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Dependence of the resistivity and the transmittance of sputter-deposited Ga-doped ZnO films on oxygen partial pressure and sputtering temperature

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Abstract Ga-doped ZnO (GZO) thin films were prepared by rf magnetron sputtering and dependence of the electrical resistivity and the transmittance of the GZO films on the oxygen partial pressure (R = the O_2/Ar gas flow ratio) and the substrate temperature were investigated. The resistivity of the GZO film decreases first and then increases with an increase in the substrate temperature (T). A minimum resistivity obtained with a substrate temperature of 300 °C is 3.3×10^{-4} Ωcm. The resistivity nearly does not change with R for $R < 0.25$. The decrease in the resistivity for $R < 0.25$ is attributed to enhancement in crystallinity, whereas the increase in the resistivity for $R > 0.25$ to precipitation of gallium oxides at grain boundaries. Optical transmittance of the GZO films is enhanced by increasing R up to 0.75. This enhancement in the transmittance is due to a decrease in oxygen vacancy concentration and a decrease in surface roughness with R.

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 (~2×10^{-4} Ωcm), 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 TC substrates, since the TC substrates are exposed to hydrogen plasma [2, 3]. Group IIIA 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 GZO has been relativity less studied than Al-doped ZnO (AZO).

The deposition temperature of a TCO film is strictly limited depending upon its applications. In the case of LCD applications it should be lower than 140 or 250 °C depending on whether the substrate material is plastic or glass [7]. For plasma display panels (PDP) applications it should be lower than 400 °C. Also for solar cell applications it should be lower than 200 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

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the substrate temperature on the electrical and optical properties of TCO films have been investigated in the temperature range below 200 °C [7–10]. 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 GZO thin films prepared by rf magnetron sputtering in a temperature range up to 400 °C.

Experimental

GZO thin films were deposited on (002) sapphire and glass substrates using an rf magnetron sputtering technique. A target (ZnO: 97 wt% and Ga_2O_3: 3 wt%) with a 2-inch diameter was used. The maximum horizontal component magnetic field strength at the target surface was 5×10^{-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 1×10^{-6} torr and oxygen and argon gas was introduced into the chamber to maintain the desired pressure (1×10^{-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 80 W. 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. Photoluminescence (PL) spectra were obtained using 40 mW He–Cd (325 nm) at room temperature.

Results and discussion

Figure 1 shows the variation of carrier concentration, carrier mobility and electrical resistivity with the substrate temperature for the GZO thin films deposited by

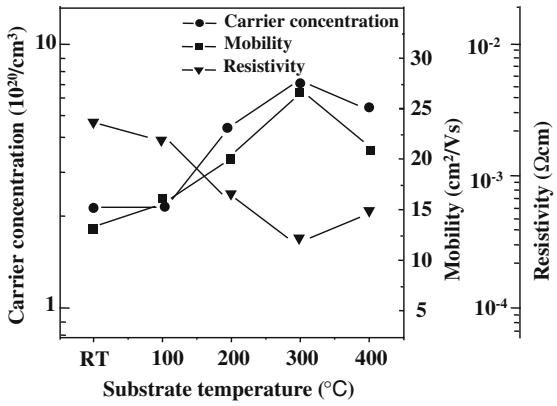

Fig. 1 The carrier concentration, carrier mobility and electrical resistivity of GZO films as a function of the substrate temperature with an O_2/Ar flow ratio (R) of 0.75

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 2.2×10^{-3} Ωcm It decreases slowly first and then rapidly as the substrate temperature increases from room temperature to 300 °C. A minimum resistivity of 3.3×10^{-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 in 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 enhancement in the crystallinity of the GZO film. As can be seen in Fig. 2, the FWHM of the XRD (002) peak for the GZO film decreases in a temperature range from room temperature to 400 °C suggesting that the crystallinity is enhanced with temperature. On the other hand, the increase in the resistivity with an increase in the substrate temperature from 300 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 (002) peak for the GZO film. It is well known that the crystallinity of a conducting material makes strong effects on the carrier concentration and mobility of the material. There are many crystallographic defects affecting the crystallinity. These defects include grain boundaries, dislocations, interstitials, vacancies, and solute atoms such as Ga atoms. All these defects induce scattering of carriers e.g. impurity scattering and grain boundary scattering and act as traps for carriers which reduces the effective carrier concentration by making carriers inactive.

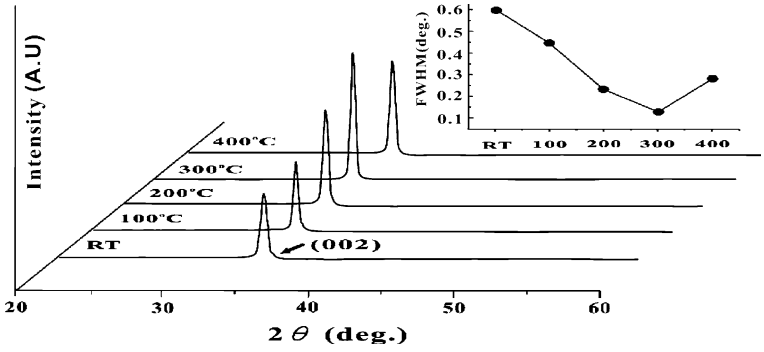

Fig. 2 X-ray diffraction patterns and the full width at half maximum (FWHM) of the (002) peak of GZO thin films deposited at different substrate temperatures with the O_2/Ar flow ratio of 0.75

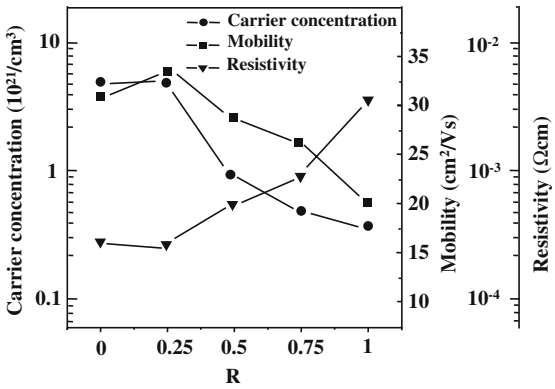

Fig. 3 The carrier concentration, carrier mobility and electrical resistivity of GZO films deposited at 300 °C as a function of the O_2/Ar flow ratio (R)

Variation of the carrier concentration, the carrier mobility and the electrical resistivity of the GZO film with the O_2/Ar gas flow ratio, R is shown in Fig. 3. 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 $R > 0.25$. This change in the resistivity can be explained as follows: The crystallinity of the GZO film seems to be enhanced as the oxygen partial pressure (R) increases from 0 to 0.5, because Fig. 4 shows that the FWHM decreases with R in this range of R. However, the decreasing rate of the FWHM for $0.25 < R < 0.5$ is lower than that for $0 < R < 0.25$ and the FWHM increases with R in the R range from 0.5 to 1.0. Particularly the increasing rate of the FWHM for $R > 0.75$ is very high. This change in the FWHM with R suggests that precipitation of gallium oxides starts at $R = 0.25$ as R increases. According to Yamamoto et al.'s report, if the oxygen partial pressure is higher than a certain level, nonconducting gallium oxides precipitate at grain boundaries due to segregation of oxygen atoms, which causes a crystalline disorder in the films [11]. 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

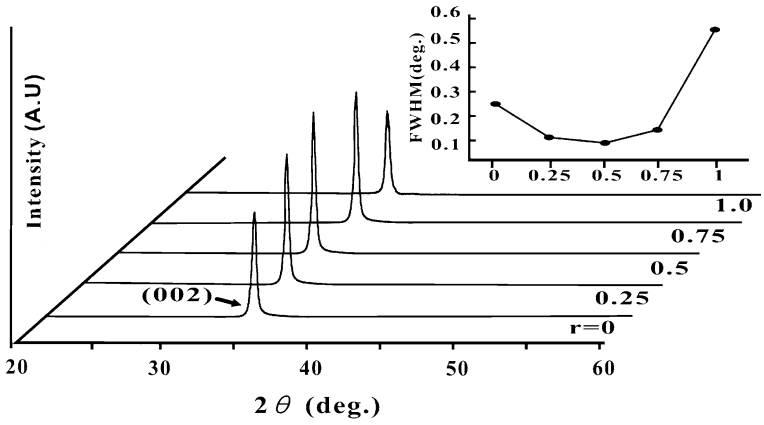

Fig. 4 X-ray diffraction patterns and the FWHM of the (002) peak of GZO thin films deposited with different O_2/Ar ratios (Rs) at 300 °C

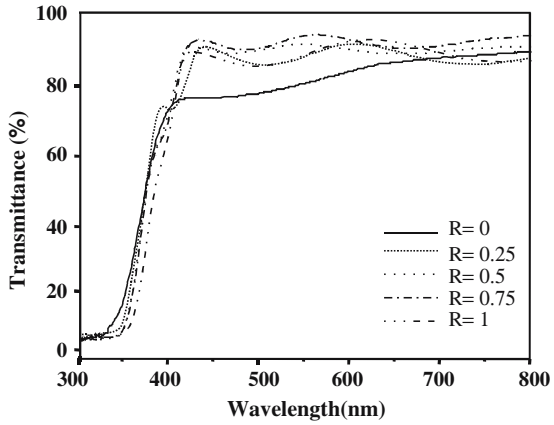

Fig. 5 The optical transmittance of GZO films deposited at 300 °C for different O_2/Ar flow ratios (Rs)

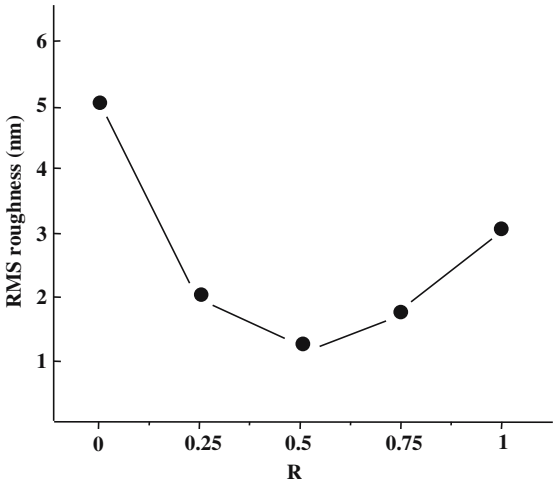

Fig. 6 The RMS surface roughness of GZO films deposited at 300 °C as a function of the O_2/Ar flow ratio (R)

prepared with $R = 0$. The lower transmittance for lower Rs is attributed to the high densities of point defects such as oxygen vacancy and Zn interstitial in the GZO films. 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 Fig. 6. The surface roughness of the GZO film decreases with R for $R < 0.5$ but increases with R for $R > 0.5$. The AFM images in Fig. 7 confirms us that the surface roughness is lowest for $R = 0.5$. The decrease in the surface roughness for $R < 0.5$ may also contribute to the increase in the transmittance.

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 3.3×10^{-4} Ωcm 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 intimately 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 ($R = 0.25$) 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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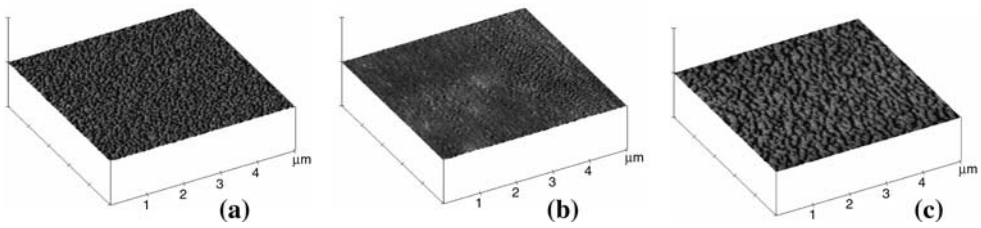

Fig. 7 The atomic force microscopic (AFM) images of GZO films deposited at 300 °C with different O_2/Ar flow ratios (Rs): (**a**) $R = 0$, (**b**) $R = 0.5$, and (**c**) $R = 1.0$

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