EFFECT OF DEPOSITION TEMPERATURE ON ELECTRICAL, OPTICAL AND STRUCTURAL PROPERTIES OF Ga-N CO-DOPED ZnO OXIDE THIN FILMS

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Received 30 April 2011; accepted 29 May 2011.

1. Introduction

Zinc oxide (ZnO) thin films doped with Al (AZO) and Ga (GZO) have been investigated as an alternative to indium tin oxide (ITO) for transparent, conducting electrodes in solar cells, liquid crystal displays (LCDs), and light emitting diodes (LEDs) due to their low resistivity ($\rho \sim 10^{-4}$ Ωcm) and high transmittance (> 85%) in the visible spectrum range [1]. The attractive electrical and optical properties have made ZnO a desirable material for an emerging transparent electronics/optoelectronics. Among the advantages of ZnO are low cost, abundant source material and eco-friendly nature. The ZnO semiconductor material has a direct band gap of ~ 3.3 eV and like other wide band gap semiconductors exhibits asymmetry doping. The lack of a good quality *p*-type that in conjunction with *n*-type can make a *p-n* junction has been the most significant hindrance to ZnO applicability for active devices fabrication. Many efforts on *p*-type doping of ZnO have focused on nitrogen doping and nitrogen-group III (Al, Ga) co-doping. As a result, *p*-type ZnO:N and ZnO:Al:N has been realised with the carrier concentrations of around 10^{13}-10^{19} cm^{-3} [2-5].

In this paper, we discuss the effect of deposition temperature of the substrate (T_S) on the electrical, optical and structural properties of gallium-nitrogen co-doped ZnO thin films (ZnO:Ga:N).

2. Experimental

ZnO:Ga:N films were deposited on Corning 7059 glass substrates using radio-frequency (rf) diode sputtering in Ar /N_2 sputtering gas (Ar, 99.999% purity and N_2, 99.999% purity). A ceramic target ZnO:Ga_2O_3 (98wt%:2wt%) was used. The rf power was 600 W for all depositions, the working pressure was 1.3 Pa and the deposition time was 30 min. The substrate temperature was a variable parameter ranging from room temperature (RT) to 300°C. The thickness of the films (23÷485 nm) was measured using a Dektak 150 instrument. The structure and film orientation were evaluated by X-ray diffraction (XRD, Model X'pert Pro using CuKα radiation, $\lambda = 0.154$ nm). The electrical parameters were measured using a Hall system and software at a room temperature. Transmittance was measured over the range of 190 - 1100 nm using a double beam spectrophotometer Specord 210.

3. Results and discussion

Variation in the substrate temperature had a profound effect on the deposition rate which decreases from 16 to 0.8 nm/min (Fig.1) as T_S increases from RT to 300°C, and to the film thickness. Since all other parameters of the sputtering process were maintained constant, reduction in the deposition rate and the film thickness could result from desorption of zinc from the film grown at an elevated T_S [6].

Hall-effect measurements showed that the substrate temperature has a strong impact on the electrical parameters, including type and range of conductivity. The films grown at 50 % N_2 at RT showed *p*-type behavior while all those grown at 200 and 300°C were *n*-type. The resistivity decreased with increasing of the substrate temperature (Fig. 1).

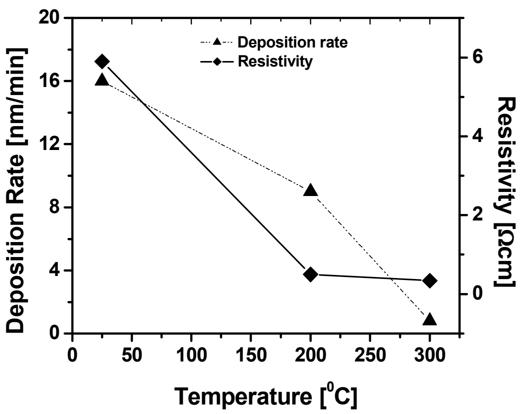

Fig. 1: *Dependence of deposition rate and resistivity on T_S for ZnO:Ga:N films deposited with 75 % N_2 in Ar/N_2 gas.*

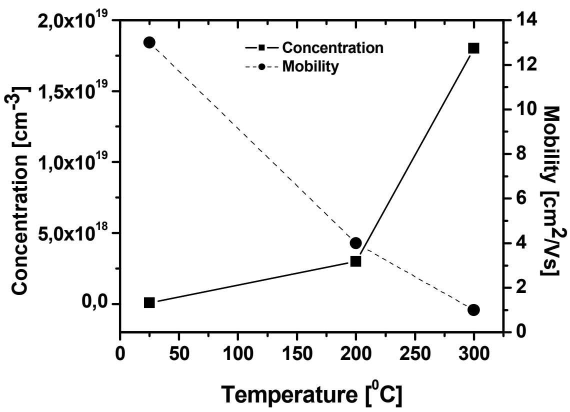

Fig. 2: *Dependence of carrier concentration and mobility on T_S for ZnO:Ga:N films deposited with 75 % N_2 in Ar/N_2 gas.*

Fig. 2 plots carrier concentration and mobility as a function of the substrate temperature.The lowest resistivity of 0.34 Ωcm at $T_S = 300°C$ resulted from the highest carrier concentration of $1.8x10^{19}$ cm^{-3} and a mobility of 1 cm^2/Vs.

Transmittance spectra are shown in Fig. 3. All ZnO:Ga:N films have an average transmittance $T > 72$ % (including the glass substrate) in the wavelength range of 390 - 1100 nm that is increasing with rise in T_S.

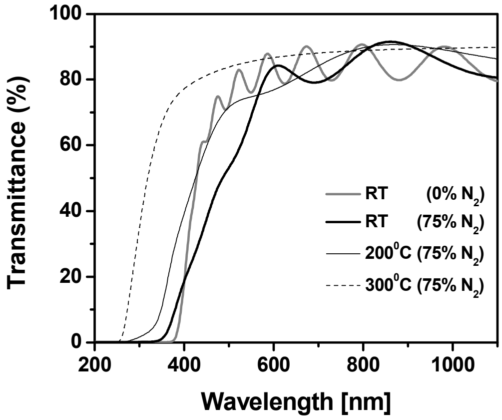

Fig. 3: *Optical transmittance spectra of ZnO:Ga (0% N_2) and ZnO:Ga:N (75% N_2) thin films deposited at T_S of RT, 200, 300°C.*

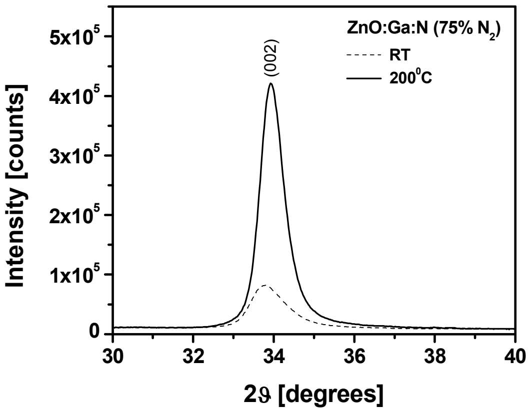

Fig. 4: *XRD patterns of ZnO:Ga:N thin films deposited at T_S of RT and 200°C with 75% N_2 in Ar/N_2 gas.*

The optical band edge shifts toward lower wavelengths with increasing temperature, which is consistent with rise in the carrier concentration. Absorption around the band edge and the yellow color of the film grown at RT (75 % N_2) have been ascribed to deep N-related states in the band gap of ZnO [5,7].

Fig. 4 shows XRD patterns of samples deposited at RT and 200°C. In both patterns can be seen only one diffraction line attributed to the (002) plane of wurtzite ZnO with a c- axis preferred orientation. The integrated intensity of this line increases with increasing temperature and the resistivity of this film (0.5 Ωcm) is reduced more than an order of magnitude. Asymmetry in the (002) diffraction line and its broadening toward higher diffraction angles results more likely from the incorporation of Ga and N atoms and formation of hexagonal and cubic gallium nitride phases.

4. Conclusions

ZnO:Ga:N films were deposited on glass substrates by rf diode sputtering at substrate temperatures varying from room temperature to 300°C. The experimental results revealed multiple effects of temperature on the film growth and its physical parameters. The deposition rate decreased from 16 to 0.8 nm/min with increasing T_S. XRD patterns reveal a strong expressed c-axis preferred orientation of the crystallites. The relationship structure – electrical – optical properties was found. The integrated intensity of the (002) diffraction line increased with the increasing growth temperature and the resistivity of this film (0.5 Ωcm) was reduced more than an order of magnitude. The highest carrier concentration of 1.8×10^{19} cm^{-3} was measured in the film with the highest average transmittance of 86 %. Shift of the optical band edge toward lower wavelengths corresponds to rise in the carrier concentration.

Acknowledgement

The work was supported by the CENTEM project, reg. no. CZ.1.05/2.1.00/03.0088 that is cofunded from the ERDF within the OP RDI programme of the Ministry of Education, Youth and Sports and within the project No. 1M06031, and Slovak VEGA projects 01/0220/09 and 1/0689/09.

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