Effects of annealing on structure, resistivity and transmittance of Ga doped ZnO films

K. Yim, H. W. Kim and C. Lee*

Effects of annealing on the electrical resistivity and transmittance properties of Ga doped ZnO (GZO) thin films deposited on glass by radio frequency (RF) magnetron sputtering were investigated. The electrical resistivity of a GZO thin film is effectively decreased by annealing in a reducing atmosphere such as $N_2+5\%H_2$. This is attributed to passivation of grain boundaries and zinc ions by hydrogen atoms resulting in increases in carrier concentration and mobility. However, annealing at a temperature >400°C is less effective. The lowest resistivity of $2{\cdot}3\times10^{-4}$ Ω cm is obtained by annealing at 400°C in an $N_2+5\%H_2$ atmosphere. The optical transmittance of the GZO film is improved by annealing regardless of the annealing atmosphere. Annealing in an $N_2+5\%H_2$ atmosphere widens the optical band gap, while annealing in an O_2 atmosphere makes the band gap narrower, which can be explained as a blue shift phenomenon.

Keywords: Ga doped ZnO, Electrical resistivity, Transmittance, Annealing atmosphere, Annealing temperature

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} Ω 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 non-toxic and much more resistant to hydrogen plasma reduction and can be grown at lower temperatures. Thus, impurity doped ZnO is more favourable 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 IIIA elements such as Al, In, Ga and B have been widely used as n type dopants for ZnO.[4–11]

Among these elements Ga has several advantages. One of them is that Ga has higher oxidation resistance than Al. Another is that defect generation is minimised when ZnO is doped with Ga since the radius of Ga^{3+} (0·062 nm) is closer to that of Zn^{2+} (0·060 nm) than that of Al^{3+} (0·053 nm), The third is that it makes less diffusion related problems since the diffusivity of Ga is lower than that of Al at the same temperature, although this is not important because there is little chance for TCOs experience a high temperature process after they are deposited. However, Ga doped ZnO (GZO) has been relatively less studied than Al doped ZnO in spite of these advantages may be because Ga is more expensive than Al.

The deposition and annealing temperatures for TCO thin films are strictly limited depending upon their applications. In the case of liquid crystal display (LCD) applications it should be lower than 140 or 250°C depending on whether the substrate material is plastic or glass.[12] For plasma display panels (PDPs) applications it should be lower than ~400°C. Also for solar cell applications it should be lower than ~150 or 400°C depending on whether the TCO film is deposited on other films such as a semiconductor film or deposited directly on glass. There are some reports on annealing of Al doped ZnO films, yet there are very few reports on annealing of GZO films. In this paper the authors has reported the effects of annealing temperature and atmosphere on the electrical resistance and optical transmittance of GZO thin films prepared by radio frequency (RF) magnetron sputtering. Annealing effects in the annealing temperature range up to 600°C were investigated to understand the effects of thermal energy and annealing atmosphere on the electrical and optical properties of GZO films better, although annealing at such high temperatures are not allowed in most TCO applications.

Experimental

GZO thin films were deposited on (002) sapphire and glass substrates using an RF magnetron sputtering technique. A target (97 wt-%ZnO–3 wt-%Ga_2O_3) with a 2 inches 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

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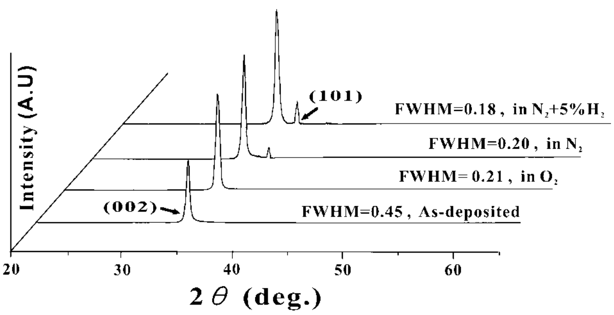
Published by Maney on behalf of the Institute
Received 5 April 2006; accepted 18 May 2006
DOI 10.1179/174328407X158514

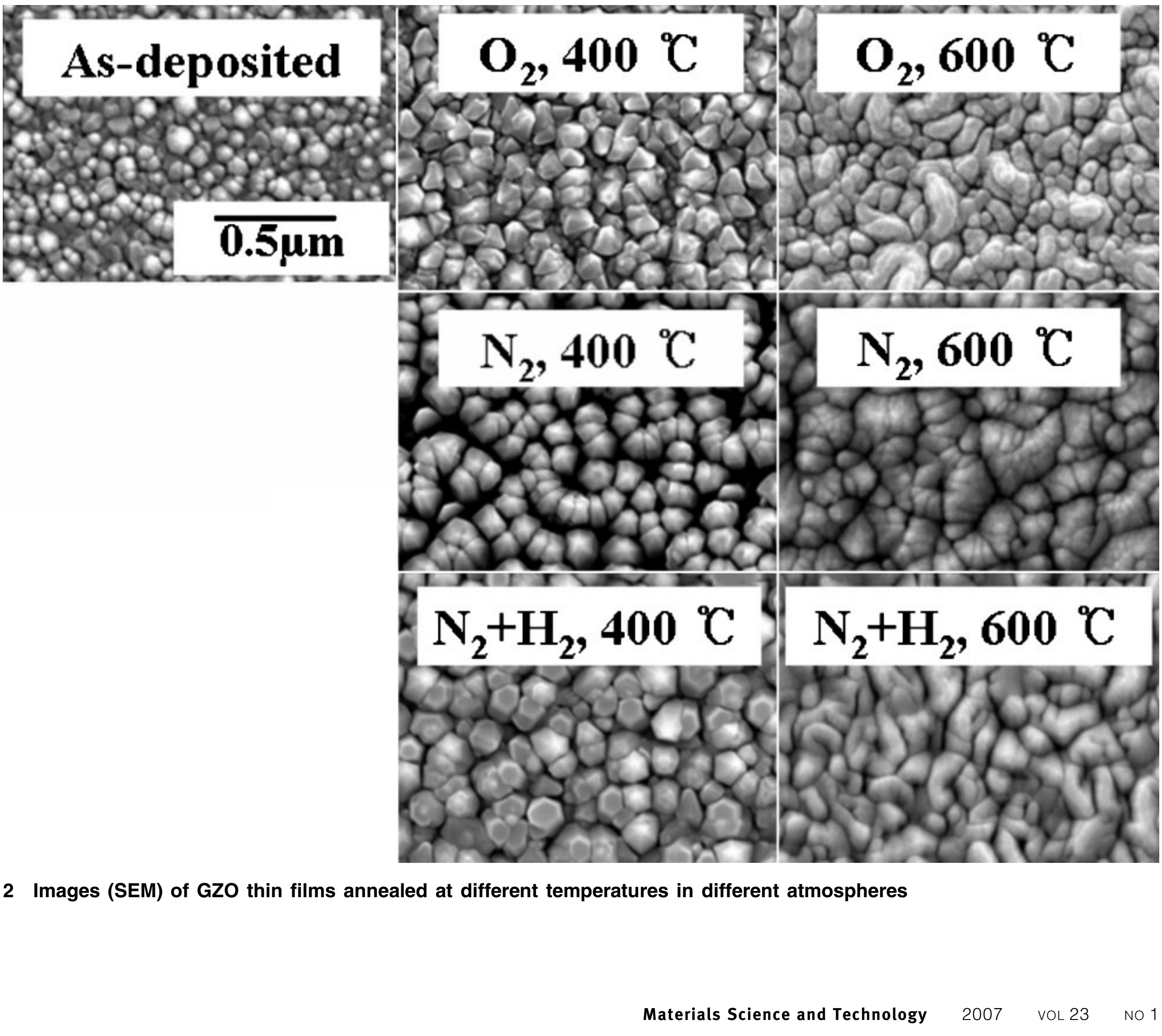


1 X-ray diffraction spectra of GZO thin films annealed at 400°C in different atmospheres along with that of an as deposited GZO film

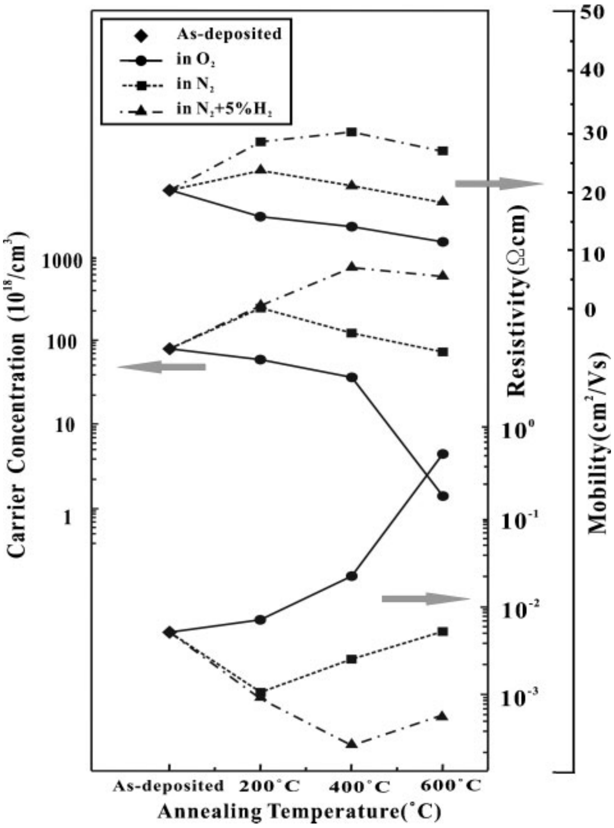
before they were introduced into the sputtering system. The deposition chamber was initially evacuated to 1×10^{-6} torr and oxygen and argon gas was introduced into the chamber to maintain the desired pressure (1×10^{-3} torr). The Ar and O_2 gas flowrates were fixed at 20 and 10 sccm respectively. The RF sputtering power and the substrate temperature were 80 W and 200°C respectively. The GZO thin film samples were annealed at 200, 400 and 600°C for 1 h in an O_2, N_2 and $N_2+5\%H_2$ atmosphere. For the prepared samples X-ray diffraction (XRD) analysis 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. Scanning electron microscopy was performed to observe the microstructures of the GZO films. The carrier concentration, carrier mobility and electrical resistivity of the films were determined by Hall effect measurement (HEM-2000). The optical transmittance measurements were made using a UV/VIS spectrophotometer.

Results and discussion

X-ray diffraction patterns shown in Fig. 1 indicate that the Ga doped ZnO thin films, as deposited and annealed at 400°C in N_2, O_2 and $N_2+5\%H_2$ atmospheres exhibit a strong *c* axis orientation perpendicular to the substrate surface. The crystallinity evaluated from the intensity and FWHM of the (002) diffraction peak is enhanced by annealing regardless of the annealing atmosphere. The enhancement in crystallinity by annealing may be explained by many causes. One of them is an increase in grain size by annealing. Figure 2 shows plan view SEM micrographs of GZO thin films for different annealing atmospheres and annealing temperatures. The grain size tends to increase and the grain shape tends to change from an equiaxed rough grain to a longish smooth grain as the annealing temperature increases from 400 to 600°C. In addition to an increase in the grain size, the concentrations of point defects such as oxygen vacancy and zinc interstitial decrease as the annealing temperature increases. This also seems to contribute to the enhancement in crystallinity by annealing. The Ga doped ZnO film annealed in an O_2 atmosphere has a texture of (002), whereas those



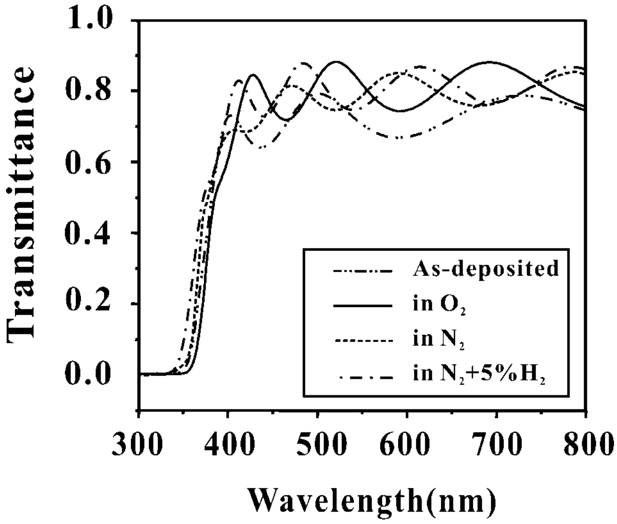
2 Images (SEM) of GZO thin films annealed at different temperatures in different atmospheres



3 Electrical properties of GZO thin films as function of annealing temperature in different atmospheres

annealed in N_2 and $N_2+5\%H_2$ atmospheres have not only an (002) diffraction peak but also an (101) peak. In the case of O_2 annealing the oxygen vacancy concentration is decreased by annealing, so that most grains tend to have an (002) preferred orientation through self-texturing. In contrast, in the case of N_2 or $N_2+5\%H_2$ annealing it seems that substitution of an oxygen atom with a nitrogen atom lowers the *c*/*a* ratio (where *a* and *c* are the lattice parameters of the wurtzite structure), which makes some of the grains have an (101) orientation.

The electrical resistivity, the carrier concentration and mobility of ZnO thin films annealed in different annealing atmospheres as a function of annealing temperature are shown in Fig. 3. It is obvious from Fig. 3 that the electrical resistivity of a GZO thin film is effectively decreased by annealing in an $N_2+5\%H_2$ atmosphere. Annealing in an N_2 atmosphere also has an effect of decreasing the resistivity although it is not as effective as annealing in $N_2+5\%H_2$. However, annealing at a very high temperature in either an $N_2+5\%H_2$ or an N_2 atmosphere is not as effective as that at lower temperatures. It should be noted that the resistivity increases as the annealing temperature increases from 400 to 600°C in $N_2+5\%H_2$ and from 200 to 600°C in N_2. In contrast to them the resistivity is increased by annealing in an O_2 atmosphere. In general, unintentionally doped ZnO films exhibit n type semiconductor characteristics owing to existence of oxygen vacancies, zinc interstitials and hydrogen impurities, whereas Ga doped ZnO films exhibit strong n type semiconductor or conductor characteristics. In the case of oxygen annealing the resistivity increases more rapidly as the annealing temperature increases. This may be attributed to



4 Optical transmittance spectra of GZO thin films as deposited and at 400°C annealed in different atmospheres

decreases in oxygen vacancy and zinc interstitial concentrations by the following reactions

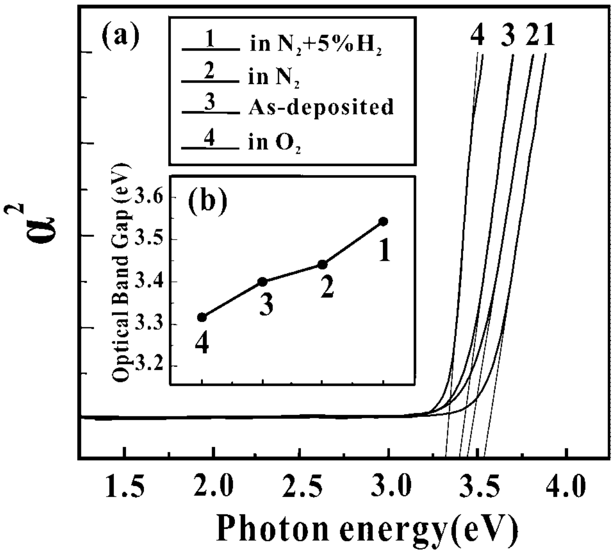
$$Zn_{Zn}+V_o+1/2O_2\rightarrow ZnO \quad (1)$$

$$Zn_i+1/2O_2\rightarrow ZnO \quad (2)$$

Decreases in oxygen vacancy and zinc interstitial concentrations would result in decreases in both carrier concentration and mobility, since they act as donors and cause impurity scattering or ionised impurity scattering. Also reactions (1) and (2) will be accelerated with increasing annealing temperature.

In the case of $N_2+5\%H_2$ annealing the resistivity decreases first and then increases as the annealing temperature increases. This may be attributed to the desorption of negatively charged oxygen species from the grain boundaries which act as trapping sites and form potential barriers during annealing.[13] The negatively charged species form depletion regions near grain boundaries decreasing carrier concentration and mobility. Hydrogen atoms would passivate the grain boundary surface during the annealing treatment in an $N_2+5\%H_2$ atmosphere and this hydrogen passivation would remove the depletion regions near grain boundaries. The removal of the depletion region, in turn, would result in increases in carrier concentration and mobility.[14] Besides such boundary passivation effect of hydrogen atoms, hydrogen impurity atoms passivate Zn grain ions, which may also contribute to the increase in carrier concentration.[15] The improvement of crystallinity by annealing, which was confirmed by XRD analysis results (Fig. 1), may also contribute to the increase in carrier mobility, but the contribution seems negligible because both the carrier concentration and mobility of the GZO film annealed in an O_2 atmosphere tend to decrease with increasing annealing temperature, as can be seen in Fig. 3.

Figure 4 shows optical transmittance spectra of GZO thin films annealed in different atmospheres as well as as deposited one. All the annealed GZO thin films have an average transmittance of >80% and one as high as ~90% especially in the visible range. It seems that the



5 *a* plot of α^2 versus photon energy and *b* optical energy band gap values of GZO thin films annealed in different atmospheres, determined by extrapolation of the α^2 versus photo energy curve in Fig. 5*a*

transmittance is improved by annealing regardless of the annealing atmosphere. This improvement in transmittance may be attributed to enhancement in the crystallinity and a decrease in surface roughness. It is well known that annealing TCO films in an oxygen atmosphere improves their transmittance. However, the transmittance of the GZO film annealed in an $N_2+5\%H_2$ or an N_2 atmosphere is also as high as that of the GZO film annealed in an O_2 atmosphere. According to Fig. 4 the average transmittance of the GZO film annealed in an $N_2+5\%H_2$ atmosphere is as high as that of the GZO film annealed in an O_2 atmosphere. The optical transmittance of a film is known to strongly depend on its surface morphology. The increase in transmittance by annealing may be attributed to an increase in the grain size as can be seen in the SEM images (Fig. 2). As the grain size increases, grain boundary scattering is reduced, so that the transmittance is improved. Absorption owing to an interband transition of ZnO occurs in the wavelength range from 340 to 380 nm.

The optical absorption coefficient α of a semiconductor with a direct band gap such as ZnO can be derived using the following equation

$$\alpha = A(h\nu - E_g)^{1/2} \tag{3}$$

where A is the proportional constant, $h\nu$ is the photon energy, and E_g is the optical energy band gap. Thus, the optical band gap can be obtained by extrapolating the linear part of the data line to the $h\nu$ axis and taking the intercept of the data line with the $h\nu$ axis in a plot of α^2 versus $h\nu$. Plots of α^2 versus $h\nu$ for the GZO films annealed at 400°C in different atmospheres and different optical band gap values obtained from this plot are shown in Fig. 5*a* and *b* respectively. The optical band gaps for the GZO films as deposited, annealed in an $N_2+5\%H_2$ atmosphere, and annealed in an O_2 atmosphere are 3·54, 3·32 and 3·40 eV respectively. Therefore, it may be said that annealing in a reducing atmosphere widens the optical band gap, while annealing in an oxidising atmosphere makes the optical band gap narrower.

The phenomenon that the optical band gap increases with increasing carrier concentration is known as the 'blueshift'. Burstein proposed the relationship between the band gap shift ΔE_g and the carrier concentration in the following equation

$$\Delta E_g = h^2 n^{2/3} / (8 m_e^* \pi^{2/3}) \tag{4}$$

where m_e* is the effective mass of the electron, n is the electron concentration, and h is Planck's constant. The optical band gap values obtained from Fig. 5 and the carrier concentration values taken from Fig. 3 for GZO films as deposited and annealed at 400°C in different atmospheres are listed in Table 1. It can be seen that ΔE_g is proportional to log n. Therefore, it can be fairly certain that the GZO films as deposited, and annealed in different atmospheres obey this relationship.

Conclusions

Effects of annealing on the structural, electrical and optical properties of GZO thin films deposited on glass by RF magnetron sputtering were investigated. The crystallinity of GZO films is improved by annealing regardless of the annealing atmosphere, but an (101) diffraction peak besides the an (002) intensity peak newly appears in the XRD patterns of the GZO films annealed in an $N_2+5\%H_2$ atmosphere and an N_2 atmosphere. It is shown that the grain size tends to increase and the surface tends to become rougher as the annealing temperature increases by SEM analysis. The electrical resistivity of a GZO thin film is effectively decreased by annealing in a reducing atmosphere such as $N_2+5\%H_2$. This is attributed to passivation of grain boundaries and zinc ions by hydrogen atoms resulting in increases in carrier concentration and mobility. However, annealing at a temperature >400°C is less effective. The lowest resistivity of $2{\cdot}3\times10^{-4}$ Ω cm is obtained by annealing at 400°C in an $N_2+5\%H_2$ atmosphere. The optical transmittance of the GZO film is improved by annealing regardless of the annealing atmosphere. Annealing in $N_2+5\%H_2$ atmosphere widens the optical band gap, while annealing in an O_2

Table 1 Optical energy band gap values and carrier concentrations for GZO films as deposited and annealed at 400°C in different atmospheres

Sample no.	Annealing atmosphere	E_g, eV	ΔE_g	Carrier concentration n, $\times10^{19}$ cm^{-3}	log n
1	$N_2+5\%H_2$	3·54	0·22	83·1	20·92
2	N_2	3·44	0·12	12·5	20·10
3	As deposited	3·40	0·08	6·25	19·80
4	O_2	3·32	0	2·60	19·42

$\Delta E_g = E_g - E_g(O_2)$.

atmosphere makes the band gap narrower, which can be explained as a blueshift phenomenon.

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