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Effect of working pressure on the characteristics of Ga-Al doped ZnO thin films deposited by the facing targets sputtering method

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Ga-Al doped zinc oxide (GAZO) transparent conductive films were deposited on glass substrates by the facing targets sputtering (FTS) method. The GAZO thin film fabricated in argon atmosphere contained Ga and Al, as confirmed by energy dispersive x-ray spectroscopy (EDX). The effects of the working pressure on the structural, optical and electrical properties of the GAZO films were investigated. As the working pressure was increased, the electrical properties were decreased and the optical properties remained constant. As a result, the GAZO thin films deposited on the glass substrates showed 90% transmittance in the visible range (400-800 nm). And we obtained GAZO thin film with the lowest resistivity of $1.186 \times 10^{-3} \Omega \cdot$ cm.

Key words: GZO, AZO, GAZO, Facing Targets Sputtering.

Introduction

Transparent conductive oxides (TCO) play an important role in the fabrication of various devices such as transparent electrodes and sensors and as window materials for displays and solar cells [1, 2]. An expensive indium tin oxide (ITO) film is currently used in most of these devices. However, a cheap and stable TCO film for deposition on transparent substrates is required to realize low-cost electronic devices. In recent years, extensive research for the next generation of low-cost TCO films (doped ZnO and SnO_2) have been carried out to replace the ITO film.

Zinc oxide (ZnO) is a promising alternative to indium tin oxide (ITO) in TCO applications, due to its low cost and relatively low deposition temperature and stability in hydrogen plasma compared with ITO and SnO_2 [3, 4]. The electrical properties of ZnO can be improved by proper doping of ZnO with a group III element (B, Al, Ga, In); Al and Ga have been most widely used as the doping elements [5]. And, more researches related to the ZnO thin film are using Al as the dopant. The Al-doped ZnO thin film with the lowest resistivity is obtained with Al_2O_3 content of 1 to 2 wt.% [6]. However, Al shows relatively low thermal stability and has degeneration problems upon long-time exposure to air ambient, originating from the high reactivity of Al. The element Ga is less reactive and more resistant to oxidation compared to Al [7, 8]. In addition, Ga has the ionic and covalent radii of 0.62 and 1.26 Å, respectively, which are more close to those of Zn (0.74 and 1.31 Å).

In this study we have used the facing targets sputtering (FTS) method which consists of two targets facing each other and substrates located to the side of the center, as shown in Fig. 1. Two target sheets are installed: one is the Ga doped ZnO (GZO) sheet and the other is the Al doped ZnO (AZO) sheet [9]. Thereby, Ga-Al doped ZnO (GAZO) films can be deposited by hetero target deposition in the facing sputtering system. The disadvantages of the Al element can be compensated for by the Ga element [10].

Only few reports have identified the effects of Ar gas pressure on the properties of GAZO thin films deposited at room temperature by the FTS method. In this study, GAZO thin films were deposited at room temperature by the FTS system at various Ar gas pressures, and their structural, optical, and electrical measurements were compared and analyzed.

Experimental

GAZO thin films were prepared by the FTS system, which consists of two target sheets and a substrate

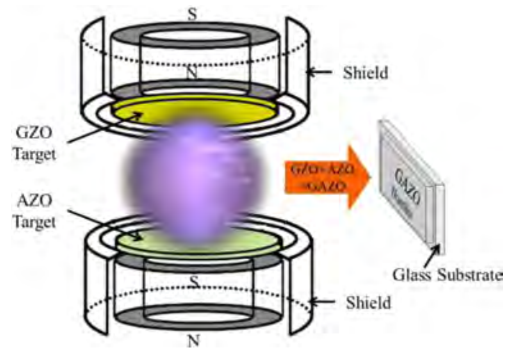

Fig. 1. Schematic of facing targets sputtering (FTS) system.

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Table 1. Sputtering Condition.

Deposition Parameter	Sputtering Conditions
Targets	4inch GZO (Ga_2O_3 3 wt.%, ZnO 97 wt.%)
	4inch AZO (Al_2O_3 2 wt.%, ZnO 98 wt.%)
Substrate	Glass
Base Pressure	1.3×10^{-4} Pa
Working Pressure	0.1-0.39 Pa
Gas Flow	Ar (10 sccm)
Input Power Density	1.1 W/cm^2 (Input Power 90 W)
Thickness	200 nm
Temperature	Room Temperature

located to the side of the center, as shown in Figure 1. Unlike the general sputtering method, the FTS system was designed target facing. Because of this structure, the energetic charged particles are restricted by the magnetic force within the plasma, which is of spiral shape and of high density. Therefore, the FTS system suppresses the bombardment of the substrate by high energy particles. As a result, FTS system can deposit high quality thin films at a low temperature. The sputtering conditions for the preparation of the GAZO thin films are given in Table 1.

The electrical, optical and structural properties were examined by hall-effect measurement, atomic force microscopy (AFM), X-ray diffraction (XRD), energy dispersive x-ray spectroscopy (EDX), scanning electron microscopy (SEM) and UV-VIS spectrometry.

Results and discussion

Fig. 2 shows the chemical component ratio of the deposited thin film by EDX. The thin film, fabricated on a glass substrate under different working pressures, contained metallic ions such as Ga and Al. The weight percents of elements Ga, Al, Zn, and O are shown in table 2. The thin film fabricated in argon atmosphere contained Ga atoms and Al atoms, confirming the formation of a GAZO thin film.

In the results of Fig. 2, as the working pressure increases, the rate of deposition decreases at over 0.13 Pa. Increasing the working pressure decreases the mean free path (MFP), which in turn increases the scattering of the sputtered atoms and decreases the deposition efficiency [11]. The effect of working pressure with increasing of Al and Ga wt%, may be thought that improved of chance at the substitution from Zn to Ga and Al. Because Ga has an ionic radius of 0.62 Å, which is more close to that of Zn (0.74 Å), GA is considered to be a more likely substitute than Al for Zn [12]. We deposited the GAZO thin film under different working pressures and then investigated its properties.

The XRD spectra of the GAZO thin films deposited on glass substrates at room temperature are shown in

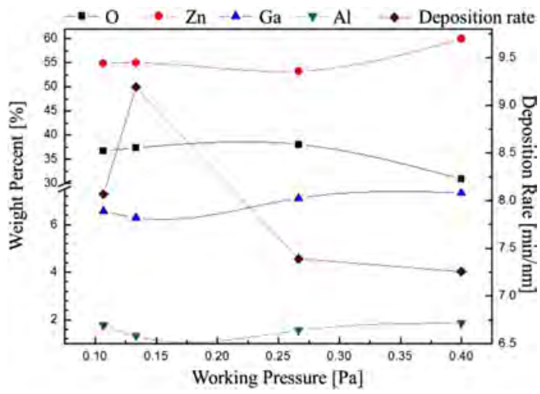

Fig. 2. EDX data and deposition rates of GAZO thin films according to working pressure.

Table 2. The weight percents of Ga, Al, Zn, and O elements.

wp.[Pa]	Ga wt.%	Al wt.%	Zn wt.%	O wt.%
0.10	6.57	1.77	54.91	36.75
0.13	6.29	1.32	55.03	37.36
0.26	7.11	1.56	53.27	38.06
0.39	7.34	1.86	59.94	30.86

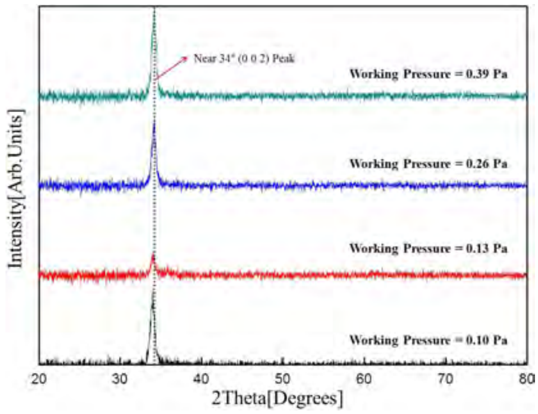

Fig. 3. XRD patterns of GAZO thin films for different working pressures.

Fig. 3. All of GAZO thin films have a diffraction peak of (002) at near 34 °, which is close to that of the standard ZnO crystal (34.45 °) [13], independent of the working pressure. However, no phases of Ga and Al elements were detected from the XRD patterns. This may be due to Ga and Al replacing Zn that was substituted in the hexagonal lattice or Ga and Al segregated to the non-crystalline in the grain boundary [14]. The crystalline quality of the GAZO thin film was improved as evidenced by the increased intensity and sharper (002) diffraction peak. However, due to the increased crystalline quality of the film, electrical properties gradually decreased (Fig. 4) [15, 16].

Fig. 4 shows the variations in electrical properties as a function of working pressure. The results showed that all the GAZO thin films were n-type semiconductors.

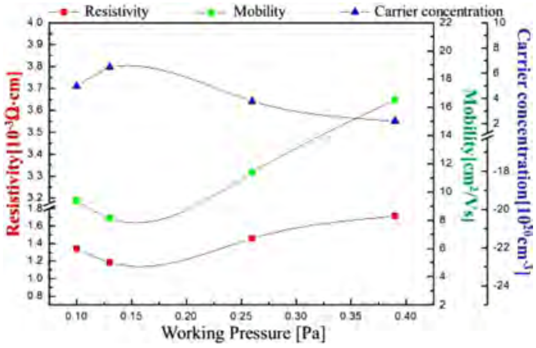

Fig. 4. Electrical properties of GAZO thin films according to working pressure.

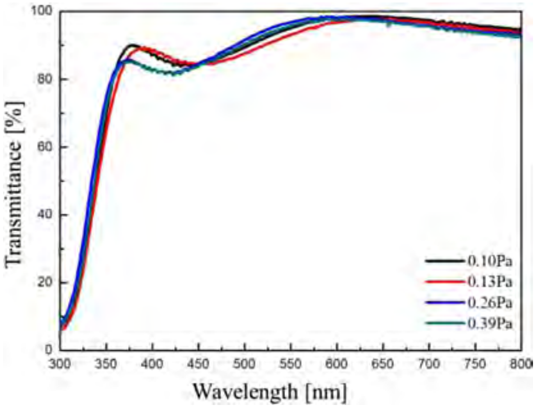

Fig. 5. Optical properties of GAZO thin films for different working pressures.

The resistivity of the GAZO films decreased from 1.186 to $1.711 \times 10^{-3}\ \Omega\cdot$cm as the working pressure was increased from 0.10 to 0.39 Pa. The electrical properties of GAZO films were closely related to the crystalline quality of the films. The high conductivity of the GAZO films might have resulted from the Ga and Al doping effect. The increase in resistivity at over 0.13 Pa working pressure may be due to the excessive supply in Ga and Al atoms, because of which GAZO thin films change from an amorphous state to a crystalline state [17].

Since the electrons in the GAZO thin films are supplied from oxygen vacancy, Ga-Al atoms and amorphous structure in the film is affected to electrical properties. It was thought that an increase of crystalline quality might be a cause of the decrease of oxygen vacancy, resulting in increase of resistivity (Fig. 3) [18].

Another important factor for the consideration of GAZO thin films as potential TCO films is their transmittance to visible light. The transmittance spectra of GAZO films as a function of the wavelength in the range of 300-800 nm are shown in Fig. 5. The average transmittance in the visible wavelength region is about 90% for all the thin films, which means that the working pressure does not have a significant effect on the transparency of the films over the visible wavelength range. According to reported results, the visible range transmittance of TCO thin films is greater than 80%

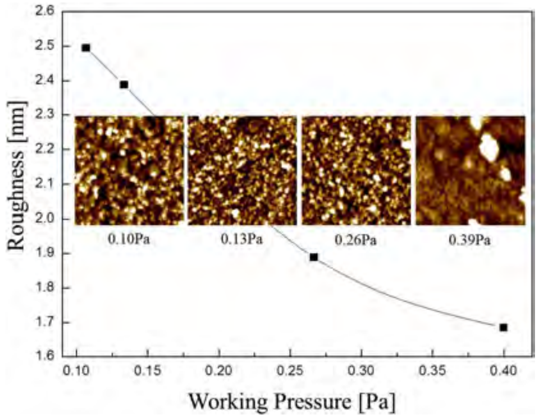

Fig. 6. Surface roughness and AFM images of GAZO thin films according to working pressure.

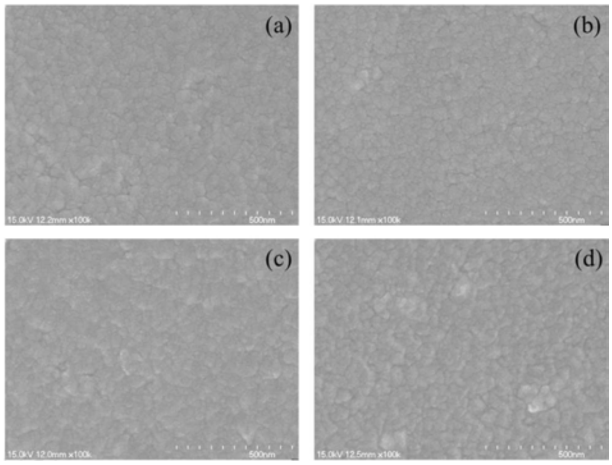

Fig. 7. FE-SEM images of GAZO thin films for different working pressures.; (a) 0.10Pa, (b) 0.13Pa, (c) 0.26Pa, (d) 0.39Pa.

[19]. This finding indicates, therefore, that the GAZO films satisfy the basic transmittance requirement of TCO films for OLED applications.

The surface roughness of GAZO thin films was revealed by the root mean square (RMS) value and AFM images, as shown in Fig. 6. The RMS roughness of the GAZO thin films decreased with increasing working pressure because the energy of the particles arriving at the surface decreased with increasing working pressure. Increased working pressure was likely to have resulted from energy dissipation due to intermolecular collisions because of a decreased MFP [20].

The GAZO thin film with surface roughness under 2 nm satisfies the requirement for OLED device applications [21].

Also, this result can be confirmed by the SEM image of Fig. 7. The as-deposited GAZO thin film showed a smooth surface without cracks or protrusions. Uniform particles are shown on the surface and because of this smoothness, the GAZO thin film, when applied to an OLED anode, can increase the luminance and efficiency of an OLED device. As an important property of an

OLED anode, the surface roughness of an OLED anode determines the luminance and efficiency of the OLED device [22]. Therefore, if considering only surface property, the as-deposited GAZO thin film appears to be suitable for OLED anode applications.

Conclusions

In this study, GAZO thin films were deposited at room temperature under various working pressures by hetero targets in the FTS system. GAZO thin films had a preferred orientation in the [002] direction. The thin film fabricated in argon atmosphere contained Ga ion and Al ion from EDX, which confirmed the formation of a GAZO thin film. However, no diffraction of the Ga and Al phase was found from XRD patterns. We confirmed that working pressure was a key parameter in determining the electrical properties and surface structure of GAZO thin films at room temperature. The thin film deposited at 0.13 Pa had the lowest resistivity of $1.186 \times 10^{-3}\ \Omega \cdot \mathrm{cm}$. The average optical transmittance of the films was 90%. The GAZO thin films deposited at room temperature have satisfactory properties, low resistivity and high transmittance, for applications as TCO films in OLED devices.

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