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Crystal Al-Doped ZnO Thin-Film Preparation by Sputtering Deposition using A Mixed-Powder Target

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***Abstract*—Al-doped ZnO films were prepared by sputtering deposition using mixtures of Al_2O_3 and ZnO powder targets. The film quality depended on the conditions of the target powder. The deposition rate, crystallinity, and transparency of films prepared with new, pressed powder targets were higher than those prepared with used, non-pressed powder targets. In addition, we found that pressurizing the new-powder target and increasing the substrate temperature resulted in thin films with high transparency and electrical conductivity.**

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

I. INTRODUCTION

Research and development to create new, highly functional materials has been proposed as a Japanese national strategy to solve social issues and to achieve the United Nations Sustainable Development Goals and 'Society 5.0'[1,2]. Moreover, the exploration of conventional materials is approaching its limits in most fields, making it necessary to expand the scope of exploration to new functional materials. However, the search for multisystem materials becomes more complex as the number of elements in the material increases.

Sputtering deposition is widely used to deposit thin films because it requires a simple apparatus, is an easy process with an expansive choice of materials, and produces high-uniformity films at high deposition rates.[3-10] In addition, it uses nontoxic gases and low energies to generate the processing plasma. Thus, it is safer than other plasma-processing methods, such as chemical-vapor deposition and pulsed-laser deposition. Sputtering has been used to deposit functional thin films composed of multiple materials[11, 12]. Preparing thin films consisting of multiple elements is difficult with conventional sputter deposition because high-density bulk targets are generally used. Therefore, it is necessary to make new targets by other methods, such as spark-plasma sintering, and/or conduct sputter deposition using multiple targets[13, 14]. These target preparations are usually time-consuming and costly.

As an alternative, plasma processes using multielement powder targets have been used to prepare functional multielement thin films in single-step processes[15-29]. In this process, several kinds of powder can be mixed and placed in a target holder in a vacuum chamber. Thin films are then deposited on a substrate mounted on the opposite side of the vacuum chamber to the target holder. It is possible to obtain a few samples with different doping densities during one cycle[11]. For example, Sn-doped SiO_2 thin films were prepared using SnO_2 and SiO_2 mixed-powder targets[13),18)]. The elemental concentrations in the thin films can be controlled by the composition of the powder mixture.

Transparent conductive films are used as liquid-crystal displays in TVs, smartphones, and other devices[30,31]. ITO is the most widespread material used in these films[32,33]. However, the demand for new transparent conductive films to replace ITO is increasing because indium is a rare metal and toxic to humans[34]. Aluminum-doped zinc oxide (AZO) has attracted attention as the most promising alternative[35]. 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[36,37]. Therefore, we have fabricated AZO thin films using conventional sputtering method. This was performed on Si and quartz substrates using bulk targets. Some of the prepared thin films had visible light transmittance of >80 %, and other showed low resistivity of $<10^{-4}$ Ω・cm[24]. In addition, the properties of the films depended on the target and the deposition conditions. The most important factor in this process is the control of the amount of Al doping. However, conventional sputtering using a bulk target lacks controllability because it is difficult to change the Al composition ratio in the target.

In this study, AZO thin films were prepared via one-step sputtering deposition using Al_2O_3 and ZnO mixed-powder targets. The film properties, such as crystallinity, composition ratio, and surface roughness, were characterized.

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II. Experimental Setup

AZO thin films were prepared using a sputter-up-type deposition system, and Al_2O_3 and ZnO mixture powders were used as the target. First, ZnO (particle diameter of 1 μm and purity of 99.99 %) and Al_2O_3 (particle diameter of 1 μm and purity of 99.9 %) powders were weighed on an electronic balance. The powders were then mixed lightly in an agate mortar, placed in a vessel, and then mixed by rotating the vessel for several hours. The target holder was then filled and the surface flattened to complete the process. If pressing was required, a press was used to produce the compact.

A schematic representation of the sputter-deposition apparatus is shown in Fig. 1. The stainless-steel deposition chamber had a diameter of 400 mm and height of 450 mm. A powder target was placed in a 50.8-mm-diameter stainless-steel target holder. The chamber was vacuumed to a base pressure of 5×10^{-3} Pa using turbomolecular and rotary pumps. The total deposition pressure was 0.3 Pa with Ar gas (99.99%) introduced at a 10-sccm flow rate. Sputtering deposition was performed with radio frequency (13.56 MHz) plasmas. The plasma was generated by applying a 100-W discharge power to the powered electrode. Prior to loading in the deposition chamber, substrates were cleaned in an ultrasonic agitator several times, followed by washing with high-purity deionized water. The surface of the substrate was not heated and was almost at room temperature.

III. Relationship Between The Target Usage Time And Film Quality

AZO thin films were prepared at room temperature using a mixed-powder target of $ZnO:Al_2O_3$ = 90:10 wt%. The deposition time was varied and the substrate was not heated (i.e. it was used at room temperature). The deposition under two conditions: (1) with the powder target replaced with a new one each time (hereafter 'new powder') and (2) without replacing the target (hereafter 'used powder').

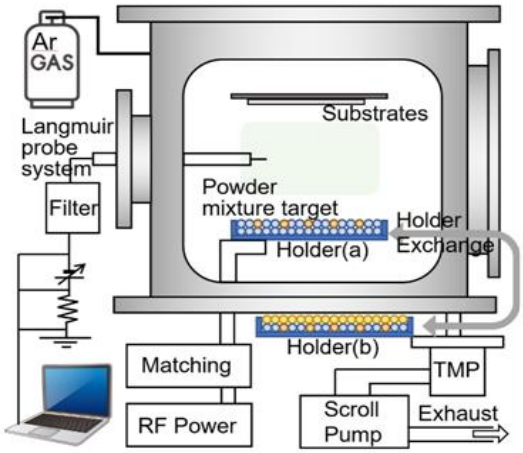

Fig. 1Schematic representation of the sputtering deposition apparatus.

A. Deposition rate

Figure 2 shows the deposition rate of AZO thin films prepared with either the new and used powder. The deposition rate using the new powder gradually decreased to 90% after a deposition time of 120 minutes. By contrast, the deposition rate for the old powder decreased to 60% after 90 minutes before reaching saturation.

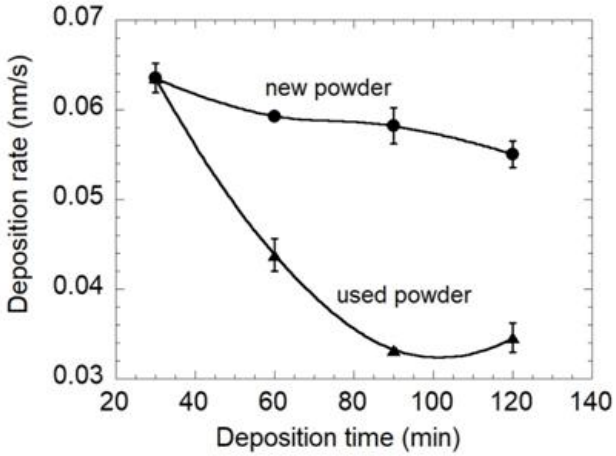

Fig. 2 Deposition rate of AZO thin films prepared using both the new powder and used powder.

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B. Crystallinity of the target surface and thin films

Figure 3 shows the XRD results before and after deposition for 300 minutes. Three diffraction peaks — ZnO(100), (002), and (101) — were observed. After 300 minutes of deposition, the diffraction peak intensity of ZnO increased, which means the crystallinity of ZnO improved. Thus, the crystallinity of the target surface changed with deposition time. The deposition rate with the used powder saturated after 90 minutes of deposition (Fig. 2), which may indicate that this change in crystallinity affects the sputtering rate.

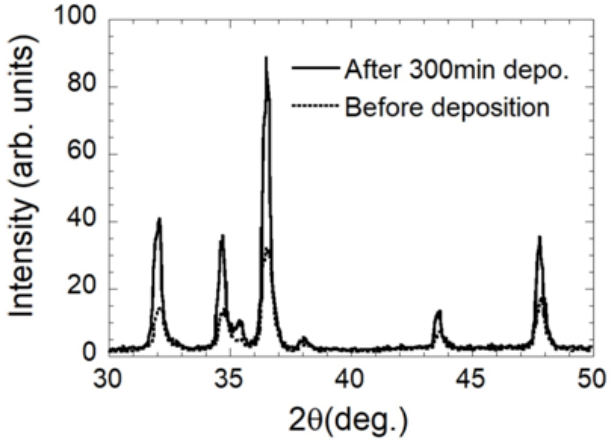

Fig. 3 XRD results before and after deposition for 300 minutes.

Figures 4 and 5 show the crystallinity of the thin films fabricated using the new and used powders, respectively. The ZnO diffraction peaks were observed in the AZO thin film. In the AZO thin film with a deposition time of 30 minutes, a strong diffraction peak was observed that appeared to be ZnO. Compared with the XRD spectrum of the target surface shown in Fig 3, the ZnO peak shifted to the low-angle side. This phenomenon indicates that the deposited film is subjected to compressive stress. For the used powder, the peak shifted to a lower angle after 60 minutes of deposition, and a decrease in peak intensity and broadening of the peak width were also observed. This suggests that the lattice constant changed owing to contamination of aluminum or oxygen in addition to the decrease in crystallinity of the target itself, or that there was crystal distortion due to compressive stress in the used powder. For the new powder, two or more peaks were observed at all deposition times because a new-powder target was used each time. We suggest that the target surface was refreshed, which resulted in the crystallinity of the film in the volume remaining high.

C. UV–visible spectra

Figure 6 shows the UV–visible spectra and surface photographs of the thin films prepared with the used powder. The transmittance decreased with increasing deposition time. In particular, the visible light (400–600 nm) transmittance decreased from 80%–90% to 30%–40%.

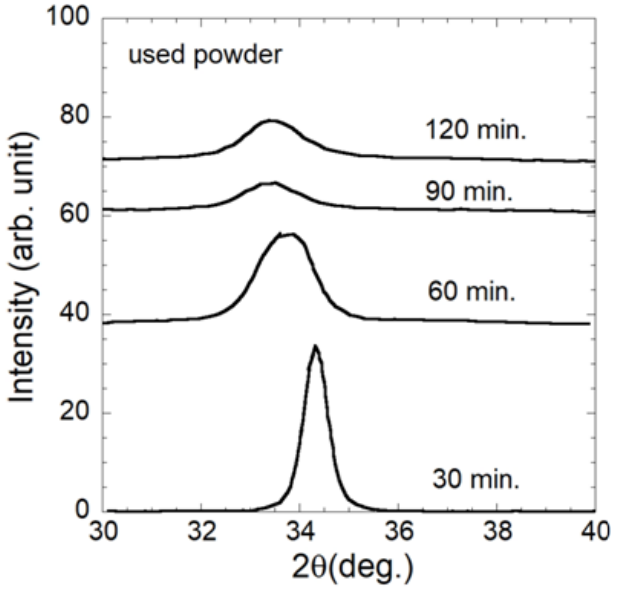

Fig. 4 Crystallinity of the thin films fabricated with the used powder.

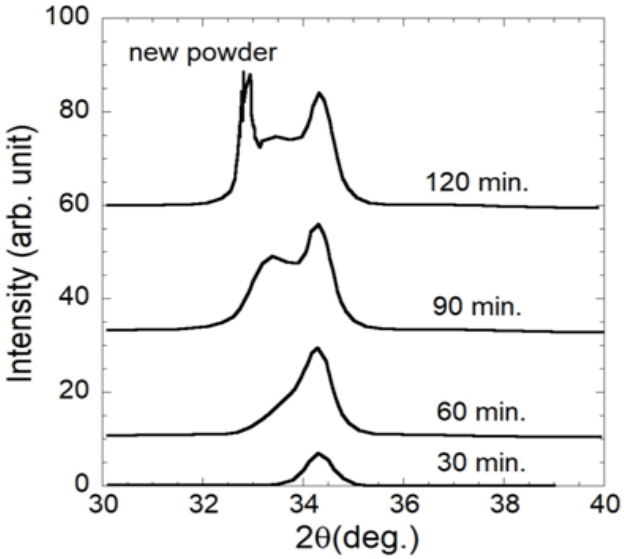

Fig. 5 Crystallinity of the thin films fabricated with the new powder.

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The photographs of the deposited films show that their appearance changed from transparent to blackish-brown as the deposition time increased. It is known that ZnO thin films prepared by conventional sputtering deposition using a bulk target turn blackish-brown as the ratio of metallic Zn in the film increases[38]. In this experiment, almost 100% Ar gas was used for the deposition. Therefore, when Ar ions strike the mixed-powder target surface, oxygen atoms are selectively sputtered out and the target surface becomes Zn-rich. Therefore, the color of the prepared film indicates a lack of oxygen in the film.

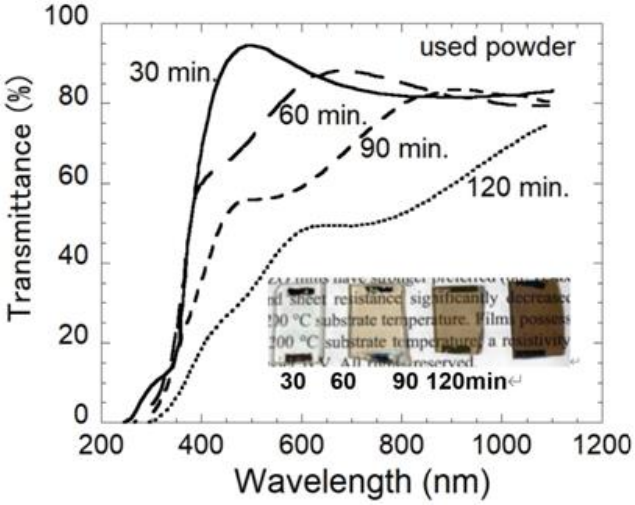

Fig. 6 UV–visible light transmission spectra and surface photographs of the thin films prepared with the used powder.

Figure 7 shows the UV–visible spectra and surface photographs of the thin films prepared with the new powder. In this case, the decrease in the transmittance of the thin film was improved compared with that of the used powder. In particular, the transmittance of infrared light (600 nm) was almost constant at 80%. However, coloration of the thin film occurred after 90 minutes of deposition, with a decrease in the transmittance of visible light to 60–70%. The resistivity of the thin film was also measured using the four-point probe method (data not shown). The resistivity was approximately 8×10^{-2} ($\Omega\cdot$cm) when the deposition time was 30 minutes, and increased with increasing deposition time.

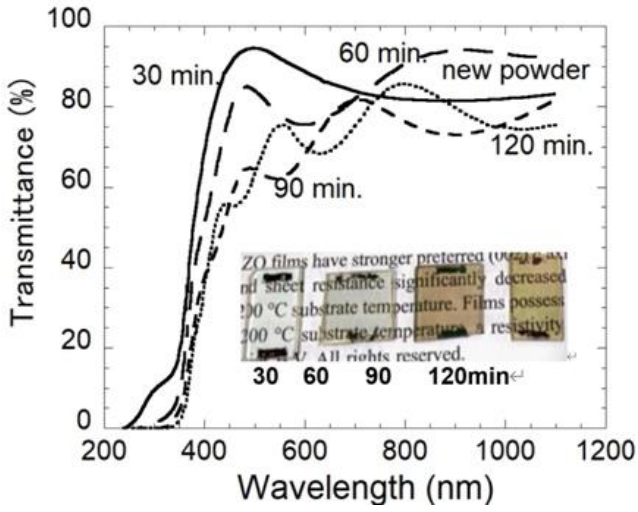

Fig. 7 UV–visible light transmission spectra and surface photographs of the thin films prepared with the new powder.

IV. Relationship Between The Properties Of The Powder Target And The Film Quality

The film quality was evaluated by preparing thin films on three different targets: untreated (#1), dried at 50 °C for 60 min (#2), and pressed under 15 MPa (#3). The densities of targets #1, #2, and #3 were 0.38, 0.34, and 1.3 g/cm^3, respectively. The target was a mixed powder of ZnO:Al_2O_3 = 98:2 wt%, and was replaced with a new target each time a film was deposited (new powder). The substrate temperature was set to room temperature (RT) or 400 °C, and AZO thin films were prepared with a 60-minute deposition time.

A. Deposition rate

Figure 8 shows the dependence of the deposition rate on the target properties. The deposition rate with the pressed target (#3) was faster than that of the non-pressed targets (#1, #2). This may be due to differences in the number of particles ejected after the Ar ions hit the target surface because of differences in the porosities of the powder targets. In addition, the deposition rate increased with increasing substrate temperature.

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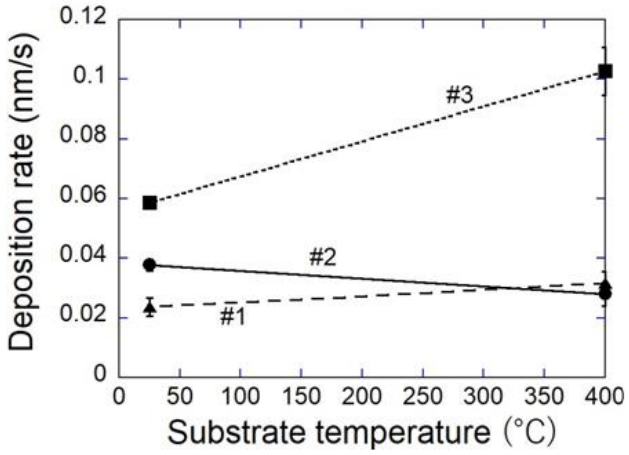

Fig. 8 Dependence of the deposition rate on the target properties.

B. Crystallinity of the prepared films

Thin films were prepared at room temperature and at a substrate temperature of 400 °C using the new powder and analyzed using XRD. Diffraction peaks of ZnO (data not shown) were observed under all conditions. Figures 9 and 10 shows the peak intensities and maximum peak shift from films prepared with targets #1, #2, and #3 at room temperature and at 400 °C. The peak intensity was almost constant for all three targets at room temperature. By contrast, at a substrate temperature of 400 °C, the peak intensity increased with increasing target density.

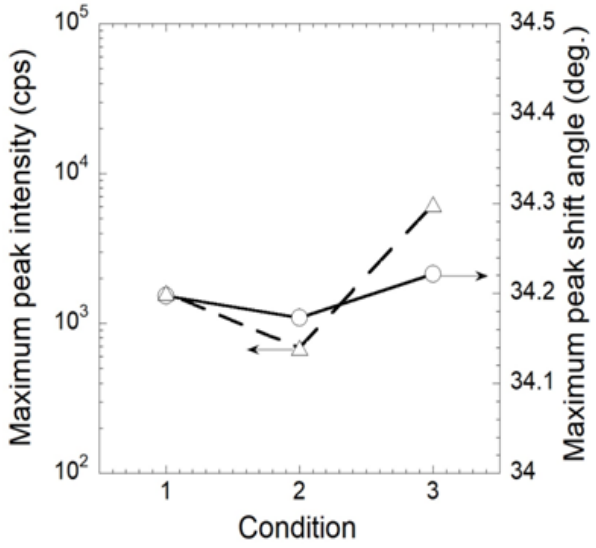

Fig. 9 Peak intensities from the prepared film for targets #1, #2, and #3 at room temperature.

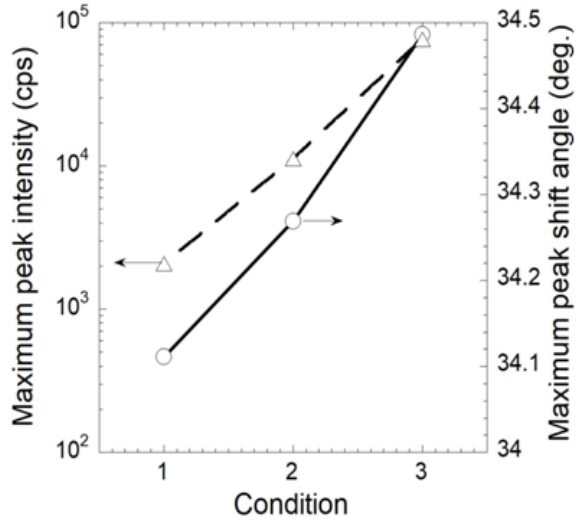

Fig. 10 Peak intensities from the prepared film for the targets #1, #2, and #3 at a substrate temperature of 400 °C.

Figure 11 shows the relationship between the resistivity and average transmittance of visible light. The thin film with the highest transparency and lowest resistivity was that fabricated with target #3 and a substrate temperature of 400 °C. These were also the conditions that resulted in the highest crystal strength. The transmittance of this thin film was comparable to that of the ITO thin films that are currently in commercial use. However, the resistivity was about one order of higher; therefore, further improvement is needed.

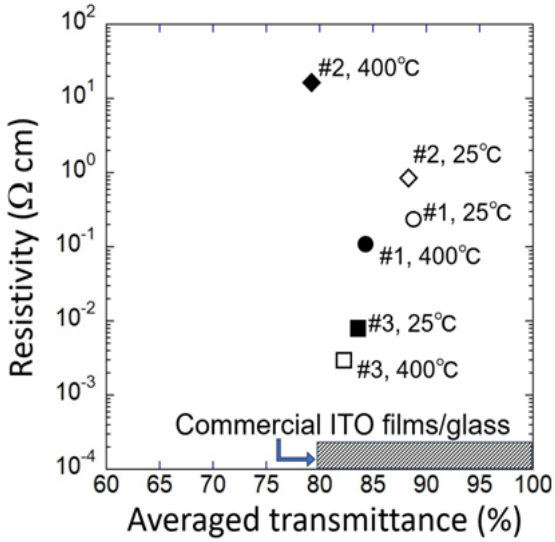

Fig. 11 Relationship between the resistivity and the average transmittance of visible light (380–780 nm).

V. CONCLUSIONS

AZO thin films were prepared by sputtering a mixture of ZnO and Al_2O_3 powder targets, with one target used continuously for more than 60 minutes and the other target changed every 30 minutes. The deposition rate, crystallinity, and transparency of the new-powder films were higher than those of the used-powder films. In addition, it was also found that using a pressurized new-powder target and increasing the substrate temperature resulted in thin films with high transparency and electrical conductivity. The results suggest that it may possible to fabricate AZO thin films with high transparency and electrical conductivity using a pressurized powder target.

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