Preparation of Al-doped ZnO Sputtering Target for Transparent Conductive Films by Pulse-Current Sintering

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Aluminum-doped Zinc oxide (AZO) sputtering targets (10 mm in diameter and 5 mm thick) were prepared by a pulse-current sintering method, where metallic Al was selected as the Al source. The ZnO sintered materials doped using metallic Al showed low electrical resistivity owing to both the Al doping and precipitation of metallic zinc. AZO thin films were prepared by RF magnetron sputtering using the prepared target, and showed an electrical resistivity of approximately $9.6 \times 10^{-4} \Omega\text{cm}$. Moreover, increase in electrical resistivity at the erosion area was small compared with that in films prepared with a conventional target.

Key words: zinc oxide, doping, sintering, sputtering target, thin film

1. INTRODUCTION

ZnO is a wide gap semiconductor ($E_g = 3.2 \text{ eV}$) and has high transmittance in the visible region as a thin film. Moreover, ZnO is nontoxic and has excellent cost performance compared with indium-tin oxide (ITO) [1]. The electrical properties of ZnO are controllable by aluminum doping. Therefore, aluminum-doped ZnO (AZO) is one of the best candidates to replace ITO transparent conductive films.

Magnetron sputtering is widely used for preparation of AZO films owing to a large deposition rate and strong contact between film and substrate. As for target materials, two types can be adopted, metallic (Al-doped Zinc) [2-3] and ceramic (Al_2O_3 -doped ZnO) [4-7]. The ceramic target type has been preferably used because it yields AZO films with higher quality and better reproducibility than those obtainable with the metallic target [4].

However, the electrical properties of AZO films prepared by magnetron sputtering are significantly influenced by the position of the substrate relative to the target. The electrical resistivity of the film increases in the region facing the erosion area of the target. This phenomenon is considered to be caused by increased bombardment of the substrate by high-energy oxygen atoms and oxygen anions in the area facing the erosion area of the target. The resulting excess oxygen atoms and ions cause an increase in the electrical resistivity of the film [8-9]. Thus, reduction of the resistivity at the region facing the erosion area is needed from the viewpoint of industrial manufacturing. This requires consideration of both the dopant and preparation process.

In the present study, an AZO sputtering target was prepared by pulse-current sintering (PCS), a method which has many advantages including a faster heating rate, lower sintering temperature, and shorter holding time than conventional sintering methods [10-11]. Metallic Al was selected as an aluminum source.

Al-doping was also intended to form an oxygen-deficient state in the sintered materials. AZO film was prepared by magnetron sputtering using the Al-doped AZO target. The electrical properties of the film were measured and compared with a film prepared using a conventional target.

2. PREPARATION OF AZO SPUTTERING TARGET

2.1 Preparation

ZnO (6N, 1–2 mm) and Al (3N, <75 mm) were used as starting materials. They were weighed to give a nominal composition of $\text{Zn}_{0.95}\text{Al}_{0.05}\text{O}$. The total weight of powder was approximately 220 g for a sintered specimen 100 mm in diameter and 5 mm in thickness. The powders were mixed by uniaxial ball mill in a nylon bottle with 300 mL ethanol and 500 g of ZrO_2 balls. Mixing was performed at 100 rpm for 20 h. After mixing, the slurry was dried in a rotary evaporator at 50 °C for 3 h.

Fig. 1 Typical sintering behavior of metallic Al-doped ZnO. Negative and positive values of electrode displacement indicate expansion and sintering, respectively.

Sintering was performed using a PCS system (CSP-V-6015, S.S. Alloy Co., Ltd., Higashi-Hiroshima, Japan). The powders were poured into a graphite die (100 mm ϕ) and a mechanical pressure of 20 MPa was applied through graphite punches. Figure 1 shows the typical sintering behavior of AZO. The samples were heated to 900 °C by applying a pulse-current (max 3000 A) under vacuum. The heating rate was approximately 45 K/min. The samples were held at 900 °C for 10 min and then cooled to room temperature. The displacement of the electrodes showed sudden shrinkage at around 600 °C, indicating the start of sintering. Thereafter, the slope of shrinkage became gradual with increasing temperature and almost constant at around 900 °C. This result indicates that sintering started at around 600 °C and completed at 900 °C. The color of the obtained sintered material was black, which was different from the undoped ZnO (white or yellow). The density of the sintered materials was 97 % of the theoretical density of ZnO. After a polishing and bonding process, the sputtering target was successfully obtained, as shown in Fig. 2.

Fig. 2 Metallic Al-doped ZnO sputtering target (100 mm ϕ , 5 mm).

2.2 Electrical properties of ZnO doped using metallic Al

To evaluate the microstructure and electrical properties of the Al-doped ZnO, 10 mm square sintered materials were prepared by the same method as that in Section 2.1, except for the use of the PCS system (Plasman kit, S.S. Alloy Co., Ltd., Japan) and mechanical pressure (40 MPa). Undoped and Al₂O₃ (4N, 1 mm) doped ZnO (nominal composition: Zn_{0.95}Al_{0.05}O) were also prepared for comparison.

Electrical resistivity and Hall coefficient were measured at 300 K by the van der Pauw method. The structure and distribution of atoms were investigated using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), respectively.

Table I shows electrical resistivity and carrier (electron) concentration for the sintered ZnO materials. The electrical resistivity was lower and carrier concentration was higher for the doped ZnO than the undoped ZnO. It is notable that the metallic Al-doped ZnO showed particularly low resistivity, owing to its high carrier concentration.

Figure 3 shows SEM micrographs of metallic

Al-doped sintered materials. From the EDX spectra, the existence of three areas, zinc oxide, zinc aluminate, and metallic zinc, was identified. This result suggested that the ZnO was reduced in part by the Al and formed the observed metallic Zn precipitates. Therefore, the low electrical resistivity of metallic Al-doped ZnO was caused by both Al substitution on Zn site and metallic Zn precipitation. Thus, a low resistive AZO target having an oxygen-deficient state was realized by the present metallic Al doping and PCS process.

Table I Electrical resistivity and carrier concentration at 300K of ZnO and AZO sintered materials.

dopant	Electrical resistivity, ρ (Ω cm)	Carrier concentration, n (cm ⁻³)
undoped	1.9×10^1	-
Al ₂ O ₃	1.5×10^{-2}	1.5×10^{19}
metal-Al	4.3×10^{-3}	8.1×10^{19}

Fig. 3 SEM image of metallic Al-doped sintered materials.

3. THIN FILM PREPARATION AND ELECTRICAL PROPERTIES

3.1 Preparation of AZO film

AZO thin films were deposited by RF magnetron sputtering on Pyrex glass substrate using the sputtering target prepared in section 2. For comparison, thin films were also deposited from the Al₂O₃ doped target prepared by the conventional sintering method. The Ar gas working pressure was 1 Pa. AZO films were deposited on the substrates at room temperature. The

Table II RF magnetron sputtering condition for preparation of AZO films.

RF input power	200 W
Working gas pressure	1 Pa
Target-substrate distance	50mm
Sputtering time	10 min
Film thickness	490–750 nm

experimental details are shown in Table II. The film thickness ranged from 490 to 750 nm.

3.2 Electrical properties of AZO film

The electrical resistivity of the AZO films was measured by van der Pauw method at room temperature. Figure 4 (a) shows electrical resistivity of the AZO films plotted in terms of substrate position. Zero on the horizontal axis corresponds to the region of the substrate facing the center of the target as shown in Fig. 4 (b). The resistivity values for film fabricated using the conventional target (Al_2O_3 -doped ZnO by pressureless sintering) is simultaneously shown in Fig. 4(a). A significant increase of electrical resistivity at the erosion area (20–25 mm) was clearly confirmed in the film prepared from the conventional target. The electrical resistivity in the region facing the erosion area was 10 times higher than that obtained near the center of the target. In contrast, in the film prepared using the metallic Al-doped target, the increase of electrical resistivity at the region facing the erosion area was substantially reduced to approximately 2.5 times that obtained in the region near the center of the target. This result may be attributed to the oxygen-deficient state of the target doped using metallic Al causing a reduction in the effect of high-energy oxygen atoms or oxygen ions bombarding the substrate in the erosion area.

Fig. 4 (a) Electrical resistivity distribution of AZO films deposited using a metallic Al-doped target (circles) and conventional Al_2O_3 -doped target (squares). (b) Substrate position and erosion areas of the target.

4. SUMMARY

A metallic Al-doped ZnO sputtering target was prepared by PCS method to obtain transparent conductive films with good electrical properties. An AZO sputtering target with low electrical resistivity and zinc precipitation was successfully prepared. AZO film prepared by RF magnetron sputtering method using this target showed only a slight increase in electrical resistivity in the region facing the erosion area of the target. Thus, the present metallic Al-doped sputtering target is effective for improvement of electrical resistivity in film regions facing the target erosion area, and is expected to be beneficial for the production of transparent conductive films.

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