Fabrication of low resistivity p-type ZnO thin films by implanting N\textsuperscript{+} ions

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Abstract. Transparent and conductive oxide films have been extensively researched in recent years for the breadth of their optically technological applications. The growth of high quality n-type ZnO films can be easily realized. One of the big challenges is the difficulty of achieving low resistivity p-type conduction for ZnO thin films. In this work, we prepared the p-type ZnO films by r.f. reactive magnetron sputtering following by N\textsuperscript{+} ions implantation and subsequent annealing in a vacuum to achieve low resistivity conductive thin films. The structural, electrical and optical properties were examined by X-ray diffraction, UV-visible, and Hall-effect measurements. The experimental results show that the films have good transmittance in the visible spectrum. The optical energy gap increases with increasing the amount of N\textsuperscript{+} ions implanted. The maximum value of the optical energy gap gained in this study is 3.30 eV when the implanted amount of N\textsuperscript{+} ions was 5\times10\textsuperscript{17} cm\textsuperscript{-2}. The film still kept p-type conduction without any obvious degradation of electric conduction. The resistivity of p-type ZnO obtained in this study varied from 1.05 \times10\textsuperscript{-1} to 9.80 \times10\textsuperscript{-1} ohm-cm.

1. Introduction

ZnO is regarded as a promising material for short wavelength light emitting diodes and laser diodes due to its direct wide band gap 3.37 eV and large exciton binding energy 60 meV at room temperature [1-3]. Interest in the study of ZnO for device applications has been heightened by recent reports on the growing of p-type ZnO layers and fabrication of p – n junction for solar cells [4-6]. One of the big challenges is the difficulty in achieving low resistivity p-type conduction for the ZnO film because of problems such as self-compensation, deep acceptor level, and low solubility of the acceptor dopants [7]. Recently, several techniques have been reported to prepare p-type ZnO films , such as the codoping of nitrogen and gallium by pulse laser deposition, nitrogen and aluminum by radio frequency sputtering [8-9]. Ion implantation is an attractive doping technique because it permits precise control of the dopant profile, and it is employed in the semiconductor industry as it is one of the most convenient techniques to realize pattern doping and device isolation. In this work, we study the...
properties of ZnO films prepared by r.f. reactive magnetron sputtering that were first implanted with N⁺ ions and subsequently annealed in an Ar atmosphere to achieve low resistivity p-type conductive thin films.

2. Experimental Details

The ZnO films were deposited on glass (Corning 1737F) substrate by an r.f. magnetron sputtering system with a base pressure of 1.33 Pa. Each substrate was ultrasonically cleaned in acetone and subsequently dried in flowing nitrogen gas before deposition. The target was material Zn (99.99% purity) and the diameter of the target was 76.2 mm. The sputtering was conducted in a mixture of oxygen and argon atmospheres with a target to substrate distance of 45 mm.

Before deposition, the chamber was pumped to an ultimate background of 10⁻⁵ torr and then a pre-sputtering process was followed for 10 minutes to clean the target surface and remove any possible contamination. The r.f. power was set in the 200 watts range, and the thickness of films was controlled by sputtering time at approximate 500nm. The implantation details of N⁺ ions by the vacuum ion beam device. The implantation parameters were as follows: Acceleration voltage: 25kV; Implanted ion energy: 30KeV; Dose of N⁺ ions density: 1~7 ×10¹⁷ ions/cm². After the implantation of N⁺ ions, the films were annealed in Ar at 300°C for 3hrs.

A conventional stylus surface roughness detector (Alpha-step 200) was used to measure the film thickness and change this value to be the growth rates divided by the sputtering time. The phases of the deposited films were studied by X-Ray diffractometer (XRD). The XRD patterns of the films were determined with a Shimadzu XD-1 diffractometer using monochromatic high intensity Cu α radiation (λ=1.5418Å), operating at 30kV with 20mA current, and a scanning speed of 3 degrees per minute. The optical transmittance measurements were performed with a UV spectrophotometer. The transmittance spectra as a function of wavelength in the range 350~850nm were performed. The electrical property of the films was measured by Hall effect measurements.

3. Results and Discussion

Fig.1 shows the XRD spectra for the ZnO films of implanted with various N⁺ dose density. The (0 0 2) preferred orientation can be clearly observed for all the deposited films. The result shows that the ZnO films have strong (002) preferred orientation. A sharp diffraction pattern of (002) is detected in thin films indicating that the films were well defined and preferentially c-axis oriented. After the implantation of N⁺ ions, the intensity of the (002) peak decreases. The second phase Zn₃N₂ peak doesn’t appear in ZnO thin films [10].The first significant observation was that the position of the (002) diffraction peak shifted to higher angles as nitrogen dose density increase. This because of the Zn-N bond legths is shorter than Zn-O bond lengths [11].This difference is relatively small, and it is concluded that compressive stress is the main reason for peak shifted to higher angles.

![Figure 1. XRD patterns for ZnO thin film densities implanted](image-url)
with various increasing dose.

The transmittance spectra as a function of wavelength in the range 350–850nm at different N⁺ dose densities are shown in Fig.2. All the ZnO films used in the experiment had a thickness of approximately 500nm. The transmittance decreases with the increasing dose density of N⁺ implantation. The decrease of transmittance is probably attributed to the light scattering induced by a large density of microstructure defects caused by ion implanted. In addition, a sharp absorption edge is observed around 380 nm for all the films, indicating a cut-off edge of pure ZnO phase. The average optical transmittance can be as high as 80% is detected in the visible spectrum for the films implanted with various N⁺ dose densities. In addition, it can be confirmed that with a N⁺ dose density of up to $3 \times 10^{17}$ cm⁻², the absorption edge shifts towards the shorter wavelength side indicating that the oxygen vacancies might be partly compensated by the implantation of N⁺ ions.

**Figure 2.** Visible optical transmittance for ZnO films of various N⁺ dose densities.

The optical gap (E_g) of the film can be obtained by plotting $\alpha^2$ vs. $\hbar v$ ($\alpha$ is absorption coefficient and $\hbar v$ is the photon energy) [12-13] and extrapolation of the straight-line portion of this plot to the energy axis, as shown in Fig.3. It is noticed that E_g increases with increasing r.f. power, and the value is within the 3.1–3.3 eV range. The result of shifting the E_g value of pure ZnO (~3.3eV) [14] is due to Burstein–Moss shift [15]. This could be explained as the variation of the carrier concentration with respect to the ion-implanted concentration and the increase of the ionized impurity scattering.

**Figure 3.** The absorption coefficient for ZnO films of various N⁺ dose densities.

The results of the Hall effect measurements are listed in Table 1. It can be seen that, as the dose density of the N⁺ ions increases, the resistivity of the zinc oxide film decreases and the conduction type changes from n-type to p-type. This indicates that the oxygen vacancies might be partly compensated by the implantation of N⁺ ions. At $7 \times 10^{17}$ ions/cm⁻² N⁺ dose densities, the carrier type...
again return to n-type conduction. When the N⁺ dose density too excess, the N acceptors are mainly compensated by O vacancies, resulting in increase resistivity and low hole concentrations. The lowest resistivity obtained is $1.05 \times 10^{-1}$ ohm-cm of p-type ZnO thin films during this study. To confirm the stability of the electrical property, the p-type ZnO films were tested again 30 days later. The film still kept the p-type conduction without any obvious degradation.

Table 1. The Hall effect measurements for ZnO films of various N⁺ dose densities.

| Dose density of N⁺ | Resistivity (Ω-cm) | Carrier concentration (cm⁻³) | Mobility (cm²/Vs) | Type |
|-------------------|--------------------|-----------------------------|------------------|------|
| Pure ZnO thin film | 2.78 $\times 10^{-03}$ | 7.12 $\times 10^{19}$ | 4.80 | N |
| 1$x10^{17}$ ions/cm² | 1.61 $\times 10^{-02}$ | 2.32 $\times 10^{18}$ | 2.69 | N |
| 3$x10^{17}$ ions/cm² | 1.05 $\times 10^{01}$ | 6.84 $\times 10^{19}$ | 1.11 | P |
| 5$x10^{17}$ ions/cm² | 9.80 $\times 10^{01}$ | 8.44 $\times 10^{19}$ | 0.87 | P |
| 7$x10^{17}$ ions/cm² | 7.24 $\times 10^{01}$ | 2.94 $\times 10^{19}$ | 2.29 | N |

4. Conclusions

We have deposited stable and low resistivity p-type ZnO films by implantation of N⁺ ions. The ZnO films obtained all exhibit (002) preferred orientation for implanted and non-implanted films. The average transmittance of most films in the visible region is above 80%, except for N⁺ ion implant dose densities higher than 5$x10^{17}$ ions/cm². After the implantation of N⁺ ions, the conduction type changes from n-type to p-type. The p-type ZnO films obtained show the lowest resistivity of $1.05 \times 10^{-1}$ Ω-cm with higher hole concentration of $6.84 \times 10^{19}$ cm⁻³.

Acknowledgments

The authors would like to thank the National Science Council of the ROC for its financial support under contracts no. NSC95-2221-E-150-097 and NSC95-2622-E-150-030-CC3

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