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Fabrication and characteristics of the low resistivity p-type ZnO thin films by nitrogen ion implantation

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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 in growing *p*-type ZnO layers and fabrication of *p* – *n* junction for solar cell[4-6].One of the big challenges is the difficult to achieve low resistivity *p*-type conduction for 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 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. Ion implantation employed in the semiconductor industry 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 were firstly implanted with N^+ ions and subsequently to annealing in Ar atmosphere to achieve low resistivity *p*-type conductive thin films.

The r.f. power was set in the 200 Watts range, the substrate temperature was maintained at 30-45 ℃, and the thickness of films was controlled by sputtering time at approximate 500nm. The implantation parameters are as follows: Acceleration voltage: 25kV; Implanted ion energy: 30KeV; Dose of N^+ ions density: 1~7 $\times 10^{17}$ ions/cm^2. After the implantation of N^+ ions, the films were annealed in Ar ambience at 300℃ for 2hr.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 degree per minute. The optical transmittance measurements were performed with UV spectrophotometer. The transmittance spectra as a function of wavelength in the range 350~850nm .The electrical property of the films was measured by Hall measurements.

2. 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 Zn_3N_2 peak haven'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.

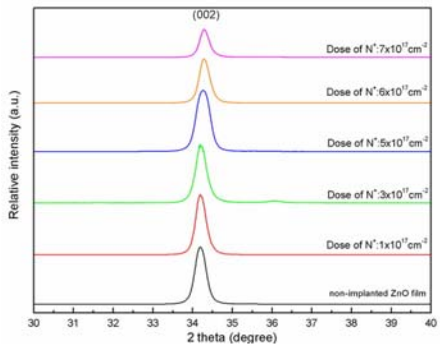

Fig.1. XRD patterns for ZnO thin film of implanted with various N^+ dose density.

The transmittance spectra as a function of wavelength in the range 350~850nm at different N^+ dose density are shown in Fig.2 All the ZnO film used in the experiment has a thickness of 500nm.The transmittance decreases with the increasing implantation of N^+ dose density. The decrease of transmittance is probably attributed to the light scattering induced by large density of defects and impurities. In addition, a sharp absorption edge is observed around 380 nm for all the films, indicating pure ZnO phase in the films. The average optical transmittance as high as 80% is detected in the visible spectrum for the films of implanted various N^+ dose density.

The optical gap(Eg)of the film can be obtained by plotting α^2 vs. hv (α is absorption coefficient and hv is the photon energy) [12-13]and speculation the straight-line portion of this plot to the energy axis as shown in Fig.3.It is noticed that Eg increases with increasing r.f. power and the value within 3.1~3.3 eV range. The result of shifting the Eg value of pure ZnO (~3.3eV) [14] is due to Burstein shift [15].The shift seen could be explained as the variation of the carrier mobility with respect to the dopant concentration and the increase of the ionized impurity scattering.

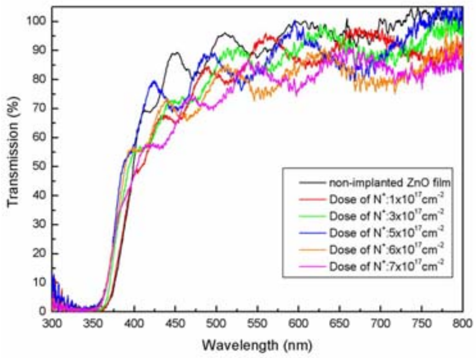

Fig.2. Visible optical transmittance for ZnO films of various the N^+ dose density.

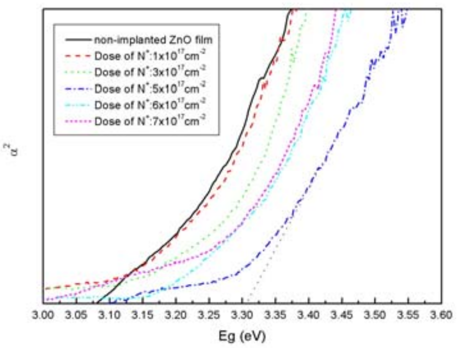

Fig.3. The absorption coefficient for ZnO films of various the N^+ dose density.

The results of the Hall effect measurements are listed in Table 1. It can be seen that, as the N^+ ions increases, the resistivity of zinc oxide film decreases and the conduction type changes from n-type to p-type. It indicates that the oxygen vocations might be partly compensated by the implantation of N^+ ions. The lowest resistivity obtained is 1.05×10^{-1} ohm-cm. To confirm the stability of the electrical property, the p-type ZnO films were tested again 30 days later. The film kept the p-type conduction without any obvious degradation. It indicates that the oxygen vocations might be partly compensated by the implantation of N^+ ions.

Table 1 The Hall effect measurements for ZnO films of various the N^+ dose density.

Dose density of N^+	Resistivity (Ωcm)	Carrier concentration (cm^{-3})	Mobility (cm^2/Vs)	Type
Pure ZnO thin film	2.78×10^{-03}	7.12×10^{19}	4.80	N
1 $x10^{17}$ ions/cm^{-2}	1.61×10^{-02}	2.32×10^{18}	2.69	N
3 $x10^{17}$ ions/cm^{-2}	1.05×10^{-01}	6.84×10^{19}	1.11	P
5 $x10^{17}$ ions/cm^{-2}	9.80×10^{-01}	8.44×10^{19}	0.87	P
6 $x10^{17}$ ions/cm^{-2}	2.13×10^{-01}	3.13×10^{19}	1.68	P
7 $x10^{17}$ ions/cm^{-2}	7.24×10^{-01}	2.94×10^{19}	2.29	N

3. Conclusions

We have deposited stable and low resistivity p-type ZnO films by ion implantation of N^+ ions. The obtained ZnO films exhibit (002) preferred orientation for implanted and non-implanted films. The average transmittance of the most films in the visible region can be above 80% except for the N^+ ion implant dose density higher than 5×10^{17} ions/cm^2.After the implantation of N^+ ions, the conduction type changes from n-type to p-type. The obtained p-type ZnO films shows a lower resistivity of 1.05×10^{-1} Ω-cm and higher hole concentration of 8.44×10^{19} cm^{-3}.

Acknowledgements

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