

Effect of the Deposition Temperature and a Hydrogen Post-Annealing Treatment on the Structural, Electrical, and Optical Properties of Ga-Doped ZnO Films

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The combined effects of the deposition temperature and a hydrogen post-annealing treatment on the structural, electrical, and optical properties of Ga-doped ZnO (GZO) films were investigated as a potential substitute for indium tin oxide transparent conductive oxide (TCO). On the as-deposited films, increasing the deposition temperature initially improved the electrical properties, but a deposition temperature in excess of 423 K resulted in the deterioration of the electrical properties due to the development of ZnGa_2O_4 and Ga_2O_3 phases originating from the excessive amount of the Ga dopant. While a post-annealing treatment of the GZO films in hydrogen leveled off the overall properties, improvement in the electrical property was observed only in films initially deposited at room temperature. This is attributed to the excessively high concentration of the dopant Ga released from ZnGa_2O_4 and Ga_2O_3 during the post-annealing treatment. It is therefore suggested that in the preparation of TCOs based on GZO films, the concentration of the dopant Ga should be carefully controlled to obtain the optimal properties by suppressing the formation of ZnGa_2O_4 and Ga_2O_3 that occurs due to the presence of excess Ga. PACS Codes: 68.55.jd; 68.55.Ln; 68.55.J-; 73.61.-r; 78.66.-w; 81.15.Cd

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1. INTRODUCTION

With the widespread use of flat panel displays and other optoelectronic devices, the demand for transparent conductive oxides (TCOs) has grown rapidly. Current TCOs are mostly based on indium tin oxide (ITO) due to factors such as its low electrical resistance, high luminous transmittance, and superior adhesion to substrates.^[1,2] However, both the rising cost of the expensive raw material indium and its toxicity have motivated the development of alternative TCOs to substitute for ITOs. Among many candidate materials, ZnO doped with n-type dopants such as Al have been extensively studied as an alternative to ITO. By doping ZnO with Al, it is possible to achieve electrical and optical properties comparable to those of ITO.^[3,4] In one demonstration, a Al-doped ZnO (AZO) film showed improved operational characteristics that were attributed to significantly lower trap charges in

the interface.^[5] Despite such promising properties, AZO films show relatively low thermal stability and degradation after long-term exposure to air ambient that originates from the high reactivity of aluminum.^[6] Thus, one alternative approach involving the use of Ga-doped ZnO (GZO) has been used recently because Ga has lower reactivity and higher resistance to oxidation as compared to Al while maintaining other desirable properties such as non-toxicity and excellent infra-red shielding.^[7] In addition, the smaller ionic radii of Ga^{3+} compared to Zn^{2+} offer comparably easy site substitution upon doping as well as higher solubility of the dopant in the matrix, which in turn suggest a desirable contribution of conduction electrons to improve the electrical properties.^[7]

One potential difficulty involved in the doping of Ga in ZnO is the formation of undesirable oxide phases such as Ga_2O_3 and ZnGa_2O_4 , which have adverse effects on the electrical properties.^[8,9] It is known that Ga_2O_3 acts as an electron trap^[10] while it is expected that the non-substitutional Ga atoms in ZnGa_2O_4 spinel structure make no contribution to

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the conduction electrons.^[8,11] In this regard, it is of primary importance to obtain GZO films with the highest possible crystalline and structural qualities to realize GZO TCOs as an alternative to AZO as an ITO substitute. In addition to the suppression of the formation of Ga_2O_3 and ZnGa_2O_4 , on the production side, ensuring higher throughput and lower production costs are of equal importance. Therefore, in an effort to establish the simplest route to the realization of GZO TCO with desirable properties, the combined effects of the deposition temperature and post-annealing in a hydrogen atmosphere on the structural, electrical and optical characteristics of GZO TCO films were investigated in this study via RF magnetron sputtering with a single ZnO target with Ga_2O_3 as a dopant source.

2. EXPERIMENTAL PROCEDURE

GZO thin films were deposited on Eagle 2000 glass (Samsung Corning Precision Glass) by RF (13.56 MHz) magnetron sputtering using a ZnO target containing 5 wt. % Ga_2O_3 (99.99%). The glass substrates were cleaned with successive rinses in ultrasonic baths of trichloroethane, acetone, methanol, and deionized water and were blown dry with dry N_2 . The substrates were then loaded in the sputtering chamber which was initially evacuated to a base pressure of approximately 1.3×10^{-4} Pa. The working pressure in the sputter system for the film deposition was maintained at 4.0×10^{-3} Pa with Ar ambient gas (99.999%) at a flow rate of 50 sccm. Before the film deposition, pre-sputtering on the shutter-closed target was carried out for 10 min to remove any contaminants on the target surfaces. GZO films were then deposited at room temperature (RT), 373 K, 423 K, and 573 K with maintaining a target RF power of 100 W. The as-deposited GZO films, after the initial characterizations, were subsequently annealed in a hydrogen atmosphere at 523 K for 30 min in a horizontal tube furnace. This temperature was chosen because it is known as the allowed maximum in typical LCD fabrication processes. The surface morphology of the GZO films was investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM) while the crystallinity and orientation of the films were investigated by x-ray diffraction (XRD) in θ - 2θ scan mode using a Ni-filtered $\text{Cu } K_\alpha$ source with the scanning angle 2θ ranging from 30° to 75° . The electrical and optical properties of the films were measured using the van der Pauw method and using a UV-VIS spectrophotometer in the wavelength range of 250 nm to 800 nm, respectively.

3. RESULTS AND DISCUSSION

Given that the film morphology is one of the most important factors that affect the electrical and optical properties of transparent electrodes, the surface morphology of the GZO

films was evaluated first. Figures 1(a) through (h) show AFM images of the GZO films deposited at various growth temperatures and in different deposited and hydrogen-treated states. These AFM images show that the surface morphologies are fairly similar irrespective of the processing conditions, except for the case of the as-deposited film grown at RT, in which relatively fine surface structures that are possibly related to the fibrous columnar microstructures formed at lower deposition temperatures^[12] can be observed. Regarding the film initially prepared at room temperature, a comparison of the morphological changes in Figs. 1(a) and (e) indicates that the post-annealing treatment in hydrogen ambient pro-

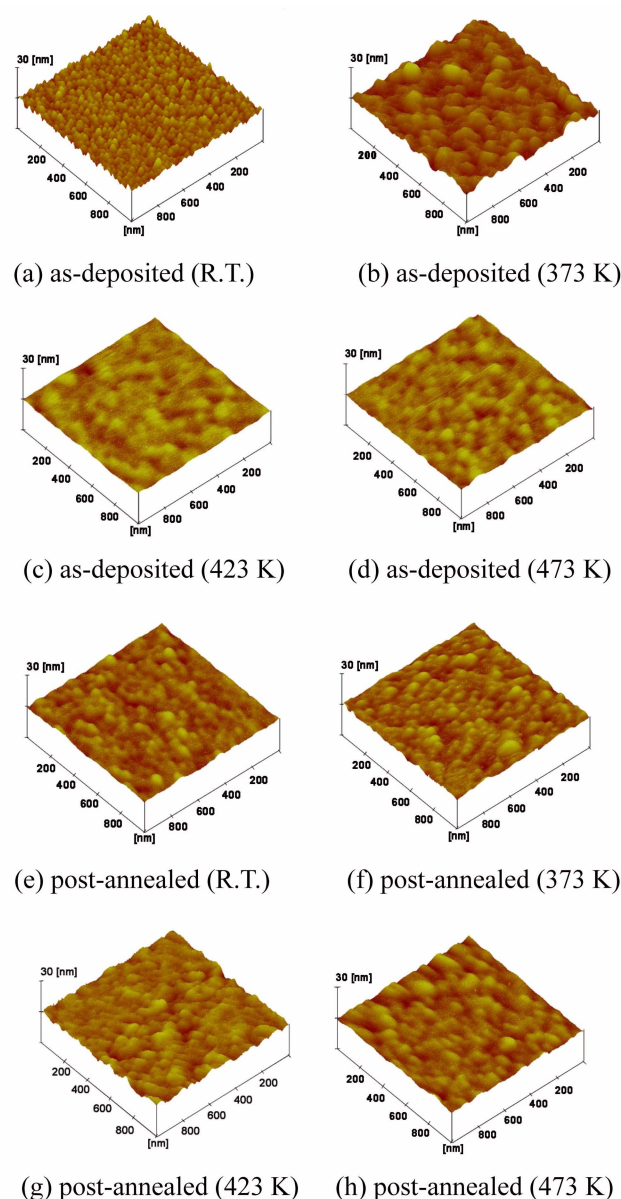


Fig. 1. AFM images of the GZO films in the as-deposited states ((a) through (d)) and post-annealed state ((e) through (h)).

vided the driving force for the lateral growth of the grains to form larger columnar structures. This in turn would result in improved physical properties.

The root mean square (rms) roughness of these films estimated from the AFM observation (Table 1) varies between 0.65 nm and 1.6 nm for the as-deposited films and between 0.81 nm and 0.97 nm for the post-annealed films. It appears that the heat-treatment in hydrogen ambient has leveled off the surface roughness, reducing the differences from 0.95 nm to 0.16 nm. However, considering that the overall thickness of the GZO films prepared in this study are approximately 100 nm, such rms roughness values and their variations are very small. Therefore, it is expected that any variation in the electrical and optical properties between films prepared under different processing conditions may not be due to the changes in the surface roughness.

Having shown that negligible morphological variations occur under different processing conditions, other factors affecting the physical properties of the GZO films were investigated. Figure 2 shows the XRD spectra of GZO films deposited at various temperatures for the as-grown and hydrogen-treated states. The most dominant peaks at $2\theta = 34.3^\circ$ are assigned to the ZnO (002), which is an indication that the GZO films have a hexagonal Wurtzite structure that

forms as a result of the textured growth along the *c*-axis regardless of the processing conditions. However, Figure 2(a) shows that these ZnO (002) peaks are substantially weaker in intensity in the films prepared at RT, even after undergoing a post-annealing treatment, implying that the room-temperature deposition process did not provide a sufficient driving force for the evolution of the crystallinity. In addition to the ZnO (002) peaks, a number of smaller peaks of which the $2q$ values are greater than that of the ZnO (002) can be observed in Fig. 2. The peaks at $2\theta = 37.4^\circ$ and $2\theta = 43.7^\circ$ are assigned to Ga_2O_3 (401) and ZnGa_2O_4 (401), respectively. It is known that when the Ga concentration exceeds a solubility limit of approximately 2.32 wt. %, the Ga_2O_3 phase is formed in the grain boundary regions.^[13] Moreover, some Ga can use non-substitutional octahedral sites to form ZnGa_2O_4 , which has been reported in the fully developed structure of GZO.^[13] These peaks related to the oxide phases are salient for samples deposited at the temperatures higher than room temperature. Furthermore, they are slightly more intense and sharper at a higher deposition temperature, which accompanies the decrease in the intensities of the ZnO (002) peaks. As the Ga concentration of the sputtering target was fixed, such XRD peak changes under a varying growth temperature imply that the dopant Ga would be activated only when relatively high deposition temperatures are adopted.

The crystallinity of the GZO films underwent various changes after the post-annealing treatment in the hydrogen atmosphere, as shown in Fig. 2 (b). The ZnO (002) peaks become more intense while the oxide phase peaks become weaker in intensity. Particularly, the ZnGa_2O_4 (401) peaks decreased substantially in the post-annealed samples. These changes in the oxide-related peaks indicate that the post-

Table 1. RMS roughness of the Ga-doped ZnO films

Deposition Temperature	RMS roughness (nm)	
	as-deposited	post-annealed
R.T.	1.36	0.81
373 K	1.60	0.90
423 K	0.81	0.97
473 K	0.65	0.89

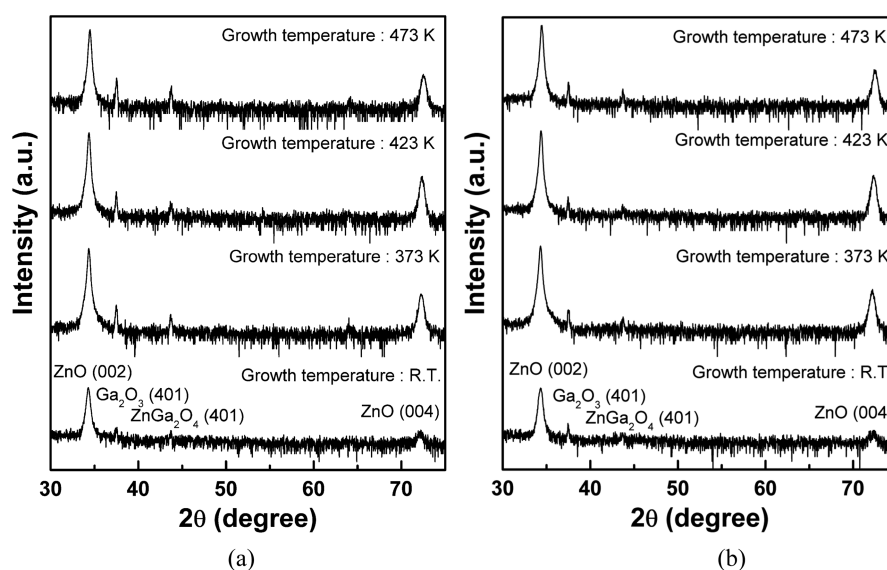


Fig. 2. XRD patterns of the GZO films (a) before and (b) after the post-annealing treatment in hydrogen.

annealing treatment in the hydrogen atmosphere decomposed the oxide phases while improving the crystalline quality of the ZnO phase. It is deduced that the decomposition of the oxide phases, ZnGa_2O_4 and Ga_2O_3 , is related to their reduction by the hydrogen atmosphere. The reduction of these oxides would then release the excess Ga, which will then contribute carrier electrons if properly located within the ZnO lattice.

Using the ZnO (002) peaks in Figs. 2(a) and (b), the average grain sizes of the GZO films were estimated using the Scherrer formula^[14]:

$$t = \frac{0.9\lambda}{B \cos \theta} \quad (1)$$

Here, t is the estimated average grain size, λ is the x-ray wavelength, B is the full width at half maximum (FWHM) of the peak, and θ is the Bragg angle. The estimated values of the grain sizes with corresponding values of B for both as-deposited and post-annealed samples are shown in Fig. 3. It can be seen that in the as-deposited films, shown in Fig. 3(a), the average grain size tends to increase from 25.8 nm to 39.7 nm with deposition temperatures ranging from RT to 423 K due to the increased surface adatom mobility at the higher growth temperature, which is typical in the evolution of the film morphology during a sputter deposition process according to the Thornton model.^[15] A slight decrease in the grain size with a deposition temperature higher than 423 K appears to be related to the excessive formation of ZnGa_2O_4 and Ga_2O_3 phases, which may hinder the grain growth. After the post-annealing treatment in hydrogen, the average grain sizes of the films initially deposited at RT and 373 K decreased slightly compared to those of the as-deposited films shown in Fig. 3(b), whereas those of the films deposited at 323 K and 473 K remained almost unchanged. In the case of the films deposited at relatively low temperatures, post-annealing at 523 K could have densified the microstructures while the

hydrogen provided a reducing ambient atmosphere to decompose ZnGa_2O_4 and Ga_2O_3 . It is believed that such a combined effect resulted in microstructural changes that decreased the grain sizes in these films. The FWHM grain size results shown in Fig. 3 reflect the observations in the AFM images in Fig. 1.

Changes in the crystalline quality under a varying deposition temperature and after post-annealing in a hydrogen atmosphere are well correlated to the electrical properties of the GZO films. Figure 4(a) shows how the concentration and mobility of carrier electrons and the resulting resistivity of the as-deposited films change after increasing the deposition temperature. First, it is seen that the carrier mobility increases substantially as the deposition temperature increases to 423 K, which is well correlated to the improving crystallinity shown at a higher intensity and decreasing FWHM of the ZnO (002) peak shown in Figs. 2(a) and 3(a), respectively. With a higher deposition temperature of 473 K, the mobility is now decreased. This is related to the intensified Ga_2O_3 (401) peaks in Fig. 2 (a), which indicate the increased grain boundary segregation of Ga_2O_3 in the ZnO matrix.^[16,17] It is expected that this grain boundary phase will act as carrier traps or as obstacles to carrier transport. Furthermore, at a higher temperature, it is expected that the dopant element Ga will be highly activated and will then act as scattering centers for carrier electrons, as in the case of many heavily doped semiconductors.^[18,19] Thus, such enhanced activation efficiency of dopant Ga as the growth temperature increases can be supported by the increased carrier concentrations at temperatures ranging from RT to 423 K shown in Fig. 4(a). However, at a deposition temperature of 473 K, the carrier concentration decreases slightly, suggesting that the intensifying ZnGa_2O_4 (400) peak is caused by the incorporation of Ga at the non-substitutional octahedral sites of its spinel structure. As ZnGa_2O_4 has a band gap energy of approximately 5 eV (indicating that it is an insulator), it is expected that the non-substitutional Ga does not contribute to the con-

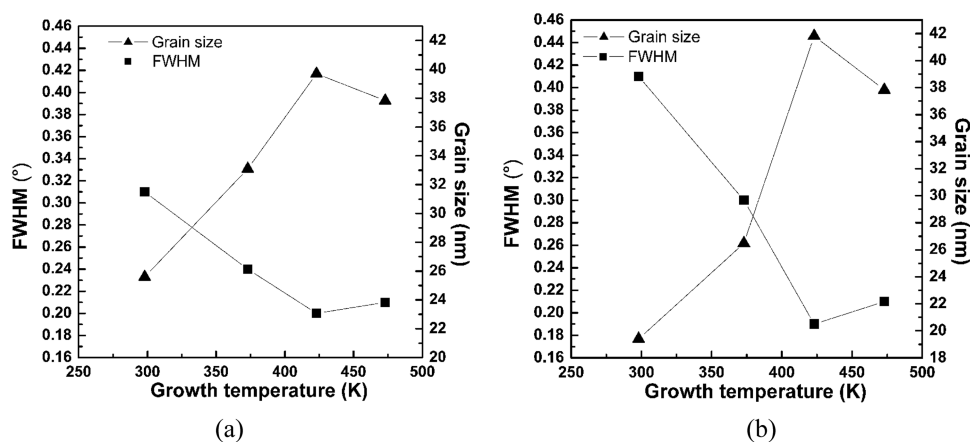


Fig. 3. FWHM of the main XRD peak and corresponding grain sizes of the GZO films (a) before and (b) after the post-annealing treatment in hydrogen.

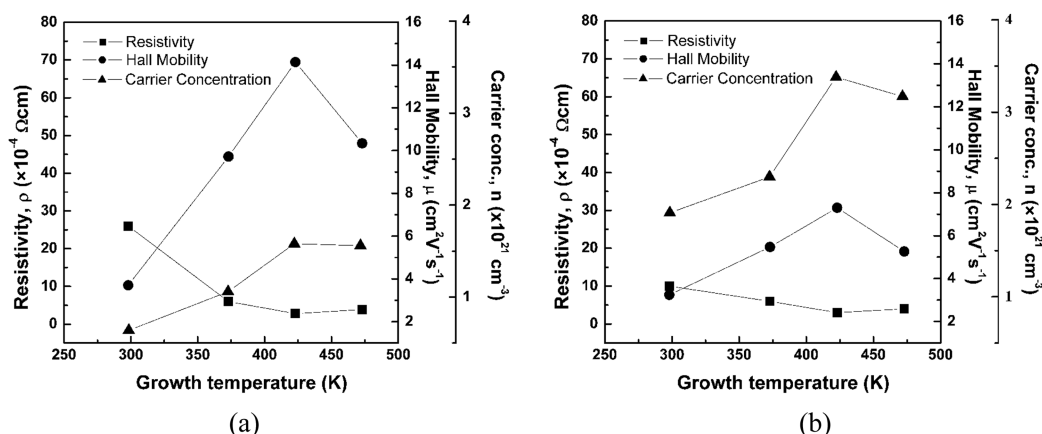


Fig. 4. Comparison of the electrical properties of (a) as-deposited and (b) hydrogen-annealed GZO films deposited at various substrate temperatures.

duction of the carriers.^[8] As a result of these combined effects, the electrical resistivity decreases from $2.6 \times 10^{-3} \text{ W cm}$ (for the film deposited at RT) to approximately $3.0 \times 10^{-4} \text{ W cm}$ (for the film deposited at 423 K) and then increases slightly to $4.2 \times 10^{-4} \text{ W cm}$ (for the film deposited at 473 K).

After the post-annealing treatment in a hydrogen atmosphere, the electrical properties of the GZO films changed somewhat, as shown in Fig. 4(b). First, a comparison between Figs. 4(a) and (b) shows that the carrier concentrations of the post-annealed films are all higher than those of their as-deposited counterparts while maintaining the same variation trend with respect to the initial deposition temperature. Referring to the changes in the XRD patterns before and after the post-annealing process, as shown in Figs. 2(a) and (b), the increase in the carrier concentration for the samples grown at deposition temperatures ranging from RT to 423 K can be attributed to the reduction of the oxide phases during the hydrogen treatment, through which reduced Ga atoms can diffuse into the ZnO matrix to function as an *n*-type dopant. Thus, the carrier concentrations range from 2.0×10^{21} to $3.4 \times 10^{21} \text{ cm}^{-3}$ in the post-annealed films, whereas these values are between 6.0×10^{20} and $1.6 \times 10^{21} \text{ cm}^{-3}$ in the as-deposited films. On the other hand, mobility is reduced after the post-annealing treatment by approximately 50%, but not in the films initially deposited at RT, in which case it decreases slightly. Regarding the variation in mobility during the annealing process, two factors can be considered. The first is the decreased amount of the secondary phase, in this case Ga_2O_3 due to the reduction in hydrogen, which contributes to the increased mobility by reducing the number of carrier traps or obstacles to carrier motion. On the other hand, a reduction of Ga_2O_3 as well as ZnGa_2O_4 releases elemental Ga into the ZnO matrix to increase the carrier concentration. As these Ga-doped films are essentially heavily doped semiconductors, it is natural that an increased carrier concentration above a certain level would reduce the mobil-

ity.^[20] In the present case, it is believed that the latter effect overwhelmed the former effect in the films initially deposited at 373 K and at higher temperatures. Consequently, the electrical resistivity decreased after the hydrogen treatment only in the films deposited at RT. In other films, the electrical resistivity remained practically unchanged.

The results discussed above regarding the electrical properties of GZO suggest that the benefits of a post-annealing treatment in hydrogen are expected only in samples prepared at RT in which the crystallinity of ZnO is not fully developed and the concentration of the dopant Ga is expected to be lower. In samples prepared at higher temperatures, hydrogen indeed serves as a reducing agent that decomposes Ga_2O_3 and ZnGa_2O_4 to release Ga into the ZnO matrix, as revealed in the reduced intensities of the XRD peaks of these oxides (Fig. 2(b)) and the increased carrier concentrations (Fig. 4(b)) after the post-annealing treatment. However, such effects are nullified by the decreased mobility of the carrier electrons, which is attributable to the excessively high concentration of activated Ga. Therefore, it is concluded that in the preparation of the GZO films in which their electrical properties are to be improved by post-annealing in hydrogen, care must be taken in the determination of the optimal Ga concentration such that the formation of secondary oxide phases is suppressed and that not too much activated Ga is present in the ZnO lattice so as to reduce the mobility.

Changes in the carrier densities in relation to the various deposition conditions are reflected in the optical properties, which have equal importance to the electrical properties in display applications of TCOs. In Fig. 5, the optical properties related to the transmittances of the GZO films prepared under various conditions are compared. This figure shows that all of the films have transmittances over 90% that of glass in the visible light range, hence fulfilling the basic requirement for display applications. It is also shown that the transmittance levels of the as-deposited films are improved

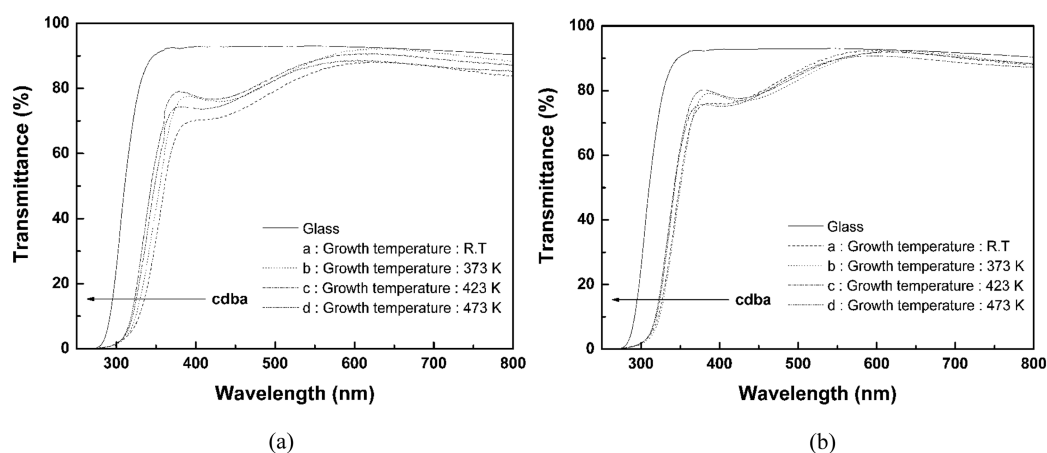


Fig. 5. Comparison of the optical properties of (a) as-deposited and (b) hydrogen-annealed GZO films deposited at various substrate temperatures.

slightly with a higher deposition temperature (Fig. 5(a)). This is attributable to the improved crystalline quality, as revealed in the XRD patterns shown in Fig. 2(a). On the other hand, hydrogen-treated films show nearly identical transmittance properties regardless of the initial deposition temperature, indicating the leveling of the crystalline quality during the post-annealing treatment.

Regarding the optical band gap, in case of the as-deposited films, it increases from nearly 3.8 eV to 3.94 eV as the deposition temperature increases to 423 K and then decreases to 3.93 eV with a further increase in the deposition temperature to 573 K. The same trend is observed in the post-annealed films, although the difference in the optical band gap is smaller. Such changes in the optical band gaps under varying deposition temperatures are well correlated to the changes in the carrier concentrations shown in Fig. 4; i.e., the optical band gap rises with higher carrier concentrations. This blue-shift in the optical band gap with an increasing carrier concentration is understood in the context of the Burstein-Moss effect, which states that the highest occupied level or Fermi level in the conduction band increases with a higher concentration of the carrier electrons, which leads to band gap broadening.^[21,22] However, assuming the relationship $\Delta E_g \sim n_e^x$, fitting the relationship between the band gap shift ΔE_g and the carrier concentration n_e causes the exponent x of n_e to be 0.296 and 0.165 for the as-deposited and post-annealed films, respectively (graph not shown). These exponents are substantially different from the exponent value of 0.667 given by the equation^[5]

$$\Delta E_g = \frac{h^2}{8m^*} \left(\frac{3}{\pi} \right)^{2/3} n_e^{2/3} \quad (2)$$

where h is the Planck's constant and m^* is the effective mass of the carrier. These large differences in the exponent of n_e between the curve-fitting and Eq. 2 imply that the depen-

dence of the changes in the optical band gap energy on the carrier concentration and the resulting Fermi level shift are not large. Instead, it is expected that the relative amounts of the insulator phases of ZnGa_2O_4 and Ga_2O_3 , which have band gap energy levels that are higher than ZnO, would affect the varying optical band gap, which again implies that the amounts of these oxide phases are not negligible, even after post-annealing in hydrogen.

4. CONCLUSIONS

In an effort to develop alternative TCO films that can substitute for ITO, the combined effects of the deposition temperature and a hydrogen post-annealing treatment on the structural, electrical, and optical properties of sputtered GZO films were investigated. The overall properties of the films fulfill the basic requirements for TCOs in display applications, especially in terms of the electrical and optical properties. The lowest resistivity of $2.9 \times 10^{-4} \text{ Wcm}$ at a carrier concentration of $3.4 \times 10^{21} \text{ cm}^{-3}$ was achieved while the transmittance relative to glass was about 90%. However, experimental observation suggests that the oxide phases of Ga_2O_3 and ZnGa_2O_4 cannot be completely eliminated by reduction during a post-annealing treatment in hydrogen once they are formed due to the presence of excess Ga dopant. Furthermore, reduction of these oxide phases did not result in an improvement of the electrical resistivity, except for films that were initially deposited at RT, although the overall properties eventually “leveled off” to a certain degree after the post-annealing treatment most likely due to the very high concentration of dopant Ga. Considering that the GZO for TCO applications is essentially heavily doped semiconductor and that both Ga_2O_3 and ZnGa_2O_4 are easily formed in GZO, the experimental results of this study suggest that the concentration of Ga should be controlled carefully during the preparation of TCOs based on GZO films.

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