Journal of Non-Crystalline Solids 356 (2010) 1779–1783

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Electrical and structural properties of multicomponent transparent conducting oxide films prepared by co-sputtering of AZO and ITO

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ARTICLE INFO

Article history:
Received 16 November 2009
Received in revised form 8 July 2010
Available online 7 August 2010

Keywords:
Transparent conducting oxides;
Sputtering;
Electrical transport properties;
Microstructure

ABSTRACT

Multicomponent transparent conducting oxide (TCO) films were deposited on glass substrates by co-sputtering of Al-doped ZnO (AZO) and Sn-doped In_2O_3 (ITO) targets. Changes in the electrical and structural properties of the films were investigated as a function of the power on ITO target at a constant AZO power. The addition of limited amounts of ITO (cation ratio of [In]/[Al + Zn + In + Sn], δ<0.28) resulted in deteriorations in the electrical properties of TCO films compared to the pure AZO film. The improvement of electrical conductivity was observed for the films having δ>0.34, where the resistivity decreased with increasing δ. Hall-effect measurements showed that there is a noticeable increase in mobility at a certain value of ITO power. X-ray diffraction analysis revealed that the transition of microstructure from polycrystalline to amorphous phase is corresponding to the increase in mobility. In addition, the introduction of H_2 (2%) into the sputtering ambient was found to increase the carrier concentration of AZO–ITO films and promote the transition into amorphous phase. Both effects resulted in further improvement of the electrical conductivity of the TCO films.

1. Introduction

Transparent conducting oxides (TCOs) have a range of highly useful applications as transparent electrodes in optoelectronic devices such as solar cells and flat panel displays. Especially, indium tin oxide (ITO) is the most popular TCO material because it has not only a fairly low electrical resistivity ($1–4\times10^{-4}\,\Omega$ cm) but also a wide bandgap (3.5–4.3 eV), and it can be easily prepared by means of magnetron sputtering of a ceramic target [1,2]. However, the development of non- or reduced-indium TCO materials has attracted much attention owing to high-cost, scarcity of indium, and toxicity of indium compound powders [3]. Therefore, Al-doped ZnO (AZO) and Ga-doped ZnO (GZO) thin films have been extensively studied as promising candidates to replace ITO because they are non-toxic and less expensive materials [1,3–5]. Furthermore, the ZnO-based TCOs are known to be durable in the presence of hydrogen plasma, which is used for the preparation of Si thin films for photovoltaic applications [6]. Since indium is a well-known dopant for n-type ZnO, a pseudobinary compound of ZnO–In_2O_3 (IZO) has been investigated by several groups [7–13]. Moriga et al. reported that amorphous and homologous $Zn_kIn_2O_{k+3}$ (k = 2,3, …) films with a high carrier concentration could be prepared by the simultaneous sputtering of ceramic ZnO and In_2O_3 targets [8,13]. According to the reports on the IZO films, a minimum of resistivity was observed at an In content [In]/[Zn + In] in the range of 0.6–0.8 [7,8,11–13]. In this paper, we report on the electrical and structural properties of multicomponent TCO films prepared by co-sputtering of AZO and ITO, both are typical TCO materials. We focused on the feasibility of multicomponent TCOs that contain a reduced amount of In. The effects of hydrogen addition in the sputtering ambient on the characteristic properties of the AZO–ITO films were also investigated.

2. Experimental

About 300 nm thick TCO films were deposited on glass substrates by co-sputtering of AZO ($ZnO:Al_2O_3$ = 98:2 wt.%, 4 in. diameter, 99.999% purity) and ITO ($In_2O_3:SnO_2$ = 90:10 wt.%, 4 in. diameter, 99.99% purity) targets with RF and DC powers, respectively. The base pressure of the deposition chamber was below 4×10^{-4} Pa and the working pressure was set at 0.4 Pa, flowing 50 sccm of Ar as the sputtering gas. The substrate temperature during the deposition was maintained at 150 °C. The distance from the center of each target to the substrate was 150 mm. In order to investigate the properties of the AZO–ITO films according to ITO content, the applied power on ITO target was varied in the range of 0–100 W while keeping the power on AZO at 150 W. Atomic compositions of cations in the deposited films as a function of ITO power are shown in Fig. 1. It can be seen that In content increases along with the ITO power. The total fraction of minor elements [Al + Sn] is in the range of 3.0–5.2 at.%. The atomic ratio (δ) of In, [In]/[Al + Zn + In + Sn], is used as a characteristic parameter which varies from 0 to 0.55 (for ITO 100 W) in this work.

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doi:10.1016/j.jnoncrysol.2010.07.024

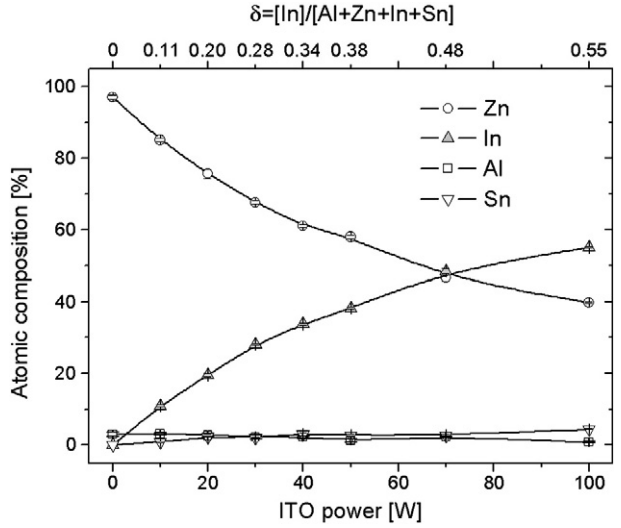

Fig. 1. Elemental composition of cations in AZO–ITO films measured by EDS.

The thickness of a deposited film was determined using a surface profiler (Tencor P-11). Energy dispersive X-ray spectroscopy (EDS) on a scanning electron microscope (SEM; JEOL, JSM 5800) operating at 20 kV was used to estimate the elemental composition of a film. Sheet resistance and electrical transport properties of a film were measured at room temperature with a four point probe (Loresta-GP, MCP-600) and a Hall-effect measurement system using a van der Pauw method (Ecopia, HMS3000). Crystallinity of a film was examined with a X-ray diffraction system (PANalytic, X'pert MPD) by using the Cu K_α line for the X-ray source. The optical transmittance and reflection spectra were obtained with a spectrophotometer (Varian, CARY5000). The surface morphology of a film was examined with a field emission SEM (Hitachi, S-4800) and an atomic force microscope (AFM; DI, MultiMode SPM) in the tapping mode.

3. Results and discussion

3.1. Electrical transport properties

Fig. 2 shows the variations in the electrical resistivity of co-sputtered AZO–ITO films as a function of ITO power. Even though the additional doping of aliovalent elements (In^{3+} and Sn^{4+}) into ZnO seemed likely to improve the electrical conductivity, the mixing of limited amounts of ITO ($\delta = 0.11$ and 0.20 for ITO power of 10 and 20 W, respectively) resulted in increase in the electrical resistivity compared to the AZO film; from 3.6×10^{-3} (for the AZO film) to $9.7\times10^{-3}\,\Omega$ cm (for ITO 10 W). Films prepared with ITO powers larger than 40 W ($\delta > 0.34$) exhibited an improved conductivity. A lowest resistivity of $7.3\times10^{-4}\,\Omega$ cm (corresponding sheet resistance is 23.6 Ω/sq) was observed for the film prepared with an ITO power of 100 W.

The variation in resistivity can be understood by considering the changes in carrier concentration (n) and mobility (μ) as a function of

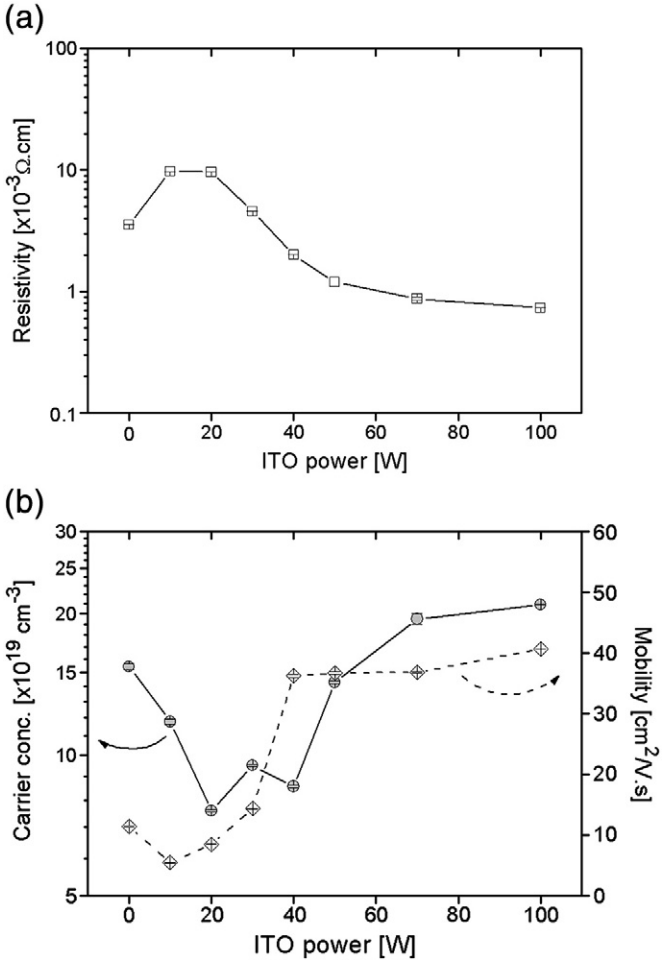

Fig. 2. (a) electrical resistivity, (b) carrier concentration and mobility. Variation in the electrical properties of AZO–ITO films according to the ITO power.

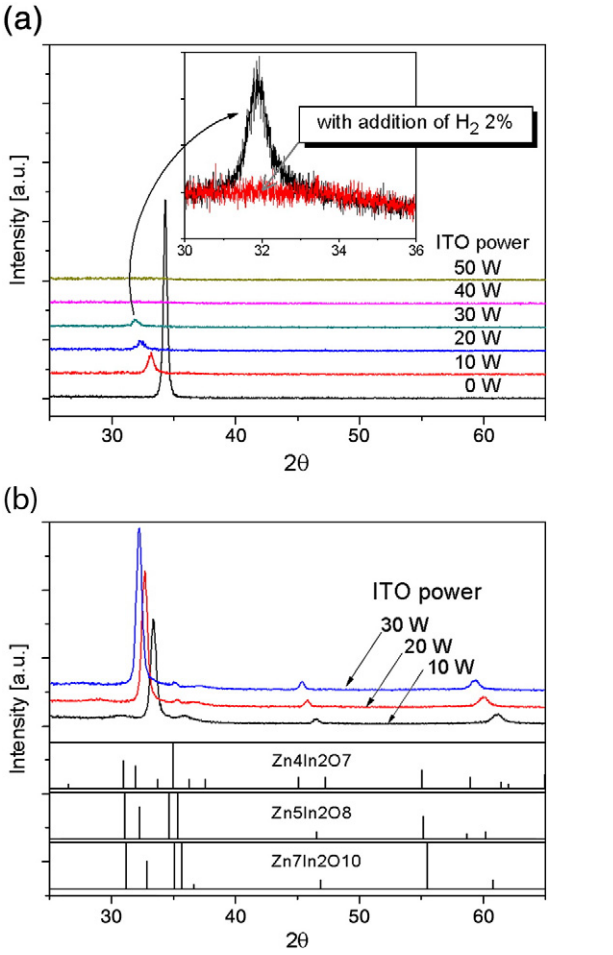

Fig. 3. X-ray diffraction patterns of AZO–ITO films prepared with different ITO powers measured (a) in conventional θ–2θ mode and (b) in glancing incidence 2θ mode. Inset in (a) shows the effect of hydrogen addition on the crystallinity of the films prepared with ITO power of 30 W.