Develop the Characteristics of AZOY Transparent Conducting Oxide Thin Film

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Abstract

Alumina (Al) and yttrium (Y) co-doped zinc oxide (AZOY), fabricated by “GfE Coating Materials Company”, are used to prepare a ceramic target. RF magnetron sputtering system is used to deposit AZOY transparent conducting metal oxide films (TCOs) on glass substrate using a. Many depositing parameters will influence the characteristics of AZOY films. In this study, the influence of oxygen concentration on the structural, electrical and optical properties of deposited AZOY films are developed. X-ray diffraction measurements show that AZOY films have high c-axis orientation as different oxygen concentration is used. AZOY Films with better texture, higher transmission, lower resistivity of $6.2 \times 10^{-3}$ $\Omega \text{cm}^{-1}$ are obtained for the samples deposited on the 0% oxygen concentration. The AZOY films deposited at the oxygen concentration of 0%~60% have the transmission higher than 85% in the visible region.

Introduction

Transparent conducting metal oxide films (TCOs) are a material group with high industrial relevance. Their unique physical properties make them interesting for a variety of other applications. They are extensively used as transparent electrodes in thin film solar cells and flat panel displays (FPDs). The performances of electro-optical systems such as solar cells and electrochromic devices are linked to the electrical properties of transparent semi-conducting oxide electrodes. Zinc oxide-based films are promising window materials satisfying above requirement due to a large band gap (~3.3 eV), high transparency and low resistivity [1]. The group IIIA metal-doped ZnO materials, particularly the Al-doped or Ga-doped ZnO (AZO), have attracted the intense interest for its great potential applications in the optically transparent conducting layers as the electrode for thin-film solar cells [2–5]. Currently, many methods are used to prepare AZO films, such as metal organic chemical vapor deposition, reactive evaporation and magnetron sputtering [6–9]. The latter method is the most widely used technique for preparing AZO films [7–10]. Furthermore, the optical and electrical properties of AZO films have greatly improved as using an oxide target rather than using a metallic target. The disadvantage of depositing AZO films using an oxide target is its lower deposition rate. However, facing targets magnetron sputtering method is adopted because of their desirable features, such as higher deposition rate and film uniformity. This technology is applied rarely and the investigation is not detailed. Therefore, it is meaningful to study the effects of the substrate temperature in order to obtain AZO films with optimal properties using facing targets magnetron sputtering. In this work, the Y$_2$O$_3$- and Al$_2$O$_3$-co-doped ZnO (AZOY), which was fabricated by “GfE Coating Materials Company”, is used as the source material [11] to fabricate the ceramic targets and RF magnetron sputtering system is used as the method to deposit AZOY films in an argon and oxygen mixing atmosphere. We will investigate the influence of oxygen concentration on the physical and electrical properties of AZOY films.

Experimental

Ceramic target was prepared by sintering the AZOY powder, which was fabricated by “GfE Coating Materials Company”, at around 1100°C. The AZOY films were deposited on 25 mm × 25 mm × 2 mm glass substrates using a RF magnetron sputtering system in which a target was situated facing substrates. The substrates were placed outside the plasma to reduce the direct bombardment and thus to improve film uniformity. The base pressure was smaller than $8 \times 10^{-6}$ torr, Ar and O$_2$ were introduced into the chamber with a total flow at 20 sccm. The RF sputtering power applied on target was kept at 120 W and deposited time was 2 hrs. The oxygen concentration ranging from 0% to 60% was controlled using a mass flow controller. The crystalline structures of AZOY films were characterized by X-ray diffraction (XRD, Bruker AXS D8) and scanning electronic microscope (SEM) measurements were performed using a field emission microscope (JEOL JSM-6700F) with the acceleration voltage of 10 kV. The substrate roughness of AZOY films was examined by atomic force microscope (AFM, NT-MDT Solver PRO-M). The electrical resistivity was measured using a four-point probe (CT 5601Y) and the optical transmission spectra of films were measured by UV-Vis spectrophotometer (Lambda 25/35/45 UV WinLab).
Results and Discussion

It is well known that AZO films deposited by sputtering are highly textured with the c-axis perpendicular to the substrate surface, and X-ray diffraction (XRD) patterns can be employed to prove the crystalline orientation. Fig. 1 shows the X-ray diffraction spectra for AZOY films deposited at different oxygen concentration. As the ratio of oxygen increases, the crystalline intensity of (103) plane apparently decreases and the crystalline intensity of (002) plane first increases and reaches the maximum at the oxygen pressure ratio of 40%. This result suggests that AZOY films depositing under this atmosphere has the optimal c-axis orientation. As more oxygen is introduced into the sputtering ambience during the AZOY films depositing process, the concentration of oxygen vacancies decreases. And that will have improvement of crystallization in the c-axis orientation (002 plane) but have no improvement in the (103) plane. When the oxygen concentration is increased to 60%, the crystalline intensity of (002) plane decreases apparently. That may be due that the adsorbed oxygen atoms exists in the grain boundary and have substitution function like Al in the sites of Zn atoms, consequently leading to the worse crystallization in the c-axis orientation.

![XRD patterns of AZOY films with different oxygen concentration.](image)

The surface roughness of AZOY films as measured using atomic force microscopy (AFM) and the results are shown in Fig. 3 as a function of oxygen concentration. All samples are scanned over a 10 µm × 10 µm area. As the oxygen concentration increases from 0% (pure argon) to 60%, the depositing surfaces become smoother. This result reflects the decrease in the grain sizes of AZOY films as the depositing oxygen concentration increases.

![SEM micrographs of AZOY films deposited at the different oxygen concentration.](image)

The resistivity of AZOY films deposited at various oxygen concentrations is shown in Fig. 4. All AZOY transparent conducting oxide films are the n-type semiconductive materials. The higher conductivity of these films results mainly from deviation of stoichiometric compositions. The conduction electrons in these films are supplied from donor sites associated with oxygen vacancies or excess metal ions. These donor sites can be easily created by chemical reduction or intentional doping. Electrons generated from oxygen...
vacancies and Zn interstitial atoms primarily dominate the conduction characteristics of ZnO. The electrical conductivity in AZOY films are higher than that of pure ZnO film, due to the contribution from the dopants of Al and Y ions on substitutive sites of Zn ions and Al and Y interstitial atoms, as well as from oxygen vacancies and Zn interstitial atoms. The resistivity has a minimum value of 6.2×10^{-3} \Omega\text{cm} at the no oxygen process, which probably results from the highest carrier concentration. As the 20% and 40 % oxygen concentrations are introduced during the depositing process, the resistivity apparently increases. As the oxygen partial pressure ratio is increased to 60%, the concentration of defects, such as oxygen vacancies or interstitials is more than 40%. Hence, the resistivity is lower than 40%.

![AFM images of AZOY films deposited at different oxygen concentration](image)

Fig. 3 AFM images of AZOY films deposited at different oxygen concentration.

Fig. 5 shows the transmission of AZOY films in the UV–Vis regions as a function of oxygen concentration. The optical transmittance spectra of AZOY films present a strong dependence on the oxygen concentration. As pure argon is used as the depositing atmosphere, the AZOY film has the lower transmission during the 380nm ~ 550 nm, in which range the AZOY films depositing under Ar-O2 mixing atmosphere have the similar results, and the optical transmission in the visible regions all exceeded 85%. It is observed that the transmission in the visible region decreases substantially at short wavelengths near the ultraviolet range for all AZOY films. At no oxygen process, the film shows a slight lower visible transmittance in visible region and the absorption of the film is shifted to the shorter wavelength region. The movement of the absorption edge to the shorter wavelength region is the Burstein-Moss shift, which is due to the Fermi level moving into the conduction band with the increase of carrier concentrations.

![Resistivity of AZOY films as a function of different oxygen concentrations](image)

Fig. 4 Resistivity of AZOY films as a function of different oxygen concentrations.

![Transmission of AZOY films as a function of wavelengths at the different oxygen concentration](image)

Fig.5 Transmission of AZOY films as a function of wavelengths at the different oxygen concentration.

**Conclusions**

Through extensive research on the performance of AZOY films, we obtain high-quality transparent conducting AZOY films by controlling the oxygen concentration during depositing process. When the oxygen concentration increases from 0% to 40%, the crystallization increases obviously, and 40% has the maximum c-axis ((002)) orientation. Using 0% oxygen concentration as the depositing atmosphere, the AZOY film has a minimum resistivity of 6.2×10^{-3} \Omega\text{cm} and a transmission toward 85% in the visible range.

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References


