# Influence of substrate temperature and oxygen/argon flow ratio on the electrical and optical properties of Ga-doped ZnO thin films prepared by rf magnetron sputtering

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Effects of substrate temperature and atmosphere on the electrical and optical properties of Ga-doped ZnO thin films deposited by rf magnetron sputtering were investigated. The electrical resistivity of Ga-doped ZnO (GZO) films decreases as the substrate temperature increases from room temperature to 300°C. A minimum resistivity of $3.3 \times 10^{-4}$ $\Omega$ cm is obtained at 300°C and then the resistivity increases with a further increase in the substrate temperature to 400°C. This change in resistivity with the substrate temperature is related to the crystallinity of the GZO film. The resistivity nearly does not change with the $O_2/Ar$ flow ratio, R for R < 0.25 but increases rapidly with R for R > 0.25. This change in resistivity with R is also related to crystallinity. The crystallinity is enhanced as R increases, but if the oxygen partial pressure is higher than a certain level (R = 0.25 ± 0.10) gallium oxides precipitate at grain boundaries, which decrease both carrier concentration and mobility. Optical transmittance increases as R increases for R < 0.75. This change in transmittance with R is related to changes in oxygen vacancy concentration and surface roughness with R.

## 1 Introduction

Indium tin oxide (ITO) has been most widely used as a transparent conducting oxide (TCO) electrode in liquid crystal displays (LCDs), organic light emitting diodes (OLEDs) and solar cells since it has high visible transmittance (~90 % at 550 nm), low electrical resistivity (~ $2 \times 10^{-4}$ $\Omega$ cm), and relatively high work function (~4.8 eV) [1]. Nevertheless, ITO is an expensive TCO since indium in ITO is a rare and expensive element. Therefore, impurity-doped zinc oxide (ZnO) has been actively investigated as an alternative to ITO. Impurity-doped ZnO is cheaper, and easier to etch than ITO. ZnO is nontoxic and much more resistant to hydrogen plasma reduction and can be grown at lower temperatures. Thus, impurity-doped ZnO is more favorable than ITO particularly for amorphous-silicon solar cells fabricated on transparent conducting (TC) substrates, since the TC substrates are exposed to hydrogen plasma [2,3]. Group A elements such as Al, In, Ga, and B have been widely used as n-type dopants for ZnO[4-6].

Among these elements Ga has a couple of advantages. One is that defect generation is minimized when ZnO is doped with Ga since the atomic radius of Ga is the most similar to that of Zn. Another one is that it makes less diffusion-related problems since the diffusivity of Ga is lower than those of Al and B at the same temperature. In spite of these advantages Ga-doped ZnO has been relativity less studied than Al-doped ZnO. Also recently there occurred a work about indium zinc oxide ($In_2Zn_2O_5$) (IZO) films as novel TCO grown by pulsed laser deposition. These films combine the advantages of the ITO and ZnO films like promising opto-electronic materials[7].

The deposition temperature of a TCO film is strictly limited depending upon its applications. In the case of liquid crystal display (LCD) applications it should be lower than 140°C or 250°C depending on whether the substrate material is plastic or glass [8]. For plasma display panels (PDP) applications it should be lower than

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400°C. Also for solar cell applications it should be lower than 200°C or 500°C depending on whether the TCO film is deposited on other films such as a semiconductor film or deposited directly on glass. Because of this deposition temperature limit for TCO films most studies on the effect of the substrate temperature on the electrical and optical properties of TCO films have been investigated in the temperature range below 200°C [8-11]. However, for the applications of solar cells and PDPs with various device structures it is necessary to investigate the effect of the substrate temperature for a wider range of temperature. In this work we report the effects of the substrate temperature and atmosphere on the electrical and optical properties of Ga-doped ZnO (GZO) thin films prepared by rf magnetron sputtering in a temperature range up to 400°C.
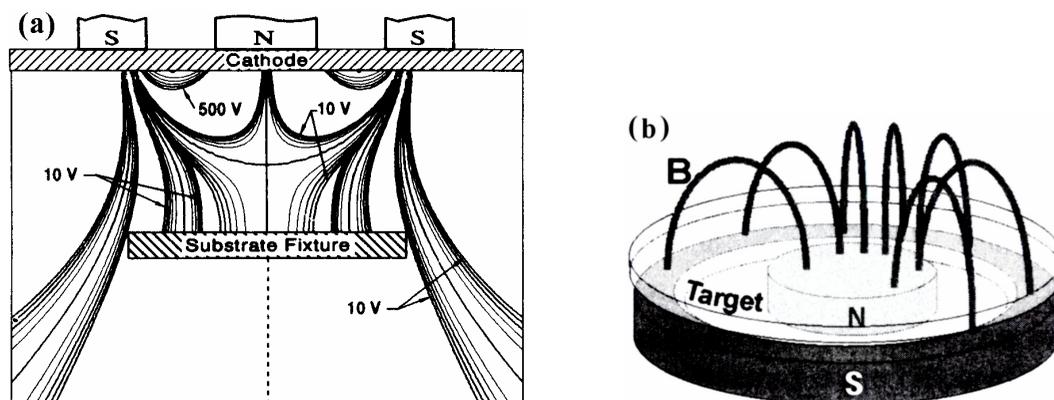


**Fig. 1** (a) Lamor potential contours and (b) the magnetic field space distribution in the sputter chamber (B: magnetic field).

## 2    Experimental

GZO thin films were deposited on (002) sapphire and glass substrates using an rf magnetron sputtering technique. A target (ZnO : 97wt% and $Ga_2O_3$ : 3wt%) with a 2 inch diameter was used. The Lamor potential contours [12] and the magnetic field space distribution in the sputter chamber are shown in figure 1 (a) and (b), respectively. The maximum horizontal component magnetic field strength at the target surface was $5 \times 10^{-2}$ T. The substrate surfaces were cleaned in an ultrasonic cleaner for 10 min with acetone and methanol, respectively and then blown dry with nitrogen before they were introduced into the sputtering system. The deposition chamber was initially evacuated to $1 \times 10^{-6}$ torr and oxygen and argon gas was introduced into the chamber to maintain the desired pressure ($1 \times 10^{-3}$ torr). The gas flow ratio (R = oxygen:argon) was varied like 0:30, 10:20, 15:15, 20:10, and 30:0. The rf sputtering power was fixed at 80W. The substrate temperature was varied in a temperature from room temperature (RT) to 400°C.

For the prepared samples X-ray diffraction (XRD) was performed to investigate the crystallinity of the GZO films. The full width at half maximum (FWHM) of ZnO (002) XRD peaks was measured from the XRD diffraction spectra to assess the crystallinity. An α-step (Dektak-3) was used to measure the film thickness. Atomic force microscopy (AFM) was used to investigate the surface roughness of the film. The carrier concentration, carrier mobility and electrical resistivity of the films were determined by Hall measurement (HEM-2000). The optical transmittance measurements were made using a UV/VIS spectrophotometer.

## 3. Results and discussion

Figure 2 shows the variation of carrier concentration, carrier mobility and electrical resistivity with the substrate temperature for the GZO thin films deposited by rf magnetron sputtering. The rf power and $O_2$/Ar flow ratio were fixed at 80 W and 10:20, respectively and the film thickness was 300 nm. The electrical resistivity of the GZO thin film deposited at room temperature was measured to be $2.2 \times 10^{-3}$ Ωcm. It decreases slowly first and then rapidly as the substrate temperature increases from room temperature to 300°C. A minimum resistivity of $3.3 \times 10^{-4}$ Ωcm is obtained at 300°C and then the resistivity increases with a further increase in the substrate temperature to 400°C. The decrease in the resistivity with an increase of the substrate

temperature from room temperature to 300°C is due to increases both in the carrier concentration and the carrier mobility. The increases of both the carrier concentration and carrier mobility with the substrate temperature may be, in turn, attributed to the enhancement in the crystallinity of the GZO film. As can be seen in figure 3, the FWHM of the XRD peak for the GZO film decreases in a temperature range from room temperature to 400°C suggesting that the crystallinity is improved with temperature. On the other hand, the increase in the resistivity with an increase of the substrate temperature from 300°C to 400°C is due to deterioration in the crytallinity of the ZnO film as can be seen from an increase in the FWHM of the XRD peak for the GZO film.
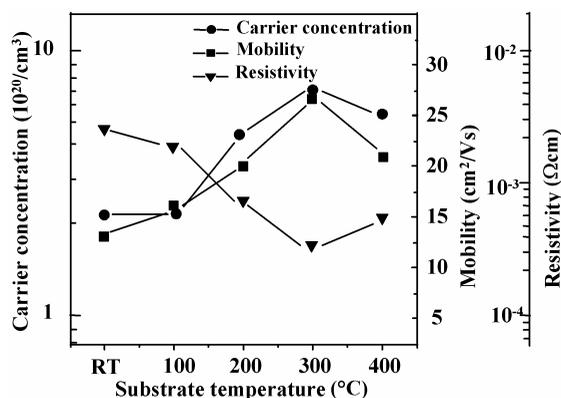


**Fig. 2** The carrier concentration, carrier mobility and electrical resistivity of GZO films as a function of the substrate temperature for an $O_2$/Ar flow ratio of 0.25.
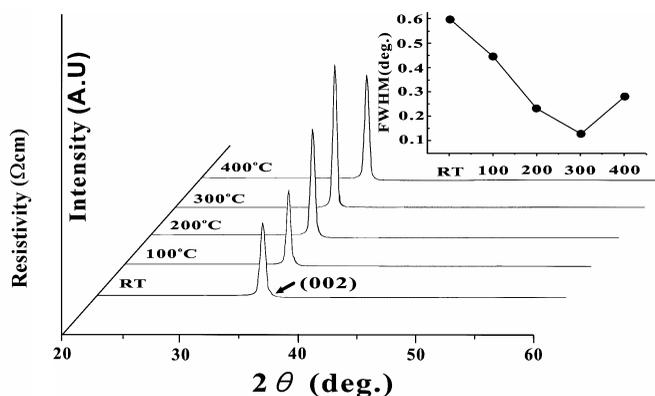


**Fig. 3** X-ray diffraction patterns of GZO thin films deposited at different substrate temperatures for the $O_2$/Ar flow ratio of 0.25.
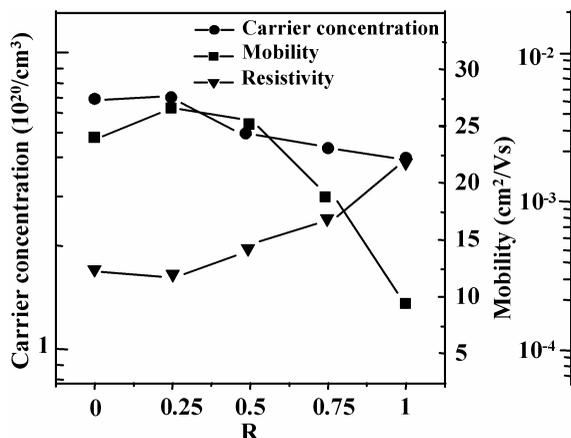


**Fig. 4** The carrier concentration, carrier mobility and electrical resistivity of GZO films deposited at 300°C as a function of the $O_2$/Ar flow ratio (R).
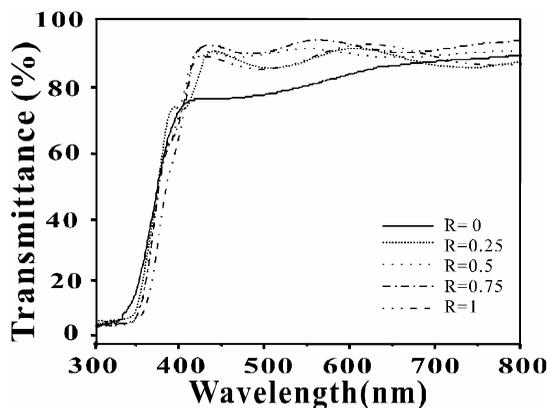


**Fig. 5** The optical transmittance of GZO films deposited at 300°C for different $O_2$/Ar flow ratios (Rs).

Variation of carrier concentration, carrier mobility and electrical resistivity with the $O_2$/Ar gas flow ratio, R is shown in figure 4. In this figure real $O_2$ and Ar gas flow rates in sccm for R = 0, 0.25, 0.5, 0.75, and 1 are $O_2$:Ar = 0:30, 10:20, 15:15, 20:10, and 30:0, respectively. The electrical resistivity nearly does not change with R for R < 0.25 but increases rapidly with R for R > 0.25. The change in the resistivity can be explained as follows: The crystallinity is enhanced as the oxygen partial pressure increases, but if the oxygen partial pressure is higher than a certain level (R = 0.25 ± 0.10), nonconducting gallium oxides precipitate at grain boundaries due to segregation of oxygen atoms, which causes a crystalline disorder in the films [13]. These gallium oxides at grain boundaries act as carrier traps rather than electron donors. In other words, acceptors such as Zn vacancies and oxygen interstitials which kill Ga donors are generated by excess oxygen. Carrier mobility also increases for R < 0.25 and then decreases for R > 0.25 with an increase of R, which is attributed to the formation of gallium oxides at grain boundaries acting as scattering centers.

Figure 5 shows the transmittance spectra for GZO thin films 300 nm thick prepared with different $O_2$/Ar flow ratios (Rs). The transmittance of the GZO thin film is higher than 90 % except that of the GZO film prepared with R=0. The lower transmittance for lower R is attributed to the bad crystallinity owing to the high densities of point defects such as oxygen vacancy, Zn interstitial, and Ga solute atoms. The Ga partially replaces the Zn in the basic matrix, which may create additional number of defective trapping levels of cationic type. These levels may play substantial role in the observed optical transmission. The $Ga_2O_3$-like carrier trapping levels can be estimated from the transmittance values of the GZO film and the energy band gap values of ZnO and $Ga_2O_3$ ($E_g$ (ZnO) = 3.3 eV, $E_g$ ($Ga_2O_3$) = 4.9 eV). The transmittance tends to increase with R for R < 0.75, which may be due to a decrease in the oxygen vacancy concentration with R. Variation of surface roughness with R is shown in figure 6. The surface roughness of the GZO film decreases for R < 0.5 and then increases for R > 0.5. The decrease in the surface roughness for R < 0.5 may also contribute to the increase in the transmittance.
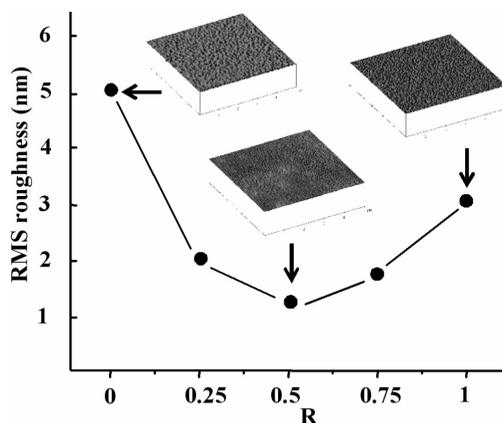


**Fig. 6** The RMS surface roughness of GZO films deposited at 300°C as a function of the $O_2$/Ar flow ratio (R).

## 4    Conclusions

The electrical resistivity of Ga-doped ZnO (GZO) films decreases first and then increases as the substrate temperature increases from room temperature to 400°C. A minimum resistivity of $3.3 \times 10^{-4}$ Ω cm is obtained at 300°C. The resistivity nearly does not change with the $O_2$/Ar flow ratio, R for R < 0.25 but increases rapidly with R for R > 0.25. Changes in resistivity with the substrate temperature and R are related to the crystallinity of GZO films. The crystallinity is enhanced as R increases, but if the oxygen partial pressure is higher than a certain level (R = 0.25±0.10) gallium oxides precipitate at grain boundaries, which decrease both carrier concentration and mobility. Optical transmittance increases as R increases for R < 0.75. This change in transmittance with R is related to changes in oxygen vacancy concentration and surface roughness with R.

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