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Characteristics of GZO thin films deposited by sol–gel dip coating

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ABSTRACT

Zinc oxide (ZnO) films were deposited by sol–gel dip coating using the acrylamide route. The films were doped with different concentrations of gallium in the range 250–1200 ppm. The films exhibited hexagonal structure. The grain size decreased from 100 to 10 nm as the dopant concentration increased. The resistivity of the doped samples decreased from 10^3 to $3\times10^{-3}\,\Omega$ cm. The band gap value shifted towards the short-wavelength region as the dopant concentration increased. XPS studies indicated doping of Ga in ZnO

1. Introduction

The properties of zinc oxide (ZnO) are currently a subject of numerous investigations, in response to the huge industrial demand for short-wavelength optoelectronic devices, transparent electrodes, and window materials for displays and solar cells. Compared to undoped ZnO, impurity-doped ZnO has a lower resistivity and better stability. Zinc oxide has been doped with Al, Ga, In, B, Si, Ge, Ti, Zr, as well as Hf and F [1–5]. The resulting minimal resistivity was about $10^{-4}\,\Omega$ cm [2,5]. Due to its lower cost and advanced properties, ZnO doped with Ga was suggested as a replacement for indium tin oxide (ITO) in a wide range of applications [6,7]. Among the metal dopants, Ga doping seems to be most successful and promising due to its advantages, such as the rather similar ionic radius and the covalent radius (0.62 and 1.26 Å) compared to Zn (0.74 and 1.34 Å, respectively),which could result in only small ZnO lattice deformations even for the case of high Ga concentrations. Also, Ga is less reactive and more resistive to oxidation compared to Al [7]. Among different substrates, the most frequently used is sapphire (a-Al_2O_3, a=4.757 Å, c=12.753 Å) due to the similarity of crystal structure, optical transparency, strength, and chemical stability, as well as availability of large area wafers with low cost. For the deposition of Ga-doped ZnO films, a number of growth techniques such as chemical vapor deposition [8], the sol–gel technique [9,10], spray pyrolysis [11], magnetron sputtering [7], pulsed laser deposition [12], and molecular beam epitaxy [13] were used. In this work, ZnO: Ga films were deposited by the acrylamide sol–gel dip coating technique. Earlier undoped ZnO was deposited by the acrylamide sol–gel technique and the properties were reported [10].

2. Experimental methods

ZnO films were deposited on cleaned glass substrates using AR grade zinc chloride, acrylamide, bisacrylamide, and ammonium persulphate. The pH of the 0.25 M zinc chloride solution was changed to 9 by adding AR grade ammonia solution. For doping with gallium 0.01 M of $GaCl_3$ was introduced in the deposition mixture. Acrylamide and bisacrylamide were then added to this solution. The temperature of the precursor mixture was kept at 70 °C. A small quantity of gelling agent ammonium persulphate was added till a viscous solution was

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obtained. The cleaned glass substrates ($2.5 \times 7.5\ cm^2$) were immersed in this solution and withdrawn at the rate of 1 cm/min. The deposit was then dried and finally post-annealed at different temperatures in the range of 400–500 °C for 120 min. The film thickness was determined using a Mutitoyo surface profilometer to be in the range 0.9–1.45 μm. The surface roughness measured by the surface profilometer was 2.34 nm. The amount of Ga doped in the ZnO lattice was determined by atomic absorption spectrometry (AAS). The doped as well as the undoped films were characterized by X-ray diffraction, optical absorption studies, and electrical studies.

3. Results and discussion

X-ray diffraction (XRD) experiments were performed using a Phillips X-ray diffractometer. CuK was used as the X-ray source. XRD spectra of the ZnO films heat treated at different temperatures are shown in Fig. 1. The standard XRD spectrum of ZnO powder (PDF80-0075) is also shown in the figure. All the films were *c*-axis oriented, i.e., the (0 0 2) axis was preferentially perpendicular to the surface of the substrate. Such *c*-axis oriented films are quite common for ZnO films grown at temperatures around 500 °C. It was observed that as post heat treatment temperature increases, the intensity of the (1 0 0) peak increases and the width of the (0 0 2) peak decreases. For the samples heated at 500 °C, the FWHM of the (0 0 2) peak was 0.194, while for the samples heated at 450 and 400 °C, the FWHM of the (0 0 2) peak were 0.241 and 0.274, respectively. This may be due to the fact that low temperatures lead to the formation of smaller grains compared to high temperatures. Doping with Ga causes changes in the structural properties of ZnO thin films. We have not observed a separate gallium oxide phase by XRD, since only peaks related to the hexagonal structure of ZnO are observed in the XRD spectra. For Ga doped ZnO thin films only two main peaks, (0 0 2) and (1 0 1), are observed simultaneously. The mutual intensity of these peaks changes with increasing Ga content and the transformation from the (0 0 2) peak for Ga-poor ZnO to the (1 0 1) peak for Ga-rich ZnO is evident. The (0 0 2) peak is dominating for 250 ppm Ga doped films, and only a weak trace of the (1 0 1) orientation peak is observed. With increasing Ga content, the intensity of (0 0 2) peak is decreased, whereas the (1 0 1) peak becomes dominant. Apparently, further increase of the Ga content is the reason for a complete change of the preferential orientations of the grains. Fig. 2 shows the XRD pattern of the Ga doped films. The suppression of the (0 0 2) peak after doping with In, Fe, or Cu was already reported earlier [14–16].

The grain size of the films from the XRD data was calculated using the Debye–Scherrer formula

$$D = 0.9\lambda/(\beta\cos\theta)$$

where D is the diameter of the crystallites forming the film, λ is the wavelength of CuK line, β is FWHM in radians, and is the θ Bragg angle. The grain size was found to decrease from 60 to 10 nm with increasing Ga doping concentration. Similar behavior was reported earlier [17].

The resistivity of ZnO films annealed from 400 to 500 °C was measured by providing Au contacts at the edges of the films. The results show that the resistivity decreases from 10,000 to 1000 Ω cm with increasing heat treatment temperature [10]. The probable reason is that the concentration of interstitial Zn decreases with increasing annealing temperature, because of Zn evaporation. ZnO contains vacancies within the crystal structure, and it can accommodate the interstitial atoms easily. The Zn interstitial atoms are easily ionized, and electrons produced by the ionized Zn interstitial atoms have large contribution to electrical conductivity. To decrease the resistivity, the films were doped with different concentrations of Ga in the range 250–1200 ppm. The resistivity was found to decrease from 1000Ω to 3.2×10^{-3} Ω cm with increase of Ga content. The carrier concentration increased from 10^{18} to $10^{20}\ cm^{-3}$ with increase of Ga concentration, the mobility increased from 0.625 to 30 $cm^2\ V^{-1}\ s^{-1}$ as the Ga concentration increased.

Optical transmittance spectra in the wavelength interval of 300–800 nm are shown in Fig. 3 for the ZnO films doped with different concentrations of gallium. It is observed that the average transmittance in the visible part of the spectra (400–00 nm) has a mean of 85% for all the films. As the gallium content increases, the absorption edge shifts to the shorter wavelength region. The movement of the absorption edge to the shorter wavelength region is the Burstein–Moss shift [17], which is due to the increase of carrier concentration. This is supported by the electrical measurements.

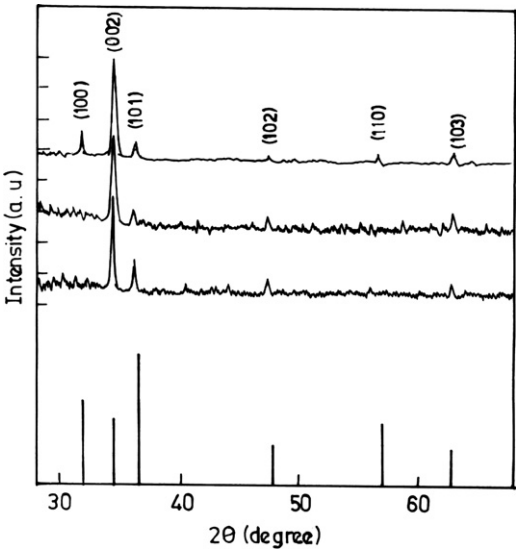

Fig. 1. X-ray diffraction patterns of ZnO films formed by heating at different temperatures: (a) 400 °C, (b) 450 °C, and (c) 500 °C.

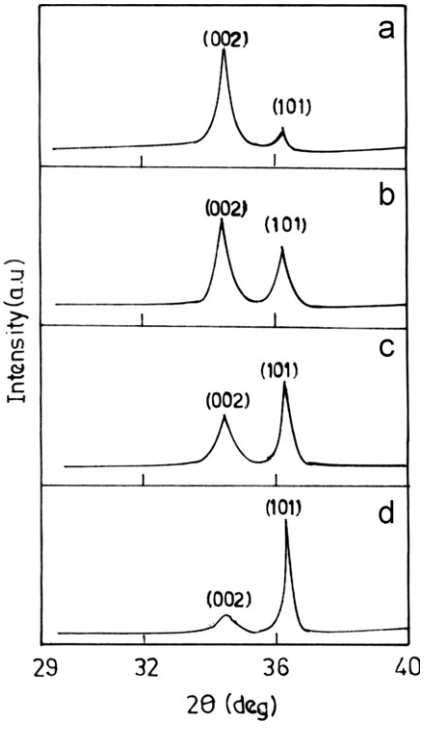

Fig. 2. XRD patterns of ZnO films doped with different concentrations of gallium: (a) 250 ppm, (b) 470 ppm, (c) 835 ppm, and (d) 1200 ppm.

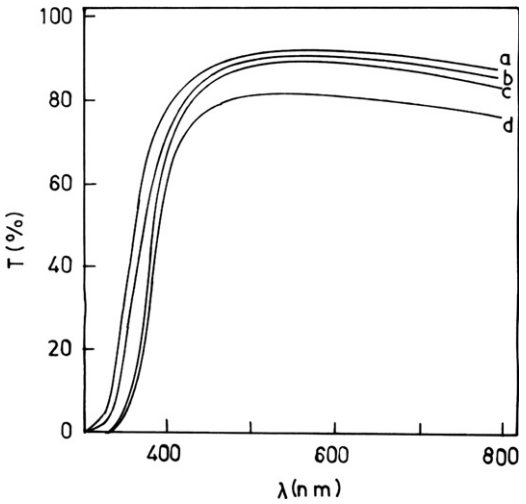

Fig. 3. Optical transmission spectra of ZnO films doped with different concentrations of Ga and heated at 500 °C: (a) 1200 ppm, (b) 835 ppm, (c) 470 ppm, and (d) 250 ppm.

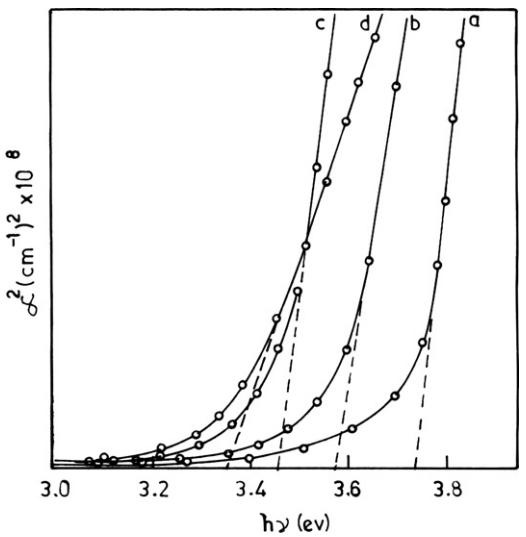

Fig. 4. $(\alpha h\nu)^2$ vs $h\nu$ plot of ZnO films doped with different concentrations of gallium: (a) 250 ppm, (b) 470 ppm, (c) 835 ppm, and (d) 1200 ppm.

A plot of $(\alpha h\nu)^2$ vs $h\nu$ (Fig. 4) yields band gap values of 3.34, 3.57,3.43, and 3.72 eV respectively, for the Ga doping from 250to 1200 ppm. The shift in the band gap can be explained in terms of the Burtsein–Moss shift since the absorption edge of a degenerate semiconductor is shifted to shorter wavelength with increasing carrier concentration. This variation of the absorption edge is due to the increase and/or decrease in free electron concentration in the films, which is the result of a large increase in the free carrier concentration and the corresponding upward shift of the Fermi level to the top of the band edge. Generally, it is well known that the broadening of the absorption edge is mainly due to the increase in disorder of semiconductor films, which leads to the appearance of localized electron and/or hole states.

The XPS spectra of Ga-doped ZnO thin films exhibited the binding energies of Ga 2p and Zn 2p peaks (Fig. 5). The Ga2p3/2 peak could be detected even in films with nominal Ga content of 250 ppm. As the post heat treatment temperatures increase the peak heights also increase, indicating that the concentration of Ga introduced into ZnO increases.

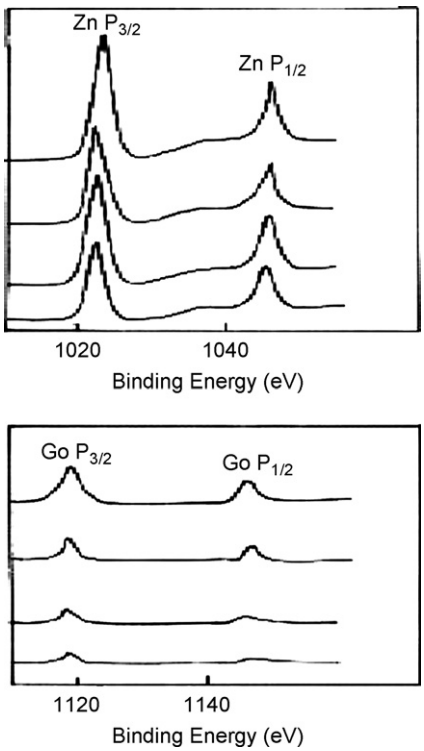

Fig. 5. XPS spectra of ZnO films doped with different concentrations of Ga: (top) 1200 ppm, (next) 835 ppm, (next) 470 ppm, and (bottom) 250 ppm.

4. Conclusion

The results of this investigation clearly shows that the sol–gel method can be used to produce low resistive GZO films with band gaps in the range 3.4–3.72 eV. Films with grain size in the range of 100–10 nm can be easily obtained.

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