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OPTICAL AND ELECTRICAL PROPERTIES OF Ga_2O_3-DOPED ZnO FILMS PREPARED BY R.F. SPUTTERING

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Optical and electrical properties of Ga_2O_3-doped ZnO films prepared by r.f. sputtering have been investigated as functions of preparation conditions and dopant concentration in an attempt to develop transparent films with low electrical resistivity and with good stability at higher temperatures. The electrical resistivity of the sputtered films depends strongly on the r.f. power density, the argon gas pressure, the Ga_2O_3 concentration and the thickness of the films when the thickness is less than about 2500 Å. The optical transparency depends on the thickness and dopant concentration and is almost independent of the sputtering conditions. Ga_2O_3-doped ZnO films become degenerate semiconductors when the carrier concentration exceeds about 10^{19} cm^{-3} and the optical band gap increases with increasing electron concentration owing to the increase in the Fermi level in the conduction band. Ga_2O_3-doped ZnO films 3000 Å thick with an optical transmission higher than 85% and with electrical resistivity lower than 10^{-3} Ω cm can be produced by sputtering a ZnO target containing 5 wt.% Ga_2O_3 with an r.f. power density of 0.84 W cm^{-2} and an argon gas pressure of 5 mTorr.

1. INTRODUCTION

Transparent oxide films with a large energy band gap and with a low electrical resistivity have attracted considerable interest in recent years, because of their potential use as transparent electrical contact in optoelectronic devices such as liquid-crystal displays and solar cells. Indium tin oxide (ITO) films are at present used as a transparent electrode for such devices. Although ITO films are widely used in optoelectronic devices fabricated at low temperatures, such as amorphous silicon solar cells, transparent films with good stability at high processing temperatures and with lower material costs are sought. For sintered CdS/CdTe heterojunction solar cells, gallium-doped CdS films[1] and chlorine-doped CdS[2] were used as the front contact as well as the window. Transparent oxide films with a wider band gap than CdS appear to have an advantage as the window layer of a heterojunction solar cell. Recently, fluorine-doped tin oxide and undoped zinc oxide thin films were successfully used as transparent electrodes in CdS/CdTe[3] and CdS/$InCuSe_2$[4] thin

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film solar cells respectively. Fabrication methods for these transparent oxides, however, are not reported. The properties of ZnO films doped with tin and aluminium have been reported[5,6], but no report is available for the properties of Ga_2O_3-doped ZnO film.

Therefore there is ample interest and motivation in investigating the effects of film preparation conditions on the properties of Ga_2O_3-doped ZnO films. In the present paper we report the results of an investigation of the electrical and optical properties of sputtered ZnO films as a function of the amount of Ga_2O_3 added to the ZnO target and sputtering conditions.

2. EXPERIMENTAL PROCEDURE

ZnO films with various gallium contents were deposited by sputtering method using an r.f. sputtering unit. A number of mixed powders consisting of ZnO powder with 99.999% purity and various amounts of Ga_2O_3 powder also with 99.999% purity were prepared to make sputtering targets. The mixed powders were pressed to obtain discs with a 126 mm diameter and a 4.2 mm thickness. The discs were sintered for 1 h in air in the temperature range from 800 to 1100 °C to form the target. The sintered density increased with increase in sintering temperature, but some warping occurred when the sintering temperature exceeded 950 °C. Thus disc specimens sintered at 900 °C were used as the target in present investigation. The films were deposited onto glass substrates (Corning 7059) placed parallel to the target surface without intentional heating. A pre-sputter etching of the target was carried out to obtain a target with a clean surface. The r.f. power density was varied from 0.42 to 2.10 W cm^{-2}, and the argon gas pressure was varied from 5 to 80 mTorr.

Ohmic contacts were provided by coating with In–Ag paste and annealing at 200 °C for 10 min in nitrogen. The electrical resistivity, carrier concentration and mobility were measured by the Van der Pauw method. The optical transmission spectra was measured in the wavelength range from 300 to 810 nm with a spectrophotometer (Varian Super Scan). Scanning electron microscopy (SEM), X-ray diffractometer and Auger electron spectroscopy (AES) were used to characterize the crystal structure, microstructure and uniformity of the films.

3. RESULTS AND DISCUSSION

Since the electrical resistivity of a very thin film depends on the thickness due to surface scattering, the resistivity of films which were prepared by sputtering from a ZnO target containing 5 wt.% Ga_2O_3 with an r.f. power density of 0.42 and 0.84 W cm^{-2} was measured as a function of thickness and the results are shown in Fig. 1. The resistivity increases sharply when the film thicknesses are less than 2500 Å. Minami *et al.*[6] also observed similar behaviour in Al_2O_3-doped ZnO films.

Figure 2 shows the dependence of the deposition rate and electrical resistivity of 5 wt.% Ga_2O_3-doped ZnO film on argon gas pressure. The resistivity shows a minimum value in the specimen that was sputtered with an argon gas pressure of 5 mTorr. This was true even after considering the thickness effect. The deposition

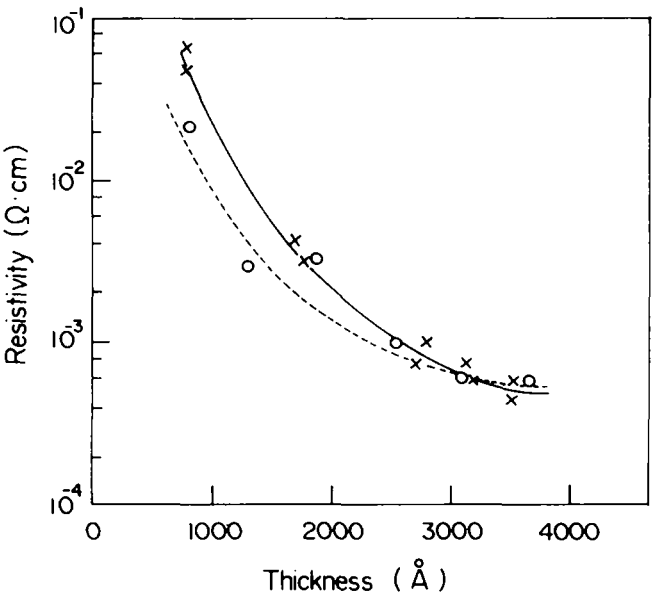

Fig. 1. Electrical resistivity as a function of thickness for Ga_2O_3-doped ZnO films sputtered with power densities of 0.42 W cm^{-2} (○) and 0.84 W cm^{-2} (×).

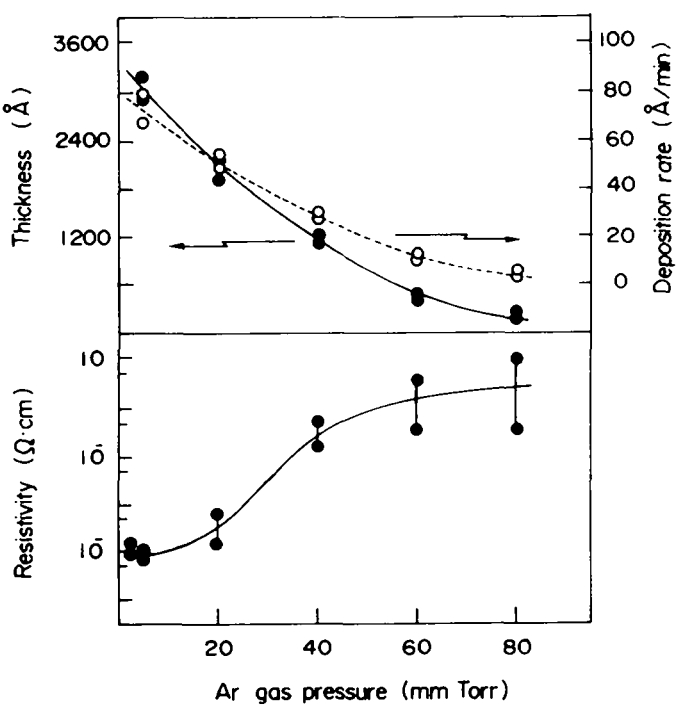

Fig. 2. Variations in the deposition rate and electrical resistivity of 5 wt.% Ga_2O_3-doped ZnO films with argon gas pressure.

rate and electrical resistivity of the sputter-deposited 5 wt.% Ga_2O_3-doped films as a function of r.f. power density are shown in Fig. 3. The deposition rate increases linearly with the r.f. power intensity. The electrical resistivity, however, again shows a minimum value at the power density of 0.84 W cm^{-2}. The increase in the resistivity with increasing power density is reported to be related to the increase in defects which were generated by fast growth rate and the energetic ion bombardment[7]. The increased value of the resistivity in the film deposited at an r.f. power density of 0.42 W cm^{-2} appears to be caused by surface scattering. The thickness of the Ga_2O_3- doped ZnO films are about 1500 Å and about 3000 Å for the specimens that were deposited with a power density of 0.42 W cm^{-2} and 0.84 W cm^{-2} respectively. The measured values of electron mobility were 2.6 $cm^2 V^{-1} s^{-1}$ and 7.0 $cm^2 V^{-1} s^{-1}$ while the electron concentration was independent of the film thickness.

The optical transmission spectra of the films with a thickness of about 3000 Å sputtered with an optimum power density of 0.84 W cm^2 and an argon gas pressure of 5 mTorr, for various amount of Ga_2O_3 content in the target are shown in Fig. 4. It can be seen that the band edges shift to short wavelengths as the Ga_2O_3 content increases from zero to 5 wt.% and then the changes are not so significant as the Ga_2O_3 content increases further. AES intensities were measured on Ga_2O_3-doped ZnO films sputtered with targets that contained 2, 5 and 10 wt.% Ga_2O_3. The zinc peak decreased and the gallium peak increased with increasing Ga_2O_3 content in the target. For a quantitative analysis, the relative Ga LMM Auger peak-to-peak

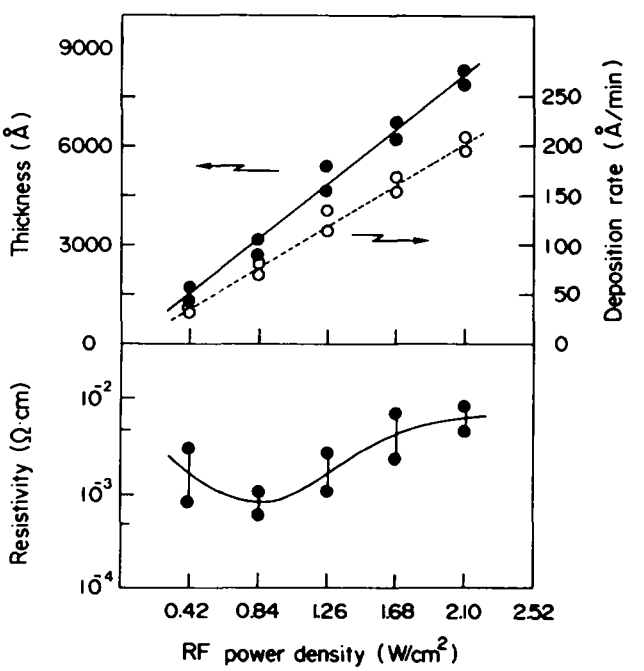

Fig. 3. Dependences of resistivity and deposition rate of 5 wt.% Ga_2O_3-doped ZnO films prepared at an argon gas pressure of 5 mTorr on sputtering power density.

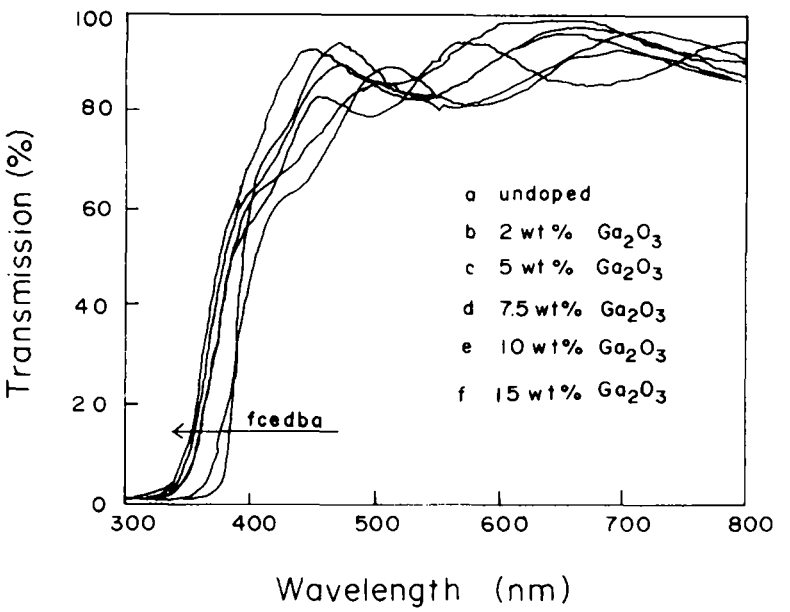

Fig. 4. Optical transmission spectra for films deposited by sputtering targets that contained various amounts of Ga_2O_3 at an r.f. power density of 0.84 W cm^{-2} and an argon gas pressure of 5 mTorr.

intensities were normalized to that for the specimen sputtered from the target that contained 2 wt.% Ga_2O_3, and the results are shown in Table I.

The normalized gallium peak-to-peak intensities of the films coincide very closely with the weight percentages of Ga_2O_3 in the targets, indicating that the composition of the sputter-deposited films is almost identical with that of the target. The depth profiles for zinc, oxygen and gallium showed that the composition of the film specimens was uniform in thickness direction.

The optical absorption coefficient near absorption edge is given by[8]

$$\alpha \approx (h\nu - E_g)^{1/2} \tag{1}$$

The value of the energy band gap determined by measuring optical transmission spectra and using eqn.(1) turned out to be 3.28 eV and 3.59 eV for undoped and 5 wt.% Ga_2O_3-doped films respectively.

TABLE I

Ga LMM AUGER ELECTRON-SPECTROSCOPY PEAK-TO-PEAK INTENSITIES OF Ga_2O_3-DOPED ZnO THIN FILMS

Amount of Ga_2O_3 in the target (wt.%)	*Amount of Ga in the target* (wt.%)	*Ga LMM Auger peak-to-peak intensity*	*Normalized peak-to-peak intensity*
2	1.86	12	1.86
5	4.65	30	4.65
10	8.48	57	8.84

Figure 5 shows the resistivity, electron concentration and Hall mobility of the films of Fig. 4. The resistivity decreases sharply with increasing Ga_2O_3 content up to 5 wt.% and then increases with further increase in the Ga_2O_3 content. The electron concentration of the undoped ZnO film is $7.5 \times 10^{17}\,cm^{-3}$ and increases with increasing Ga_2O_3 concentration up to 5 wt.% and then stays at about the same value of about $10^{21}\,cm^{-3}$ with further increase in the amount of Ga_2O_3. The electron mobility, on the contrary, decreases continuously with increasing amount of Ga_2O_3. The density N_c of states in the conduction band at room temperature was calculated, using the value of electron mass reported by Ziegler *et al.*[9], to be $4 \times 10^{18}\,cm^{-3}$. Thus the effect of the trap density at a grain boundary on the carrier concentration should be negligible for the Ga_2O_3-doped ZnO films since their electron concentrations are larger than $10^{20}\,cm^{-3}$ and the films are degenerate semiconductors.

No reports on the phase diagram of ZnO–Ga_2O_3 system and solubility of gallium in ZnO are available. If we assume that the gallium doping is substitutional, the solubility of gallium in ZnO at 200 °C, at which the electrode contacts were annealed, is of the order of $10^{21}\,cm^{-3}$ since the electron concentration of the 5 wt.% Ga_2O_3-doped film is about $10^{21}\,cm^{-3}$ and stays constant with further increase in Ga_2O_3 content. The 5 wt.% Ga_2O_3 in the ZnO target is equivalent to a gallium concentration of about $1.5 \times 10^{21}\,cm^{-3}$ in ZnO. If the above assumption is correct, then it implies the possibility of gallium segregation at a grain boundary when the Ga_2O_3 content exceeds about 5 wt.%. There was some evidence that a secondary phase existed in the specimen that contained more than 7.5 wt.% Ga_2O_3 in the X-ray diffraction patterns.

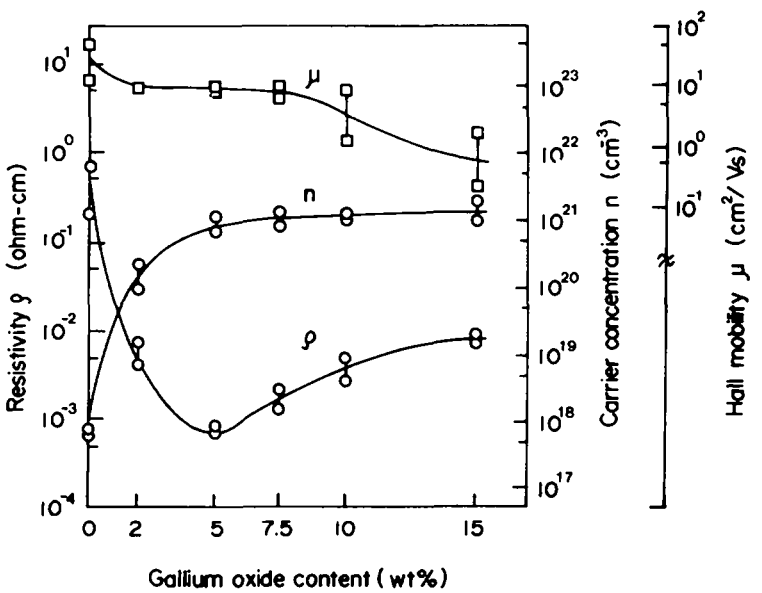

Fig. 5. Dependences of electrical resistivity, electron concentration and Hall mobility on Ga_2O_3 content in the target of the films of Fig. 4.

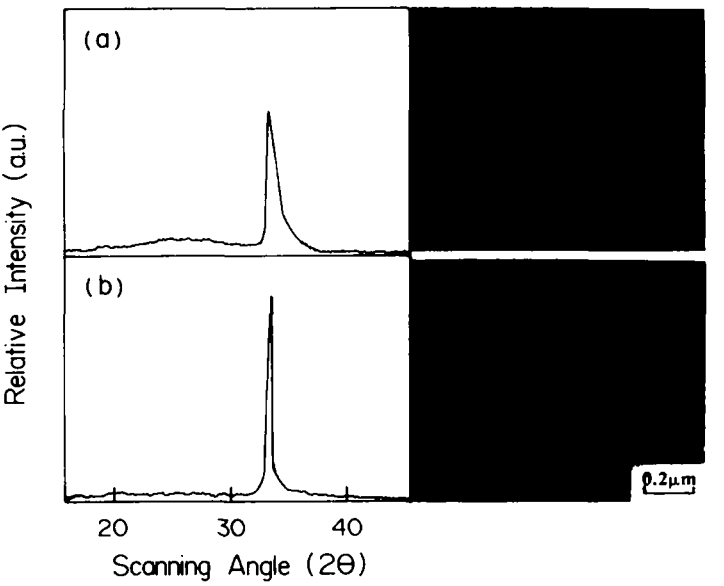

Fig. 6. X-ray diffraction patterns and microstructures for (a) undoped and (b) 7.5 wt.% Ga_2O_3-doped ZnO films.

The microstructures of an undoped and 7.5 wt.% Ga_2O_3-doped ZnO films are shown in Figs. 6(a) and 6(b) respectively. The average grain size in the undoped film is about 500 Å and that in the doped film is about 1000 Å. The microstructure of specimens prepared by sputtering targets that contained from 2 to 15 wt.% GaO_3 were similar to that in Fig. 6(b). Although the increase in the average grain size is not quite clear in the micrographs, the X-ray diffraction patterns shown in the figure indicate that the grain size of the doped film is larger than that of the undoped film (narrower peak widths). Figure 6 also shows a strong peak intensity at $2\theta = 33.5$ which indicates that the grains are strongly oriented (c axis of the hexagonal ZnO grains normal to substrate surface). Thus, considering the microstructure alone, the carrier mobility should be larger in the doped ZnO film.

However, the electron mobility decreases rather sharply from about 30 $cm^2 V^{-1} s^{-1}$ in the undoped specimen to about 7 $cm^2 V^{-1} s^{-1}$ in the 2 wt.% Ga_2O_3-doped film and decreases further with increasing Ga_2O_3 content (Fig. 5). The potential energy barrier for the carrier at the grain boundary in the Ga_2O_3-doped films should again be negligible since the carrier concentration is larger than 10^{20} cm^{-3}. Thus it appears that the decrease in the mobility is mainly caused by ionized impurity scattering for the films doped with Ga_2O_3 up to 5 wt.%.

The further decrease in electron mobility as the amount of Ga_2O_3 exceeds 7.5 wt.% may have been caused by additional scattering due to gallium segregation at grain boundaries.

The increase in the optical band gap with the increase in electron concentration is related to the increase in the Fermi level in the conduction band of a degenerate semiconductor. This phenomenon is known as the "blue shift", and the relation

between ΔE_g and the carrier concentration n is given by [10]

$$\Delta E_g \approx \frac{h^2}{8m^*}\left(\frac{3}{\pi}\right)^{2/3} n^{2/3} \tag{2}$$

The measured ΔE_g as a function of the electron concentration is shown in Fig. 7 with the results reported by Roth *et al.*[11] and Caporaletti[12]. It is seen that our data indicated by crosses extend the data (indicated by open circles) reported by Roth *et al.* well for ZnO films deposited by the chemical vapour deposition method. The deviation from the full line which represents eqn. (2) is not quite clear, but Roth *et al.* explained it in terms of band gap narrowing due to the overlap of the wavefunction of donor states as the donor density increases.

4. CONCLUSIONS

Ga_2O_3-doped ZnO films on glass substrates were prepared by r.f. sputtering, and their optical and electrical properties have been studied by measuring optical transmission spectra, electrical resistivity, carrier concentration and Hall mobility. The composition, microstructure and uniformity of the sputtered films were also investigated with AES, X-ray diffraction and SEM techniques.

The composition of the r.f.-sputtered Ga_2O_3-doped ZnO film is almost identical with that of the target. An r.f. power density of 0.84 W cm^{-2} and an argon gas pressure of 5 mTorr are the optimum conditions to obtain transparent Ga_2O_3-doped ZnO films with low electrical resistivity. The electrical resistivity increases rather sharply when the thicknesses of the sputtered films become less than 2500 Å. A gallium dopant concentration of about 1.5×10^{21} cm^{-3} in ZnO films results in a minimum value of the resistivity because the electron concentration increases with increasing gallium concentration up to about 1.5×10^{21} cm^{-3} and stays at the same value with further increase in the Ga_2O_3 content while the electron mobility decreases continuously with increasing Ga_2O_3 content in the ZnO films.

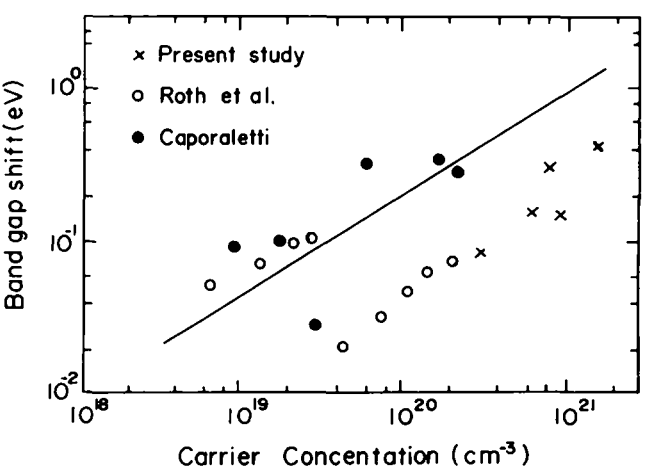

Fig. 7. Optical band gap shift as a function of carrier concentration in ZnO films.

The electron concentration stays at about the same value of about $1.5 \times 10^{21}\,cm^{-3}$, suggesting that the solubility of gallium in ZnO at 200 C is approximately $1.5 \times 10^{21}\,cm^{-3}$.

The optical band gap increases from 3.28 eV for undoped ZnO with an electron concentration of $10^{18}\,cm^{-3}$ to 3.69 eV for Ga_2O_3-doped ZnO with an electron concentration of $1.5 \times 10^{21}\,cm^{-3}$, mainly because of the increase in the Fermi level in the conduction band of the degenerate ZnO semiconductor.

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