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Electrical and optical properties of gallium-doped zinc oxide films deposited by dc magnetron sputtering

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Abstract

Gallium-doped zinc oxide (GZO) films were deposited by dc planar magnetron sputtering using a GZO ceramic target. Deposition was carried out under various conditions of substrate temperature (RT–700 °C), residual water pressure (1.61×10^{-4}–2.2×10^{-3} Pa), and $H_2/(Ar+H_2)$ flow ratio (0–15%). A relatively low resistivity of 5×10^{-4} Ω cm was obtained for films deposited at 400 °C, attributed to an increase in carrier density and Hall mobility. In the case of 100% Ar gas, the grain size and electrical properties of the GZO films deposited on RT substrates were heavily affected by residual water pressure in the deposition chamber. The resistivity increased from 3.0×10^{-3} to 3.1×10^{-2} Ω cm and the grain size of the films decreased from 24 to 3 nm when the residual water pressure was increased from 1.6×10^{-4} to 2.2×10^{-3} Pa. However, the introduction of H_2 to decrease the resistivity resulted in a decrease of grain size in proportion to H_2 flow ratio.

Keywords: Gallium-doped zinc oxide; Hydrogen introduction; dc Magnetron sputtering; Residual water pressure; Transparent conductive oxide

1. Introduction

Transparent conductive oxides (TCOs) have a range of highly useful applications such as transparent electrodes in opto-electronic devices [1]. Most previous research on TCO films has focused on ITO or SnO_2, however recently, TCO films based on zinc oxide (ZnO) have been promoted as promising alternatives of ITO and SnO_2 films, with advantages of low cost, resource availability, and nontoxicity [2,3]. Furthermore, the ZnO-based TCO films are more durable than to the SnO_2- or In_2O_3-based films in the presence of hydrogen plasma [4,5]. Stoichiometric non-doped ZnO films usually have high resistivity due to the low carrier density. Al, In and Ga have been reported to be effective for the carrier generation in ZnO films as the dopants. The Al-doped ZnO films (AZO) have typically been prepared by metal organic chemical vapor deposition [6], evaporation method [7] or magnetron sputtering [8]. However, there have been few reports on the deposition of Gallium-doped zinc oxide (GZO) films by dc magnetron sputtering which is expected to be suitable for large-area uniform coatings.

In this study, GZO films were deposited by dc magnetron sputtering using a GZO ceramic target under various deposition conditions of substrate temperature (T_s) and water partial pressure (P_{H_2O}). The crystallinity and electrical properties of the GZO films were analyzed in detail and the effects of H_2 introduction to the deposition process were investigated.

2. Experimental details

GZO films of thickness 290–330 nm were deposited on #7059 glass, SiO_2-coated Si, and fused silica glass substrates by dc magnetron sputtering using a ceramic oxide target (5.7 wt.% Ga_2O_3, Asahi Glass Co. Ltd). Substrate temperature (T_s) was controlled during deposition in the range from RT to 700 °C. Sputtering was carried out under a total gas pressure of 1.0 Pa of Ar with 0–15% H_2. The films were then deposited under various residual water partial pressures (P_{H_2O}: 1.6×10^{-4}–2.2×10^{-3} Pa). P_{H_2O} were monitored using a quadrupole mass spectrometer (Transpector XPR2,

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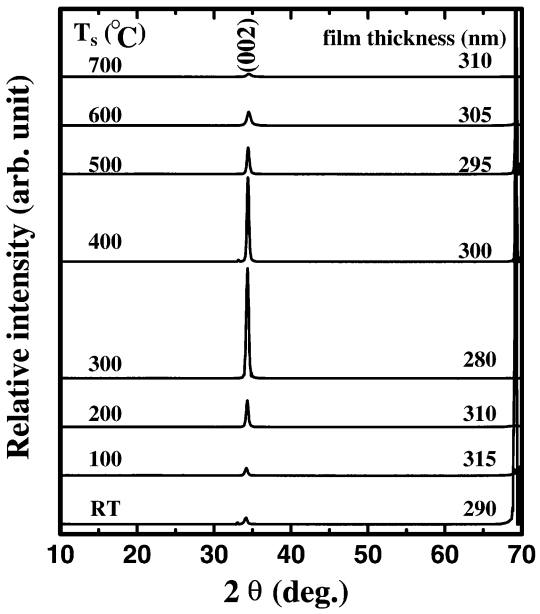

Fig. 1. XRD patterns for GZO films deposited on SiO_2-coated Si substrates at various substrate temperatures (T_s) in 100% Ar gas.

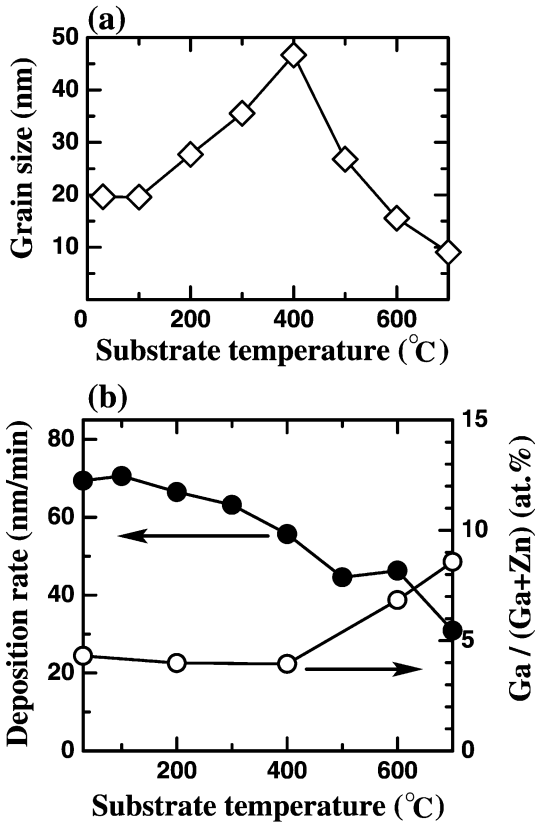

Fig. 2. (a) Grain size and (b) deposition rate and concentration ratios of Ga/(Zn+Ga) of GZO films deposited on SiO_2-coated Si substrates at various substrate temperatures (T_s) in 100% Ar gas.

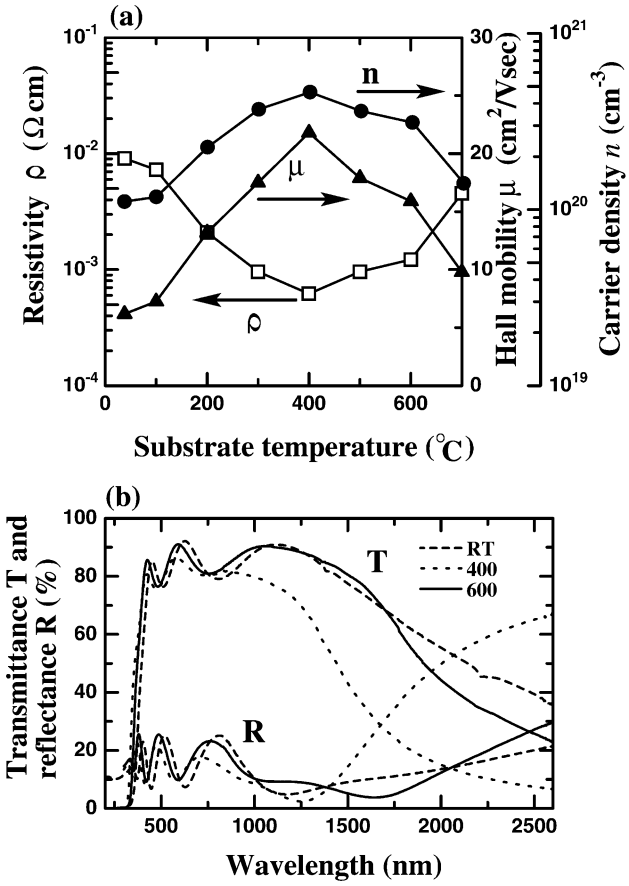

Fig. 3. (a) Room temperature resistivity (□), carrier density (●), and Hall mobility (▲) and (b) transmittance and reflectance of GZO films deposited at various substrate temperatures (T_s) in 100% Ar gas.

Inficon) and it was controlled by base pressure. The distance between the target and the substrate was 45 mm, and dc sputtering power was maintained at 100 W for all depositions. Film thickness was measured using a surface profiler (Dektak 3, Sloan Tech.), and X-ray diffraction (XRD) patterns were obtained with 40 kV–20 mA CuK_α radiation (XRD: 6000, Shimadzu). Precise XRD measurements were performed in step-scan mode at a step interval of 0.01° in order to estimate the grain size from the FWHM of the XRD peaks by the Scherrer method [9]. The atomic concentrations of Zn and Ga in the GZO films were estimated by X-ray photoelectron spectroscopy (XPS, ESCA 750, Shimadzu). Before XPS analysis, the sample surface was ion-etched by Ar^+ sputtering for 3 min with an acceleration voltage of 1 kV and beam current of 10 mA. The resistivity (ρ), Hall mobility (μ) and free carrier density (n) were estimated by the four-point probe method and Hall-effect measurement in the van der Pauw geometry (HL 550PC, Bio-rad). The optical transmission and reflection of the films were measured using a UV–VIS–NIR spectrophotometer (UV-3150, Shimadzu).

3. Results and discussion

Fig. 1 shows the XRD patterns of GZO films deposited on SiO_2-coated Si substrates in 100% Ar gas at various substrate temperatures (RT–700 °C). All films exhibited ZnO-polycrystalline structure with ⟨0 0 1⟩ preferred orientation. The intensity of the (0 0 2) peak increased remarkably for the films deposited at 300 and 400 °C, but the peak intensity decreased with further increase in T_s (500–700 °C). Fig. 2 shows (a) grain size and (b) deposition rate and concentration ratio of Ga/(Zn+Ga) in GZO films deposited in 100% Ar gas as a function of T_s. The grain size increased from 19 to 47 nm when T_s was increased from RT to 400 °C, then decreased at higher T_s. The concentration of Ga showed no clear changes in the T_s range from RT to 400 °C, and then increased remarkably for the films deposited at T_s higher than 400 °C. It is considered that the decrease in the concentration of Zn is attributable to the higher vapor pressure of Zn than the one of Ga at the same temperature, which should result in the decrease in the grain size of the films deposited at T_s higher than 400 °C. Therefore, the remarkable decrease in deposition rate at the higher T_s could be also related to the higher vapor pressure of Zn, which gives rise to partial re-evaporation of Zn atoms [10].

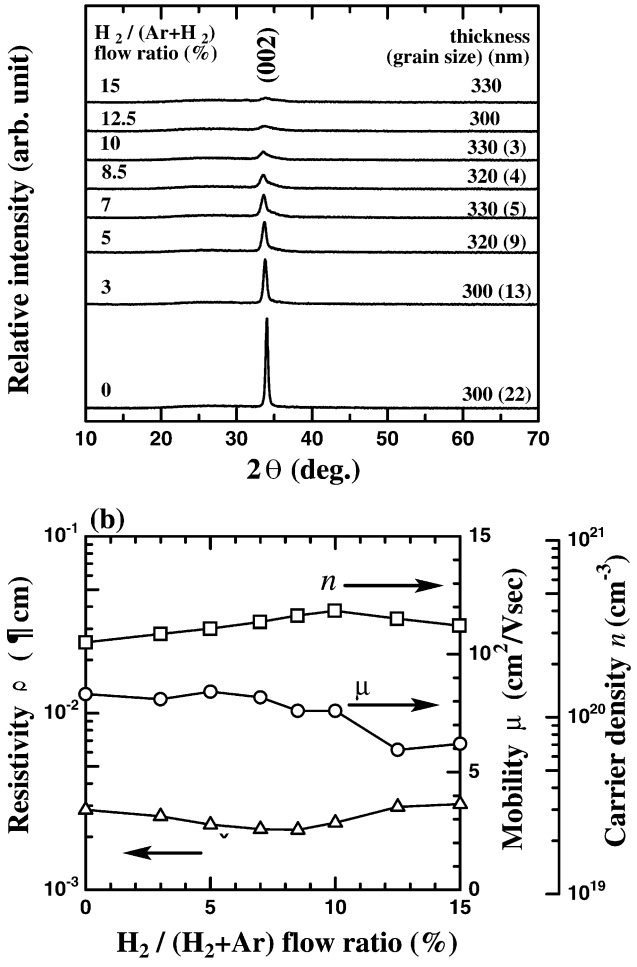

Fig. 4. (a) XRD patterns and (b) electrical properties (resistivity △, carrier density □, Hall mobility ○) for GZO films deposited on RT substrate at various H_2 flow ratios.

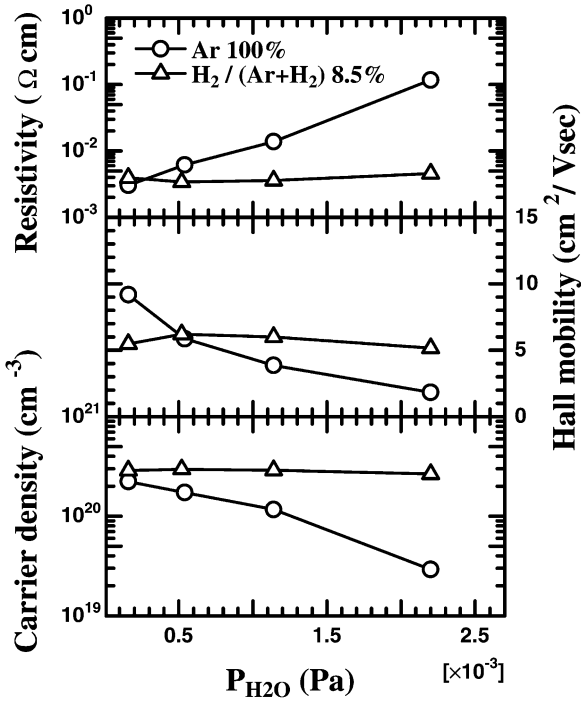

Fig. 5. Room temperature resistivity, carrier density and Hall mobility of GZO films deposited on RT substrate under various H_2O partial pressures (P_{H_2O}) using 100% Ar gas (○) or mixture gases of Ar+H_2 (H_2: 8.5% (△)).

Fig. 3 shows (a) room temperature resistivity ρ, free carrier density n, Hall mobility μ and (b) transmittance (T), reflectance (R) of the GZO films deposited at various T_s. Both n and μ increased with increase in T_s from RT to 400 °C, and the film deposited at 400 °C exhibited the lowest resistivity of 5×10^{-4} Ω cm. At T_s higher than 400 °C, resistivity increased significantly along with the decrease of n and μ. The variation of μ can be explained by grain boundary scattering [11,12], because mean free path of free electrons approximately corresponds to the grain size. All films exhibited high transmittance (85–90%) in visible light (550 nm). The film deposited at 400 °C had relatively lower transmittance and higher reflectance in near-infrared region, which can be explained by the increase in plasma frequency (ω_p) of free carriers with increasing n [13].

Fig. 4 shows (a) XRD patterns and (b) resistivity, carrier density and Hall mobility for GZO films deposited with Ar+H_2 mixed gas and without substrate heating. The intensity of (0 0 2) XRD peak decreased systematically with the increasing H_2 flow ratio. The μ remained relatively constant for the films deposited at a flow ratio of $H_2/(Ar+H_2)$ lower than 10%, but decreased at higher flow ratios. The n increased steadily with $H_2/(Ar+H_2)$ up to 10%, which could be attributed

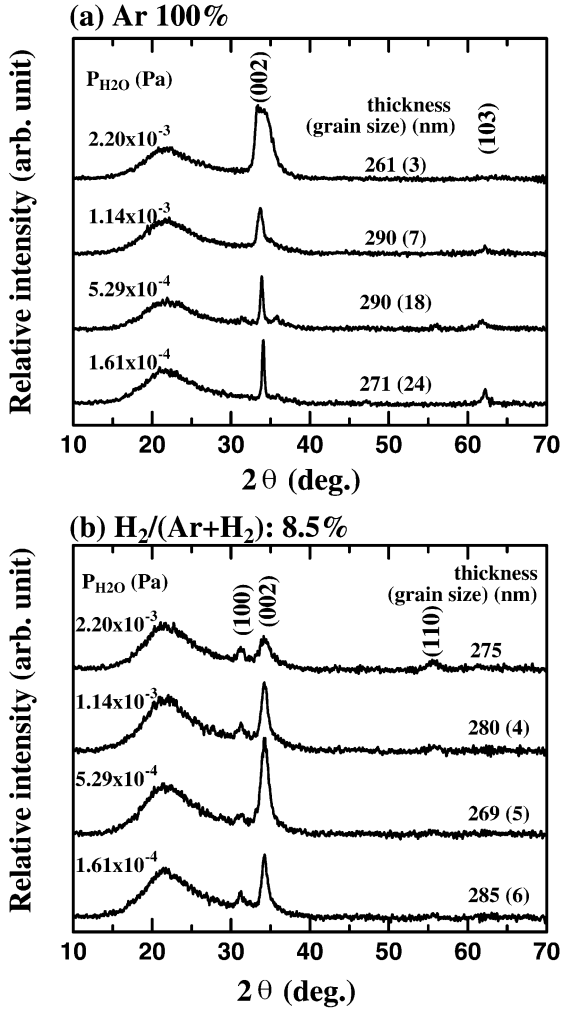

Fig. 6. XRD patterns of GZO films deposited on RT substrate under various H_2O partial pressures (P_{H_2O}) in (a) 100% Ar gas and (b) mixture gases of $Ar+H_2$ (H_2: 8.5%).

to an increase in oxygen vacancies, and then decreased at $H_2/(Ar+H_2)$ higher than 10%. Resistivity decreased gradually with increasing $H_2/(Ar+H_2)$ up to 8.5% because of the increase in n, while ρ increased at $H_2/(Ar+H_2)$ higher than 10% due to decreasing n and μ.

Fig. 5 shows the variation in ρ, n and μ for the GZO films deposited at T_s = RT under various partial pressure of water (P_{H_2O}) in 100% Ar or $Ar+H_2$ (H_2: 8.5%). With increasing P_{H_2O}, ρ of the GZO films deposited in 100% Ar increased remarkably due to decreases in both n and μ. Such degradation in ρ with increase in P_{H_2O} was not observed when the films were deposited at T_s = 400 °C. The GZO films deposited at T_s = RT in the presence of H_2 gas exhibited no changes in ρ, n and μ with increasing P_{H_2O}. As for the variation of n, the H_2 introduction has a possibility to suppress the carrier traps at the crystal defects, probably by the relaxation of defect levels, similar to H termination at the dangling bond in a Si:H [14]. The logarithm plotting of the absorption coefficient versus energy showed clear decrease in 'Urbach tail' for the films deposited with the H_2 introduction, however further investigation should be necessary for the conclusive discussion. Fig. 6 shows the XRD patterns for the GZO films deposited at various P_{H_2O} in (a) 100% Ar gas and (b) mixtures of $Ar+H_2$ (H_2: 8.5%). In the case of 100% Ar, the intensity of the (0 0 2) peak decreased gradually and grain size decreased clearly from 24 to 3 nm as P_{H_2O} increased from 1.61×10^{-4} to 2.2×10^{-3} Pa. The absorption of H_2O molecules at the growing film surface caused the decrease in the grain size, leading to the increase in secondary nucleation density. The decrease in μ could be explained by the decrease in grain size. In the presence of H_2, the decrease in grain size was only 6–4 nm over the same P_{H_2O} range, which corresponds to the almost constant μ. The films deposited in $Ar+H_2$ exhibited smaller grain size than those deposited in Ar under the same P_{H_2O}.

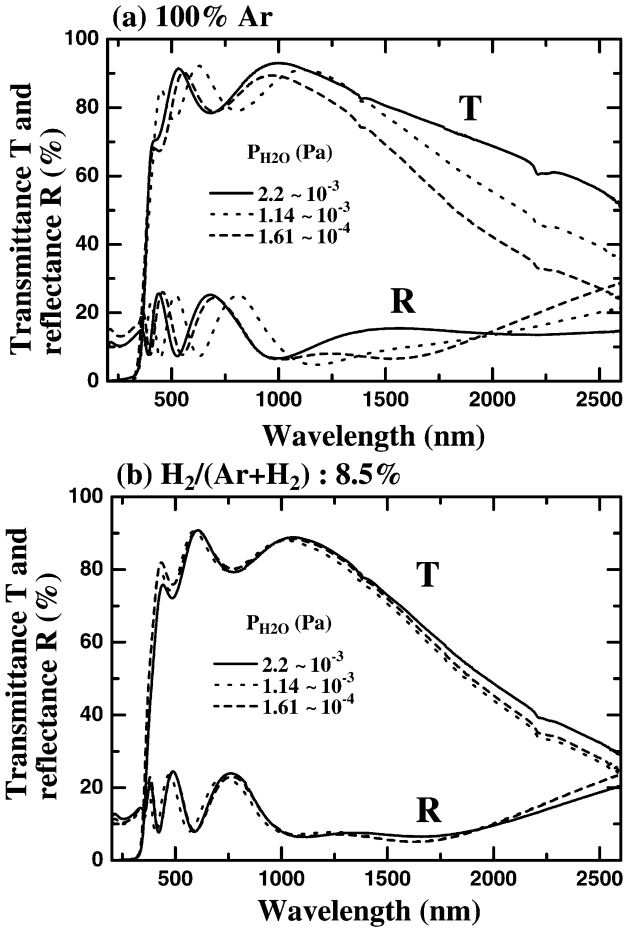

Fig. 7. Transmittance (T) and reflectance (R) of GZO films deposited under various H_2O partial pressures (P_{H_2O}) in (a) 100% Ar gas and (b) mixture gases of $Ar+H_2$ (H_2: 8.5%).

Fig. 7 shows the transmittance and reflectance of the GZO films deposited using (a) 100% Ar and (b) Ar+H_2 (H_2: 8.5%) as a function of P_{H_2O}. The near-infrared transmittance of the films deposited in 100% Ar decreased with decreasing P_{H_2O}, whereas the transmittance of films deposited in Ar+H_2 remained unchanged. These changes in the optical properties are consistent with the changes in electrical properties, where the decrease in near-infrared transmittance corresponds to an increase in carrier density.

4. Summary

GZO films deposited at 400 °C in 100% Ar gas exhibited relatively large grain size and low resistivity as a result of the high carrier density and Hall mobility. The resistivity of GZO films deposited on RT substrate in 100% Ar gas increased drastically with increasing water partial pressure (P_{H_2O}) of residual gas, due to a decrease in both carrier density and Hall mobility.

On the other hand, the electrical properties of the GZO films deposited in Ar+H_2 mixture were improved, even though the grain size of film was degraded in proportion to the H_2 flow ratio. A lower resistivity was obtained for the films deposited at an H_2 flow ratio of 8.5%. Moreover, the GZO films deposited with H_2 exhibited no degradation in the electrical properties (resistivity, carrier density and Hall mobility) with increasing P_{H_2O}, even though the crystallinity of the films became poorer with increasing P_{H_2O}.

Acknowledgments

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