that p-type ZnO thin film on p-Si substrate is formed by dopants diffusion.

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1. Introduction

ZnO is a wide band gap semiconductor, which has many optoelectronic applications, such as light emitting diodes, invisible field effect transistors, Schottky diodes and laser diodes [1–4]. Recently, the researches of ZnO thin film are concentrated on fabricating p-type ZnO since ZnO is an n-type material as grown and it is difficult to obtain p-type ZnO layer. Hatanaka and co-workers reported I–V characteristics of the p–n junction formed by excimer laser doping technique [5]. Joseph et al. presented highly resistive p-ZnO thin films obtained by co-doping method of N and Ga [6].

In this paper, the fabrication of p-ZnO thin film on Si substrate is investigated using rf magnetron sputtering followed by Zn\textsubscript{3}P\textsubscript{2} diffusion process. The crystalline, optical and electrical properties of ZnO thin films have been characterized by the X-ray diffraction (XRD) method, the photoluminescence (PL) measurement, the secondary ion mass spectrometry (SIMS) measurement and the current–voltage (I–V) characteristics. XRD results clearly exhibited ZnO (0 0 0 2) and PL showed ZnO thin film has high intensity in visible wavelength range after the diffusion. The I–V characteristic curve proved to be the p–n junction characteristics. From the results, the utilization and capability of p-type ZnO thin films can be verified as the material for light emitting devices.
2. Test structure fabrication and measurements

ZnO thin films were deposited on Si (1 1 1) substrates by rf magnetron sputtering. A 4 in. diameter, 5N-purity ZnO target was used to deposit the films. The silicon substrates were cleaned with a standard cleaning procedure and were etched in chemical solution with HF:D.I. water = 1:30 for 10 s. Prior to deposition, the target was pre-sputtered for 10 min in order to remove any contamination. Deposition of ZnO thin films was carried at the condition of rf power of 150 W and Ar ambient gas. The working pressure was 10 mTorr and the substrate temperature was fixed at room temperature. After deposition using rf magnetron sputtering, the Zn diffusion processes were performed by sealed ampoule technique using diffusion furnace maintaining temperature at about 495 °C in flowing N\textsubscript{2} gases with varying the process conditions. The ampoule in a quartz boat was loaded in the pre-heating zone and waited for 10 min before diffusions. After the diffusion process was performed for a certain amount of time, the ampoule was pulled out of diffusion furnace and cooled rapidly by dropping it into water. Then, Zn diffusion profiles were measured with SIMS using a Cameca-IMS 4F instrument; 5.5 keV Cs\textsuperscript{+} primary ions were used. The CsZn\textsuperscript{+} ions were detected to monitor the secondary ion counts with respect to the sputtering time.

In order to investigate the optical properties of ZnO films, the PL measurements were performed using an Ar-ion laser which had an excitation wavelength of 351 nm and a power of 100 mW. All spectra were taken at room temperature by using a grating spectrometer and a photomultiplier tube (PMT) detector. In addition, the XRD method was used to characterize the structural properties of ZnO thin films. The $I$–$V$ characteristics are measured by Keithley 236 source measure unit (SMU) and probe station to verify electrical properties of ZnO thin films.

3. Results and discussion

Fig. 1 exhibits the PL spectra of ZnO thin films after Zn\textsubscript{3}P\textsubscript{2} diffusion for 30 and 60 min. It is observed that a band edge emission peak of ZnO material, appearing at about 370 nm, is significantly decreased comparing with the defect peak, appearing at about 430 nm. It is believed that the defect states originate from donor-to-acceptor pair (DAP) transitions. It is reported that O vacancies and Zn interstitials are located at 0.20 eV below conduction band [7–9].

![Fig. 1. Photoluminescence spectra of ZnO/Si structure after Zn\textsubscript{3}P\textsubscript{2} diffusion: (a) diffusion time, 30 min; (b) diffusion time, 60 min.](image1)

![Fig. 2. The 20 XRD scan after Zn\textsubscript{3}P\textsubscript{2} diffusion: (a) diffusion time, 30 min; (b) diffusion time, 60 min.](image2)
The DAP transition is considered by the effect of Zn interstitials and P dopants, which corresponds to about 400 meV in dopant energy level, verified by PL measurement in Fig. 1. It is explained that diffusion process can activate more dopants by dopant diffusion and annealing effect. In addition, 60 min diffusion can incorporate more dopants in the film compared with 30 min diffusion indicating that the time of diffusion process is critical for the dopant diffusion and the improvement of optical properties of ZnO thin films.

In order to examine the crystallinity of ZnO thin films, XRD analysis is performed and the results are shown in Fig. 2. From the plot of XRD 20 scan, it is observed that ZnO (0 0 0 2) and Si (1 1 1) diffraction peaks were appeared at about 34 and 63°.
respectively. The XRD intensity of 60 min diffused ZnO thin film is almost three times stronger than that of 30 min diffused one indicating that the 60 min diffused ZnO thin film shows better crystalline quality compared with 30 min diffused one. In addition, 60 min diffused ZnO film exhibits the ZnO (1011) diffraction due to the long diffusion process.

Fig. 3 exhibits the secondary ion counts versus the sputtering time for ZnO thin film before and after Zn3P2 diffusion. In Fig. 3a, the secondary ion counts of P are detected at the order of 10 before Zn3P2 diffusion whereas those of Zn and O are estimated at the order of 10^4. After Zn3P2 diffusion in ZnO thin film, it is observed that the secondary ion counts of P are increased at the order of 10^2 and those of Zn are decreased at the order of 10^2 where those of O remains at the order of 10^4–10^5 indicating that P dopants diffused into ZnO thin film replace the Zn interstitials whereas the Zn diffused out from ZnO thin film to Si substrate. It is also observed that the secondary ion counts of P abruptly increase in Si substrate region as shown in Fig. 3b indicating that Si substrate is doped with phosphor and changed its electrical characteristic from p-type to n-type.

In order to verify the electrical properties of ZnO/Si structure, the I–V characteristics for ZnO/Si structure were investigated and shown in Figs. 4 and 5. Fig. 4 shows the I–V characteristics between n-type ZnO thin film and p-type Si substrate after sputtering followed by annealing at 500 °C for 1 h. It is observed that ZnO thin film has n-type characteristic as grown. Fig. 5a shows that the I–V characteristics after sputtering followed by 60 min Zn3P2 diffusion. It is obtained that the expected I–V characteristic of ZnO/Si structure is reversed which indicated that n-type ZnO thin film is changed to p-type and p-type Si substrate is changed to n-type. To verify the results, additional diffusion experiment was performed using p-type Si substrate sample. After 25 min Zn3P2 diffusion on p-Si substrate, the I–V characteristics were measured and plotted in Fig. 5b. The I–V characteristics shown in Fig. 5b explain the physics of Zn3P2 diffusion on Si substrate. The I–V characteristics for p-Si substrate after Zn3P2 diffusion represent the p–n junction characteristics. This fact implies that p-Si substrate is changed to n-type by Zn3P2 diffusion.

Based on the SIMS results and I–V measurement results, it is verified that n-ZnO thin film is changed to p-ZnO by Zn3P2 diffusion. The secondary ion...
counts of Zn significantly decrease and are comparable to the secondary ion counts of P and it is explained that P dopants are penetrated into the site of Zn interstitials in the ZnO thin film indicating that the ZnO thin film changed from n-type to p-type characteristic. The fabrication process from n-ZnO/p-Si structure to p-ZnO/n-Si is schematically summarized in Fig. 6.

Fig. 5. The $I$–$V$ characteristics of ZnO/Si substrate after the sputtering followed by Zn$_3$P$_2$ diffusion: (a) p-ZnO vs. n-Si; (b) n-Si vs. p-Si.
4. Conclusion

Characteristics of ZnO/Si structures fabricated by rf magnetron sputtering followed by Zn$_3$P$_2$ diffusion have been investigated. From PL measurement, indigo blue visible spectrum, which includes a peak at about 430 nm associated with donor-to-acceptor pair transitions, was observed. It is concluded that p-ZnO thin film was obtained from SIMS analysis and $I$–$V$ characteristics of ZnO/Si structure. Thus, this ZnO/Si structure can be applicable for the fabrication of LEDs.

References