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Influence of thermal annealing on electrical and optical properties of Ga-doped ZnO thin films

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ABSTRACT

Influence of thermal annealing on electrical properties of GZO films has been studied by means of Hall effect measurements and optical characterization based on Drude model analysis for transmission and reflection spectra. Electrical resistivity increased with increasing annealing temperature. Changes of electrical properties were compared between air and N_2 gas atmosphere. Thermal stability in the air was worse compared to the N_2 gas atmosphere. Annealing at rather high temperature caused decrease in the Hall mobility and increase in optical mobility. The difference between the Hall mobility and the optical mobility was attributed to carrier scattering at grain boundaries. Three kinds of deposition method, ion plating using DC arc discharge, DC magnetron sputtering, and RF power superimposed DC magnetron sputtering were compared in terms of the thermal stability.

1. Introduction

Transparent conductive oxides (TCO) are an essential material in the opt-electrical devices as transparent electrodes. Indium-tin-oxides (ITO) presently used in industry as transparent electrodes have some concerns regarding its future availability, instable supply, and increased cost of indium. Accordingly, requirement for development of substitute materials for ITO is growing. Ga-doped ZnO (GZO) has attracted much attention because of its low resistivity, high transparency and nontoxicity [1–3]. Low resistivity polycrystalline GZO films have been successfully deposited on glass substrates by ion plating [2–4], magnetron sputtering [5–7], pulsed laser deposition (PLD) [8–10], and metal-organic chemical vapor deposition [11]. However, from view points of practical applications of GZO films, there are still some problems to be solved. One of the issues is thermal stability.

In this study, we aimed application of GZO films as common transparent electrodes on color filters in liquid crystal displays (LCD). Low temperature depositions are required for the common electrodes on color filter, normally consists of organic materials. During fabrication process of LCD panels, the electrodes are generally exposed to some process temperature higher than the deposition temperature. So far, we have studied thermal stability of GZO films in N_2 gas atmosphere [12]. However, thermal stability in air is important for the practical fabrication of LCD panels. In the case of Al-doped ZnO films, thermal stability in air ambient was worse compared to in Ar gas atmosphere [13]. Thermal instability of Ga related donors in GZO films in oxidizing atmosphere was also reported by Sans et al. [14]. In this paper, we report influence of thermal annealing in air and in N_2 gas atmosphere on electrical properties of GZO films.

2. Experimental

150 nm thick GZO films were deposited on alkali-free glass substrates by an ion plating (IP) method with direct current arc discharge, direct current magnetron sputtering method (DC-MS), and radio frequency power superimposed direct current magnetron sputtering method (RF/DC-MS). Considering thermal stability of color filters, the films were deposited at a substrate temperature of 150 °C. In the IP method, a sintered ZnO target containing 4 wt.% Ga_2O_3 was used as starting material. Using the ceramic target, we have obtained the lowest resistivity [15]. On the other hand, a ZnO ceramic target containing about 5 wt.% Ga_2O_3, which was suitable Ga concentration to obtain low resistivity in our sputtering system, was used in both DC-MS and RF/DC-MS deposition methods. In order to examine thermal stability, the GZO films were annealed in air or in pure N_2 gas (purity: 99.9995%) atmosphere for 30 min at annealing temperatures, T_{an}, between 200 and 450 °C.

Electrical properties of films were characterized by Hall effect measurements in the van der Pauw geometry at room temperature. Optical transmission (T) and reflection (R) spectra were measured by an ultraviolet to near infrared spectrophotometer (HITACHI, U4100) with an angle of incidence for light at 5°.

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3. Results and discussion

Electrical properties of as-deposited films prepared by IP, DC-MS, and RF/DC-MS methods were summarized in Table 1. The resistivity of the films deposited by the IP method was lower than the films deposited by the sputtering methods. The Hall mobility of the GZO films deposited by IP is higher than that of sputtering methods. The difference in the Hall mobility can be tentatively attributed to the different crystallinity of GZO films. The carrier concentration of GZO films deposited by RF/DC-MS was higher than that of DC-MS. Since the target with same doping concentration of Ga was used in both cases, the difference in the carrier concentration was possibly caused by some intrinsic defects in the GZO films.

Fig. 1(a) shows change of resistivity of GZO films deposited by the IP after annealing in air and in the N_2 gas atmosphere. We can see that the resistivity was stable or slightly decreased up to 350 °C with increasing the T_{an} in N_2 gas atmosphere. Then the resistivity turned to increase beyond the critical temperature of 350 °C, and it drastically increased at the T_{an} of 450 °C. This behavior is consistent with the previously reported results in GZO films deposited by the IP at a slightly higher substrate temperature of 200 °C [12]. In the case of annealing in air, the critical temperature was slightly lower compared to the case of N_2 gas atmosphere. As shown in Fig. 1(b), the resistivity was stable up to 230 °C. Then, it increased with increasing the T_{an} beyond the critical temperature of 230 °C.

In order to get insight into the difference between air and N_2 gas atmosphere, the Hall mobility, μ_{Hall}, and carrier concentration, N_{Hall}, were plotted on Fig. 1(b). In the case of N_2 gas atmosphere, the μ_{Hall} increased with increasing the T_{an} up to 400 °C, while the N_{Hall} decreased in this range. By the annealing at 450 °C in N_2 gas atmosphere, both the μ_{Hall} and N_{Hall} drastically decreased. These observations were also consistent with our previous report [12]. The change of electrical properties below 400 °C has been discussed in relation with desorption of interstitial Zn from GZO films [12,16]. In addition, segregations of Ga at grain boundary was observed after annealing at 600 °C in N_2 gas atmosphere, and the segregation was proposed as one of degradation processes of electrical properties in the GZO films [12].

In the case of annealing in air, changes in electrical properties were basically similar to the case of N_2 gas atmosphere except the lower critical temperature at which the resistivity started to increase. The μ_{Hall} increased and the N_{Hall} decreased with increasing the T_{an} up to 300 °C, and both the μ_{Hall} and the N_{Hall} drastically decreased at the T_{an} higher than 300 °C. Considering the previously reported phenomena observed in the case of N_2 gas atmosphere [12], one possible explanation is that oxygen in air might encourage desorption of Zn and segregation of Ga at grain boundary. However, it has been discussed that excess oxygen causes degradation in electrical properties in ZnO based TCOs [17,18]. This is believed to be due to adsorption of oxygen at the grain boundary which traps carrier and reduces the mobility. While, Sans et al. reported segregation of Ga in other crystalline structures, like as spinel $ZnGa_2O_4$, after air annealing of GZO films deposited by PLD [14].

In either case on annealing in the air and in the N_2 gas atmosphere, situations at the grain boundaries may play an important role in electrical transport because the Hall mobility could be affected by scattering at the grain boundary. Comparison between the Hall mobility and optical mobility can provide some insights of influence of the grain boundaries on the electron transport [19,20]. The optical mobility

Table 1
Sheet resistance, resistivity, Hall mobility, carrier concentration of as-deposited GZO films.

Deposition method	R_S (Ω/sq)	ρ ($\times 10^{-4}$ Ω cm)	μ (cm^2/Vs)	N ($\times 10^{20}$ cm^{-3})
IP	19	2.8	25	8.7
DC-MS	54	8.0	16	5.0
RF/DC-MS	25	3.7	16	10.0

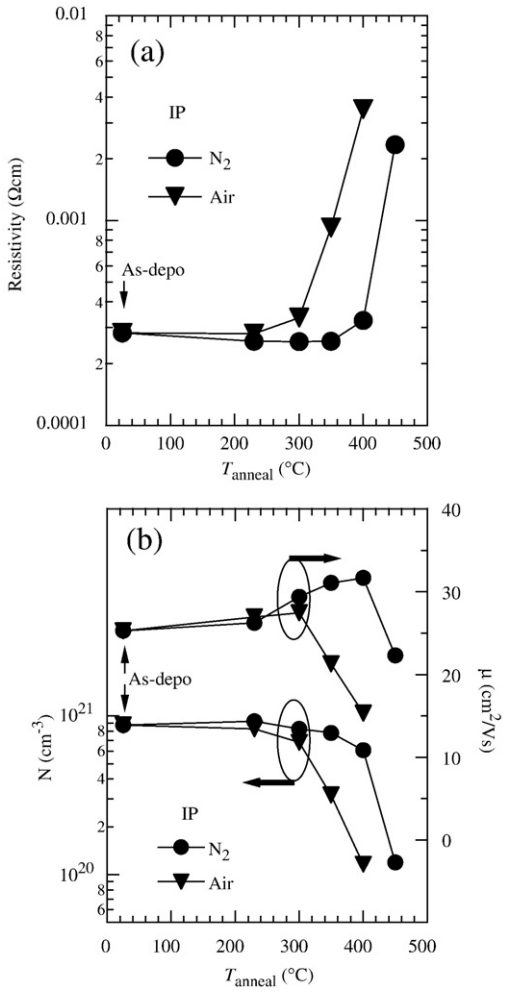

Fig. 1. (a) Resistivity of GZO films deposited by the IP after annealing in air or in the N_2 gas atmosphere as a function of annealing temperature. (b) Hall mobility and carrier concentration evaluated by Hall effect measurements.

represents the oscillating motion of free carriers in high frequency electric field. The motion is confined within the grains in the polycrystalline films composed of grains with size of several tens of nanometers. Accordingly, effects of the grain boundary on the optical mobility are considered to be avoided. Actually, average in-plane grain size of the as-deposited GZO films was characterized by grazing incident in-plane X-ray diffraction measurements by means of Williamson–Hall plot [21]. And the grain size was estimated to be 27, 26, and 29 nm, for the GZO films deposited by IP, DC-MS, and RF/DC-MS, respectively.

Fig. 2 showed optical reflection and transmission spectra measured for the as-deposited GZO film prepared by the IP method. In the near infrared region, the transmittance, T, decreases and the reflectance, R, increases with increasing the wavelength. These are typical characteristics of TCO films due to free carrier contribution to the dielectric functions.

The dielectric functions of polycrystalline GZO films were reported by Fujiwara and Kondo based on detailed analysis by spectroscopic ellipsometry [22]. Here, we estimated the optically evaluated carrier concentration, N_{opt}, and optical mobility, μ_{opt}, according to their analysis. It is known that estimation of dielectric functions by T and R spectra includes some errors. Spectroscopic ellipsometry may give reliable data, however, the T/R measurements also give some insight as adopted before [19,20]. In the model, a Tauc–Lorentz function was used to express optical band gap transition between the valence band and the conduction band transition in the TCOs [22]. For the free carrier response in the near infrared region, a conventional Drude model was used to express the dielectric functions of the GZO films. Then, the