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Relation between target property and prepared film qualities by sputtering deposition with mixed powder targets

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***Abstract*—Relation between target property and prepared film qualities were studied by sputtering deposition with mixed powder targets. Experimental results suggest that Al doped ZnO films can be prepared using the Al_2O_3 and ZnO powder mixture targets by the sputtering deposition method, and the film quality depends on the target powder condition. Deposition rate and crystallinity of the prepared film increased with increasing powder pressed force. Crystallinity of the film also increased using pressed force of the target. Therefore, it is considered that band gap increased with increasing target pressed force.**

***Keywords*—Sputtering deposition, Powder target, Thin film, Al doped ZnO, Multi-elements**

I. Introduction

Transparent conductive films are used as liquid crystal displays in TVs, smartphones, and other devices [1,2]. ITO is currently the most widespread transparent conductive film material [3,4]. However, demand for a new transparent conductive film to replace ITO is currently increasing, because indium is rare metal and toxic to humans [5]. Aluminum-doped zinc oxide (AZO) has attracted attention as the most promising alternative [6]. AZO is a direct transition semiconductor with a band gap of about 3.3 eV at room temperature, and the raw material Zn is abundant, inexpensive, and nontoxic [7,8]. Therefore, we have fabricated this AZO thin film by conventional sputtering method. In our previous experiment, AZO thin films have been prepared on Si and quartz substrates by the conventional sputtering method using bulk targets. Some of the prepared thin films have visible light transmittance of >80 %, and the other shows low resistivity of < 10^{-4} Ω · cm, respectively [9]. In addition, the properties of the films depend on the target and deposition condition. The most important factor in this process is the control of the amount of Al doping, but the conventional sputtering method using bulk target lacks the controllability because it is difficult to change the Al composition ratio in the target.

Sputtering deposition method is techniques used in various fields among the plasma processes [10-20]. We have fabricated a variety of thin films by the methods [21-24], and we succeeded in fabricating high quality thin films in all of them. However, it is difficult to fabricate functional thin films with mixtures of multiple elements. To solve this problem, a new sputtering deposition method has been developed using several kinds of powder target. Because of the simple way by which the doping density can be changed the target powder mixture, the sputtering deposition method may become more attractive. This process has been applied to the preparation of different functional thin films, such as magnetic and/or optical functional thin films. As those experimental results, functional thin films whose properties are generated by elemental mixing can be prepared using a mixture powder target. In addition, the element mixture in the prepared film can be controlled by the powder target [25-27].

In this study, Al doped ZnO thin films were prepared by sputtering deposition using powder targets. In addition, relation between the target conditions and properties of the deposited thin films.

II. EXPERIMENTAL SETUP

Figure 1 shows the experimental apparatus of this experiment. Al and ZnO elements composed thin films were deposited on Si and quartz plate substrates by a radio frequency sputtering deposition. The deposition was performed in the vacuum chamber. It was evacuated to about $5\times10{-}3$ Pa with a molecular pump and a scroll pump. After that argon gas was feed into the experimental system

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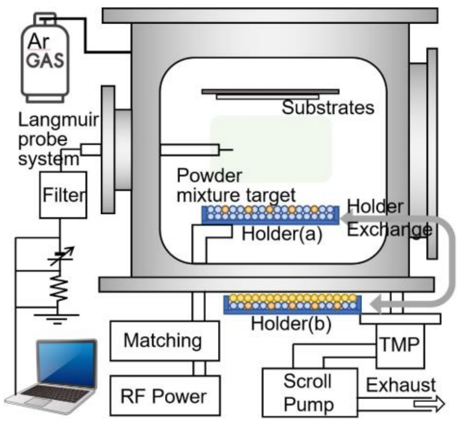

Fig. 1 Schematic representation of the sputtering deposition apparatus.

to 10 Pa by controllable gas introduction equipment. Several kinds of powder mixture targets were prepared using hand maid particle mixer.

Al doped ZnO thin films were prepared using Al_2O_3 and ZnO mixture powder targets. In this study, Al_2O_3 powder of a mean diameter 74µm with 99.9% concentration, and ZnO powder of a mean diameter of 150 µm with 99.9% concentration were used as a target material. The targets for preparation were mixed with the Al_2O_3 and ZnO targets so that the weight ratio ZnO:Al_2O_3 were 70:30 ~ 98:2 wt%. The mixed powder is then placed in an agate medium bowl and mixed by rubbing together. The mixed powder is placed in a V-shaped container, attached to a mixer, and mixed by a motor at 30 revolutions per minute for 10 hours. After mixing, mixture powder targets were just put on the target holder, and they were placed to the counter side of 30 mm from the substrate surface covered with the target powder. The powder was level on the target, and the substrates were not heated. The discharge power was 100 W, and deposition time of 1 hour.

An optical spectrometer with optical fibers was used to observed atomic and molecule emission in the processing plasma made by Ocean Optics (MAYA2000). After the deposition, film properties were measure as follows. Atomic force microscopy (JSTM-4100 made in JEOL) were used for the surface morphology and roughness. An alpha-step profilometer (ET4000A made by Kosaka Lab.) was measured for the film thickness. X-ray diffraction (RINT2100V made by Regaku) was used for the crystalline structure, and XPS (JPS9010 made in JEOL) was used for the composition of the films.

III. Results and discussion

A. Optical emission spectra of the processing plasma using powder targets by emission measurement

Optical emission spectra of the processing plasma generated from the powder targets were measured, as shown in Fig. 2. Fig. 2(a) shows the emission spectrum of the sputtering plasma using ZnO powder target, 2(b) shows that of AZO bulk target, 3(c) shows that of ZnO:Al_2O_3=90:10 wt% powders mixture target and 3(d) shows that of ZnO:Al_2O_3=70:30 wt% powders mixture target. All of the spectra contained strong peaks consistent with Ar I (400~450, 750~850 nm) and O I (777 nm) emissions. Detailed observation of the Fig. 2 reveals an Al I atom-derived emission peak (308.2nm, 309.9 nm, 344.5 nm, 345.8 nm, 394.6) at 300~400 nm. This emission peak increases with the mixing ratio of Al powder. It is also revealed that Zn I atom-derived emission peaks of 463. 0 nm, 468.0 nm, 472.2 nm and 481.0 nm appeared for the ZnO powder targets.

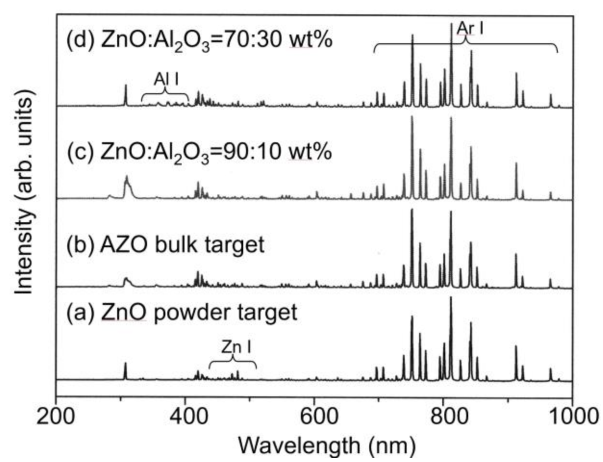

Fig. 2 Optical emission spectra of the processing plasma generated from the powder targets

B. Transparency of thin films prepared using mixture powder targets

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Figure 3 shows the transparency of thin films prepared on the quarts glass substrate, corning 7059, using mixture powder targets. Transparency of the prepared film depends on the Al_2O_3 powder mixture concentration in the target. High transparency thin films were prepared using 0~10% Al_2O_3 powder mixture in the target. However, The transparency decreased with increased with Al_2O_3 powder mixture. The prepared film prepared using >30% Al_2O_3 powder mixture is not transparent. The color of them were brown.

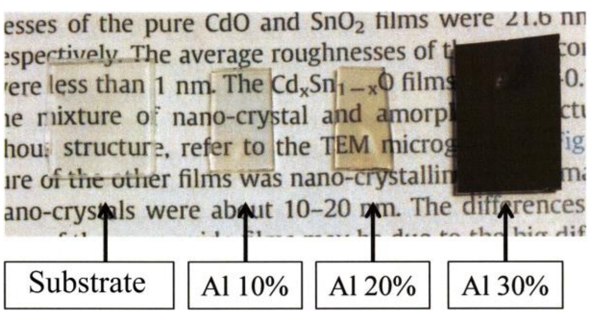

Fig. 3 Transparency of thin films prepared on the quarts glass substrate, corning 7059, using mixture powder

C. Qualities of the prepared film

Figure 4 shows the XRD spectrum of the prepared film. XRD spectra of ZnO and Al_2O_3 were also shown in Fig. 4. The spectrum shows both spectrum of the ZnO(002), ZnO(101) and Al_2O_3(113) peaks, which means that the prepared film was Al and ZnO composed film. Figure 5 shows XPS spectra of the prepared film. The results suggest that Al (Al 2p), Zn (Zn 2p) and O (O1s) peaks were observed.

IV. RELATIONSHIP BETWEEN THE PROPERTIES OF THE POWDER TARGET AND THE FILM QUALITY

A. Relation between deposition rate the powder condition.

To investigate relation between the film quality and target condition, Al doped ZnO film were prepared on the Si substrate by sputtering deposition using 4 types of the powder target. The targets mixture of the Al_2O_3 and ZnO powders was ZnO:Al_2O_3 were 98:2 wt% in weight ratio. After mixing, 4 types of the targets were prepared on the same target holders, that were (1) Unprocessed; without

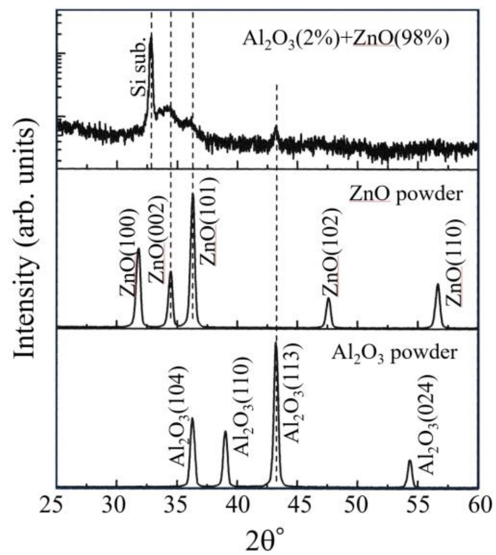

Fig. 4 XRD spectrum of the prepared film. XRD spectra of ZnO and Al_2O_3.

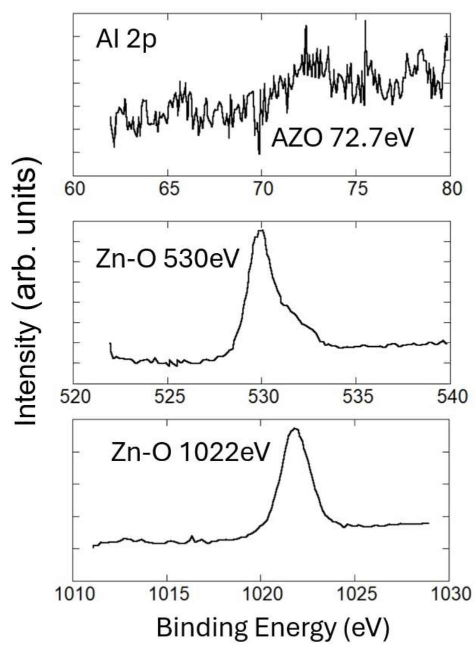

Fig. 5 XRD spectrum of the prepared film. XRD spectra of ZnO and Al_2O_3.

heated and pressed, (2) Heated; heated by 150 degree C and without pressed, (3) Soft pressed; heated by 150 degree C and pressed by 153 kgf/cm^2, (4) Hard pressed; heated by 150 degree C, and pressed by 4.5 t, as shown in Fig. 6. Using these targets, thin films were deposited to investigate

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about the relation between target condition and film qualities using powder targets in this experiment.

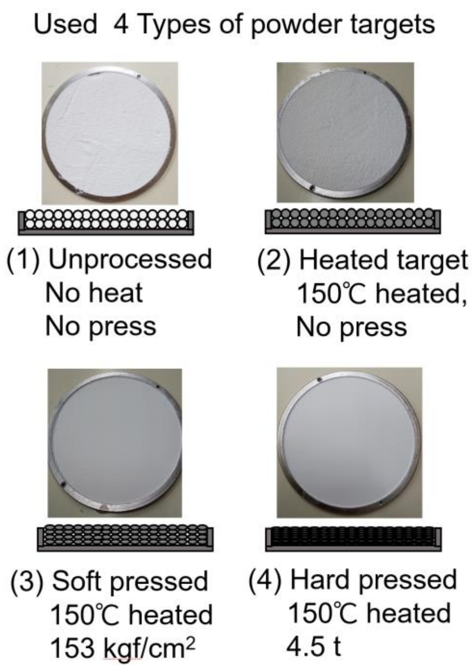

Fig. 6 4 types of the targets which used in this prepareation (1) Unprocessed; without heated and pressed, (2) Heated; heated by 150 degree C and without pressed, (3) Soft pressed; heated by 150 degree C and pressed by 153 kgf/cm^2, (4) Hard pressed; heated by 150 degree C, and pressed by 4.5 t

At first, relation between the deposition rate and target condition which were (1)~(4) as mentioned above. Deposition rate was measured by film thickness and deposition time. Film thickness was measured by alpha-step profilometer. Deposition rate of the each target were as follows; 2.56~5.38×10^{-2} nm/s for target (1), 2.21~2.44×10^{-2} nm/s for target (2), 6.85~7.91×10^{-2} nm/s for target (3), 8.46~8.79×10^{-2} nm/s for target (4). As the results, heating does not so affect for deposition rete. However, target press affected for the deposition rate. In our experiments, deposition rates were increased with increasing pressing force. Figure 7 shows dependence of the transmittance of the prepared films on the grass substrate on the target conditions of (1)~(4). Transparency of the prepared film was >80 % at >500nm, and they are independent for the target conditions. The results also show that the film thickness increased with increasing target press force, because of the number of fluctuations due to interference in

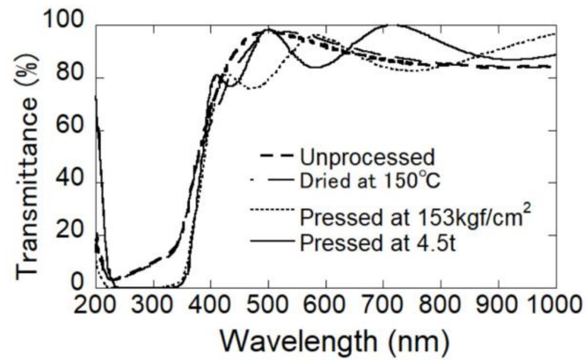

Fig. 7 Dependence of the transmittance of the prepared films on the grass substrate on the target

transmittance. This result is consistent with the dependence of deposition rate and target condition. Next, dependence of the XRD spectra of the target on the target condition as shown in Fig. 8. As the results, ZnO(002) peaks were observed, and peak intensity increased with increasing target press force. In addition, peak position shifts to large 2q direction. The results suggest that film crystallinity and band gap increased with increased target press force.

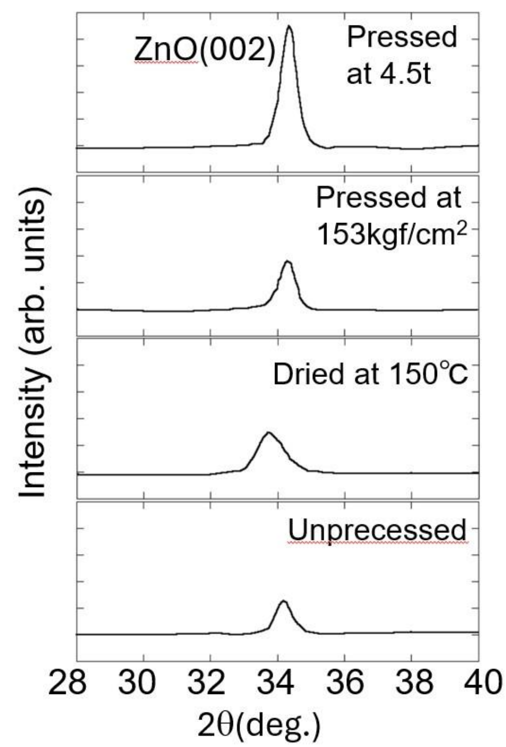

Fig. 8 Dependence of the XRD spectra of the target on the target condition.

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B. Relation between thin film preparation process and the powder condition.

Al doped ZnO film preparation by sputtering deposition process using the Al_2O_3 and ZnO powder target has been investigated. Emission spectra of the sputtering plasma shows the Al I and Zn I emission were observed in the plasma. This result suggests that Al and Zn atom exist in the sputtering plasma. XRD results suggsest that crystallized Al doped ZnO thin film can be prepared using Al_2O_3 (0~30%) and ZnO (100~70%) powder mixture targets. Film color changed by powder mixture of the Al_2O_3 targets, especially transparency decreased and color change transparency to dark-brown with increasing Al_2O_3 powder mixture. This result suggests that Al concentration in the prepared film increased with increasing sputtered Al atom density in the plasma. However, it was suggested that deposition processes affected by target conditions such as powder press force. To investigate relation between the film quality and target condition, Al doped ZnO film were prepared using 4 types of the powder target (1)~(4) with the targets mixture of Al_2O_3 : ZnO = 98:2 wt% in weight ratio. Experimental results suggest that deposition rate and crystallinity of the prepared film increased with increasing powder pressed force. In general, deposition rate of the conventional sputtering using high density target is high compared with that of low density. This may be due to increase net Ar ion irradiation energy, because of dielectric constant change by powder target pressed. Crystallinity of the film also increased using pressed force of the target. Therefore, band gap increased with increasing target pressed force.

V. CONCLUSIONS

Al doped ZnO film were prepared by sputtering deposition process using the Al_2O_3 and ZnO powder target. Experimental results suggest that Al doped ZnO film can be prepared by the sputtering deposition method and the film quality strongly depends on the target powder condition. Deposition rate and crystallinity of the prepared film increased with increasing powder pressed force. In general, deposition rate of the conventional sputtering using high density target is high compared with that of low density. This may be due to increase net Ar ion irradiation energy, because of dielectric constant change by powder target pressed. Crystallinity of the film also increased using pressed force of the target. Therefore, band gap increased with increasing target pressed force.

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