Properties of GZO thin film deposited at various positions in the plasma plume in PLD method

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Ga-doped ZnO (GZO) thin films were prepared by pulsed laser deposition (PLD) method on a large substrate at room temperature in vacuum. Two regions of apparently different optical transmittance were found in the deposited area, and their properties such as thickness, sheet resistance, optical and electrical properties and composition ratio were measured. The transparent region has low sheet resistance and high carrier density and mobility, while the black region has high sheet resistance and low carrier density and mobility. From XPS measurements it was found that the difference of the film properties results from the difference of oxygen content in the film. This seems to result in the spatial distribution of plasma parameters in the directional plume produced by the asymmetric laser beam.

Keywords: Ga doped ZnO, PLD, room temperature, In-plane inhomogeneity

1. Introduction

Recently, transparent conductive oxide (TCO) films have been widely used as transparent electrodes in flat display panels and solar cells. Indium tin oxide (ITO) has been widely used as TCO materials. However, depletion and rapid price rise of indium is concerned as well as other rare metals. Impurity-doped ZnO thin film such as GZO thin film, which has high transmittance and low resistivity, has attracted attention as alternative materials to ITO film [1, 2]. Nowadays, demands for the low temperature process of the film preparation are rapidly growing for manufacturing of products such as polymer based flexible flat panel display (FPD). PLD method and sputtering method have been mainly used for the low temperature preparation of the doped ZnO [3, 4]. Particularly, the low-temperature process by sputtering method was studied to deposit doped ZnO thin films on low heat-resistive substrates. In the preparation of ITO and doped ZnO thin films by sputtering method at room temperature, it is found that in-plane inhomogeneous films are formed due to the non-uniform erosion of the target [5-8]. In general, it has been found that PLD methods can prepare low resistivity TCO films on substrates and are unsuited for use in the large-area preparation. In our study, by placing the substrate in 280 mm from the target, the large-area uniform doped ZnO thin film (100 mm × 100 mm) was prepared by PLD method at room temperature in vacuum. [9]

In this study, Ga-doped ZnO thin films on large substrate are prepared by pulsed laser deposition (PLD) method at room temperature in vacuum. In-plane inhomogeneous optical transmittance of the film is observed. Film properties such as thickness distribution, sheet resistance, transmittance, electrical properties and composition ratio were examined to reveal the origin of the in-plane inhomogeneous film properties distribution.

2. Experimental setup

The GZO thin films were prepared by PLD method using a GZO target (ZnO : Ga_2O_3 = 95 : 5 wt.%, 30 mm $\phi \times$ 5 mm thickness) of purity 99.99 % in a vacuum chamber (under 9.0×10^{-3} Pa). A KrF excimer laser (λ = 248 nm, 25 ns pulse duration) was used to ablate the target at fluence of 2 J/cm^2 and repetition rate of 10 Hz for 30 minutes. The distance (70 mm × 70mm, #7059, Corning) from the target to the substrate was 4.5 cm. The target rotated at constant speed. The substrate temperature was room temperature. There was no ambient gas in the chamber. The transmittance from 250 nm to 1100 nm of the deposited films was measured by a UV-visible spectrophotometer consist of a spectrometer (Ocean Optics, HR4000), a light source (Ocean Optics, DT-MINI) and an optical fiber (Ocean Optics, P400-025-SR). The sheet resistance was measured using four-probe method. Resistivity, carrier mobility, carrier density were measured using both van der Pauw method and Hall measurement.

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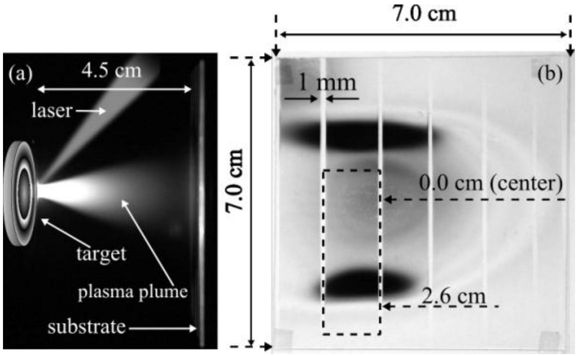

Fig. 1 (a) The arrangement of the target, plasma plume and substrate, (b) The picture of the prepared GZO thin film.

The film thickness was measured by stylus surface measurement (Dektak-3ST, ULVAC). The atomic composition of the film was measured by X-ray photoelectron spectrometer (XPS, VG Scientific, Sigma Probe).

3. Results and discussion

Figure 1 (a) shows the arrangement of the target, plasma plume and substrate. Figure 1 (b) shows the picture of the prepared GZO thin film. From Fig. 1(a), nodules occurred around the laser pattern on the target surface. The laser ablated nodules on the track of laser pattern. As a result, it is considered that nodules were deposited on the substrate as shown Fig.1 (b). To measure the film thickness, stripes areas (width: 1 mm) without film deposition are formed in the film as shown in Fig. 1. The square surrounded with dotted line in Fig.1 shows the measurement area of the prepared GZO thin film. We measured the in-plane inhomogeneous distribution of the film properties such as film thickness, sheet resistance and transmittance at every 1 mm step from 0.0 (center) to 2.6 cm.

3.1 Film thickness and sheet resistance

Figure 2 shows the distribution of the film thickness and sheet resistance. From Fig. 2, the film thickness decreased with the position from 0.0 (center) to 2.6 cm. In general, film thickness distribution, which was prepared by PLD method in vacuum, follows the Gaussian distribution. We fitted the film thickness distribution of the prepared GZO thin film with the Gaussian distribution (Fitting I). The film thickness profile in the range from 1.7 to 2.3 cm, which corresponds approximately to black region in Fig.1, differs from the Gaussian profile. As shown in Fig.2, the film thickness profile can be expressed with two different thickness distribution profiles shown as the Fitting I and the Fitting II. The prepared GZO thin film was mainly composed of the film thickness profile Fitting I. The increase of film thickness in the range from 1.7 to 2.3 cm expressed with the profile Fitting II seems to result from non-uniformity of the plasma plume. The sheet resistance in the range from 0.0 (center) to 1.7 cm was almost constant (approximately 6.0 Ω/□) as shown in Fig. 2. In contrast, in the range from 1.7 to 2.6 cm it increased drastically. The solid line shows the calculated sheet resistance using the film thickness profile Fitting I and the resistivity (8.3×10^{-4} Ω·cm) measured at the center (Table I). Comparing the measured sheet resistance with the calculated one, these vales are almost consisted with each other in the range from 0.0 (center) to1.5 cm. However, the measured values in the range from 1.5 to 2.6 cm were higher than the calculated ones. It is considered that the sheet resistance distribution was affected by the film thickness profile Fitting II.

Figure 3 shows the resistivity calculated from the film thickness and the sheet resistance in Fig. 2. From Fig. 3, the resistivity at 0.0 cm (center), 0.5 cm and 1.0 cm were 8.3×10^{-4} Ω·cm, 8.7×10^{-4} Ω·cm and 8.8×10^{-4} Ω·cm, respectively. The resistivity in the range from 0.0 (center)

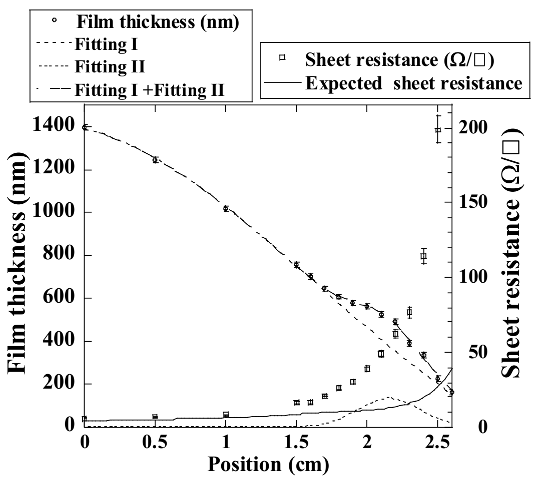

Fig. 2 The distribution of the film thickness and the sheet resistance.

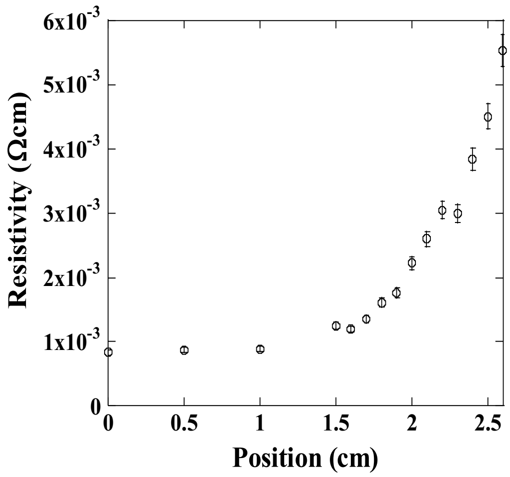

Fig. 3 The resistivity profile calculated from the film thickness and the sheet resistance.

to 1.7 cm was almost constant. However, the resistivity in the range from 2.0 to 2.6 cm increased drastically. From the result, it is shown that the prepared GZO thin film has the in-plane inhomogeneous distribution of film thickness and sheet resistance at the area corresponding to the Fitting II in Fig. 2.

3.2 Optical transmittance

Figure 4 shows the variation of transmittance from 0.0 (center) to 2.5cm. From Fig.4 (a), the transmittance in the range from 0.0 (center) to 1.2 cm increases with decrease of the film thickness. The prepared GZO thin film in the range from 0.0 (center) to 1.2 cm has the large transmittance in the visible wavelength and the low transmittance at the near infrared range. The decrease of transmittance over 750 nm is caused by the reflection due to the high carrier density in the film. In general, materials with high carrier density has metallic luster since the plasma frequency becomes large enough to cut off the incident light. We calculated the plasma frequency using Drude rule with the carrier density measured at 0.0 cm (center), and they are shown in Table I. The calculated plasma frequency is approximately 3.3×10^{14} s^{-1}. From the result, the decrease of the transmittance of the film at the wavelength over 900 nm in Fig. 4 (a) is due to the reflection. From Fig. 4 (b), the transmittance at the wavelength range from 300 to 750 nm decreases with the position from 1.2 to 2.0 cm and it becomes less than 5% at 2.0 cm. From Fig. 4 (c), the transmittance in the range from 2.0 to 2.5 cm increases due to the decrease of the film thickness. In Fig. 5 the variation of the average transmittance in the visible range (400 – 800 nm) is shown together with the resistivity distribution. From the figure, low resistivity and relatively high average transmittance are seen at the position from 0.0 (center) to 1.2 cm shows. While, high resistivity and low average transmittance from 1.7 to 2.3 cm are found, which corresponds to the black area shown in Fig. 1.

3.3 Hall measurement

Table I shows results of the Hall measurement. The properties at the four different positions of the film, 0.0-0.5 cm, 1.5-1.7 cm, 1.7-2.3 and 2.3-2.6 cm, are shown. From Table I, at 0.0-0.5 cm the carrier mobility μ of 6.8 cm^2/Vs, the carrier density n of 1.50×10^{21} cm^{-3}, and the resistivity ρ of 6.14×10^{-4} $\Omega\cdot cm$ are obtained. In contrast, at 1.7-2.3 cm low value of $\mu = 3.03$ cm^2/Vs and $n = 9.74\times10^{20}$ cm^{-3} and high ρ of 2.12×10^{-3} $\Omega\cdot cm$ are calculated. The properties μ and n decreases drastically in the area corresponding to the black region. It is found that the inhomogeneity exists in the carrier mobility and the carrier density as well as the sheet resistance and resistivity.

3.4 Composition ratio

Figure 6 shows the depth profile of composition ra-

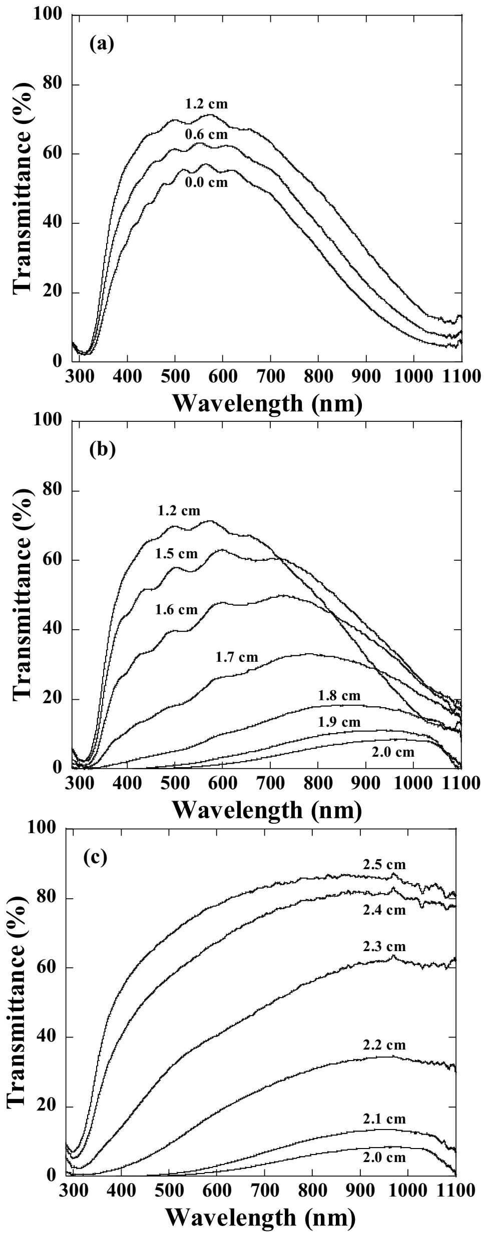

Fig. 4 The transmittance at various position of the film (a) 0.0 (center) - 1.2 cm, (b) 1.2 - 2.0 cm, (c) 2.0 - 2.5 cm

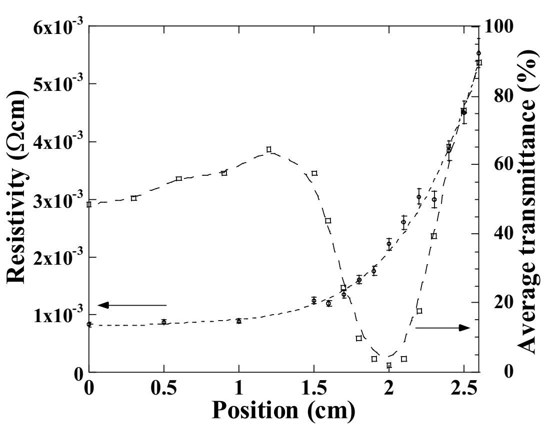

Fig. 5 The resistivity shown in Fig. 3 and the average transmittance (400nm-800nm) distribution.

Table I Resistivity (ρ), carrier mobility (μ) and carrier density (n) and average film thickness (t) at various positions in the GZO film.

Position [cm]	ρ [Ωcm]	μ [cm^2/Vs]	n [cm^{-3}]	t [nm]
0.0 ~ 0.5	6.14×10^{-4}	6.80	1.50×10^{21}	1320.5
1.5 ~ 1.7	9.48×10^{-4}	5.71	1.15×10^{21}	700.6
1.7 ~ 2.3	2.08×10^{-3}	3.03	9.92×10^{20}	543.2
2.3 ~ 2.6	5.24×10^{-3}	1.59	7.49×10^{20}	279.2

tio at the black region (from 1.7 to 2.3 cm). The high oxygen content at the surface of the prepared GZO thin film seems to result from adsorbed oxygen molecules and adsorbed H_2O molecules. The average composition ratio at the constant profiles in the film is Zn : O : Ga = 68.4 : 20.8 : 10.8. From our previous study, composition ratio of optimized GZO thin films were Zn : O : Ga = 52.6 : 42.9 : 4.5. Comparing the results, the oxygen content at the black area of 1.7-2.3 cm is half of the optimized one. It is considered that the low oxygen content may result in the both low carrier mobility and low carrier density. The in-plane inhomogeneous distribution of the film properties in the prepared GZO thin film may be caused by the non-uniform spatial distribution of plasma plume which depends on laser fluence distribution at the target surface, because plasma parameters such as electron temperature and density in the plasma plume strongly relate to the film properties.

4. Conclusion

In this study, we investigated the in-plane inhomogeneous distribution of the film properties in the GZO thin film, which was prepared by PLD method in vacuum at room temperature. The measurement results of film thickness, sheet resistance and transmittance distribution indicated that the prepared GZO thin film was composed of two regions. One had low sheet resistance and high transmittance, the other contrastively had high sheet resistance and low transmittance. As the result, the presence of two regions in the prepared GZO thin film caused the in-plane inhomogeneous film properties distribution. The composition ratio measurement indicated that the film properties difference in two layers was caused by oxygen content rate. It seems that the oxygen content rate distribution depends on the asymmetrical plasma plume, which is affected by the ablation parameters such as laser fluence distribution and laser beam pattern at the target surface.

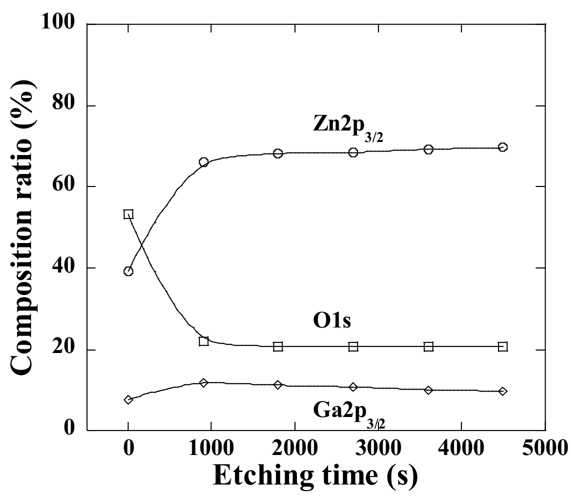

Fig.6 The depth profile of composition ratio

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