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Polycrystalline films of tungsten-doped indium oxide prepared by d.c. magnetron sputtering

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Abstract

Electrical and optical properties of polycrystalline films of W-doped indium oxide (IWO) were investigated. These films were deposited on glass substrate at 300 °C by d.c. magnetron sputtering using ceramic targets. The W-doping in the sputter-deposited indium oxide film effectively increased the carrier density and the mobility and decreased the resistivity. A minimum resistivity of 1.8×10^{-4} Ω cm was obtained at 3.3 at.% W-doping using the In_2O_3 ceramic targets containing 7.0 wt.% WO_3. The 2.2 at.% W-doped films obtained from the targets containing 5.0 wt.% WO_3, showed the high Hall mobility of 73 cm^2 V^{-1} s^{-1} and relatively low carrier density of 2.9×10^{20} cm^{-3}. Such properties resulted in novel characteristics of both low resistivity (3.0×10^{-4} Ω cm) and high transmittance in the near-infrared region.
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Keywords: Electrical properties; Thin films; Sputtering; Transparent oxide

1. Introduction

It is well-known that n-type semiconducting oxides of In, Zn and Sn have characteristics of both excellent conductivity and high transparency in visible region [1–4]. Above all, Sn-doped indium oxide (indium–tin-oxide, ITO) exhibits low resistivity (1–3×10^{-4} Ω cm) and high transmittance (over 85%) in visible region. ITO films obtained by sputtering method and electron beam evaporation method, have been widely used as transparent electrodes of many kinds of devices such as flat panel displays [5] and solar cells [6]. The electrical properties and the optical properties of ITO films have been studied well [7–10] and reported to be very sensitive to deposition techniques, deposition parameters, and postdeposition treatments.

There are some reports concerning In_2O_3-based transparent conducting oxide other than ITO. Kanai [11] examined the effect of dopants such as Ti, Zr, Hf, Nb, Ta, or W on the electrical resistivity of In_2O_3 single crystal and revealed that only Hf and Zr were the effective dopant in improving conductivity while the other elements including W were not effective. Our previous study [12] showed the properties of amorphous indium oxide films containing W prepared by d.c. magnetron sputtering at ambient substrate temperature. The amorphous films exhibit a low resistivity of 3.2×10^{-4} Ω cm and an average transmittance of over 85% in the visible region at W content of 0.57 at.%.

This paper is concerned with the electrical and optical properties of polycrystalline films of W-doped indium oxide (indium–tungsten-oxide, IWO). The polycrystalline IWO films were prepared by d.c. magnetron sputtering method using ceramic targets at substrate temperature of 300 °C.

2. Experimental procedure

Films of polycrystalline IWO were prepared by d.c. magnetron sputtering using the ceramic targets (6 in. ϕ×5 mm t, purity of 99.99%, Sumitomo Metal Mining Co., Ltd.). The conditions of film preparation were as follows. The sputtering gas was a mixture of Ar and O_2 (0–2.0 vol.%) and the total gas pressure in the deposition was 0.6 Pa. The input d.c. power density was 0.88–1.65 W/cm^2. Attained vacuum pressure of chamber before deposition was 2×10^{-4} Pa or below. The presputtering period was 20 min followed by the sputtering deposition for 2–10 min. The polycrystalline IWO films with the thickness of 400–600 nm

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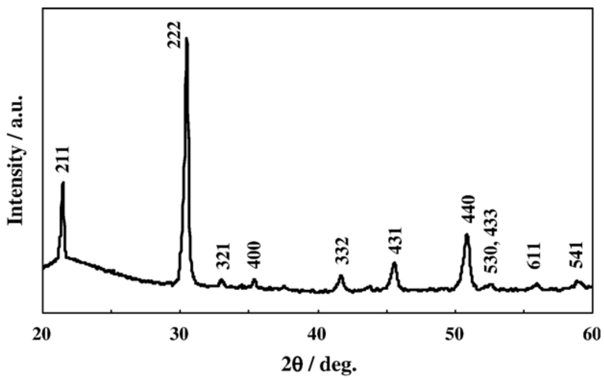

Fig. 1. XRD pattern ($\theta/2\theta$ scans) taken with CuKα radiation of IWO(5.0) film deposited at 300 °C under the total sputtering gas pressure of 0.6 Pa and oxygen content of 0.5 vol.% in sputtering gas. Film thickness: 400 nm.

were deposited on the quartz glass substrate or the fused silica glass substrate at the substrate temperatures (T_s) of 300 °C. These films are herein abbreviated as IWO(x), where "x" means relative WO_3 content (wt.%) in the sputtering target used, that is, WO_3/(In_2O_3+WO_3) (wt.%). As a reference, non-doped In_2O_3 (IO) films and the conventional ITO films were also prepared using the ceramic target (6 in. ϕ × 5 mm t purity of 99.99%, Sumitomo Metal Mining Co., Ltd.) under the same conditions as the above. The target of indium oxide containing 10 wt.% SnO_2 was used for the preparation of ITO films.

The characterizations of the prepared thin films were as follows. Film thickness was measured with a surface texture-measuring instrument. The sheet resistance and resistivity (ρ) were determined with a four-point prove. Hall mobility (μ_H) and carrier density (n) measurement were made using Van der Pauw method at room temperature in a magnetic field of 5 kG. The optical properties such as transmittance and reflectance in the wavelength of 200–2600 nm were measured by using a double-beam spectrophotometer. The dopant content in the film was analyzed by inductively coupled plasma emission spectroscopy and electron probe microanalysis. The structure and the phase of the films were determined by X-ray diffraction (XRD) analysis with Ni filtered CuKα radiation. The microstructure of the films was observed by scanning electron microscopy (SEM).

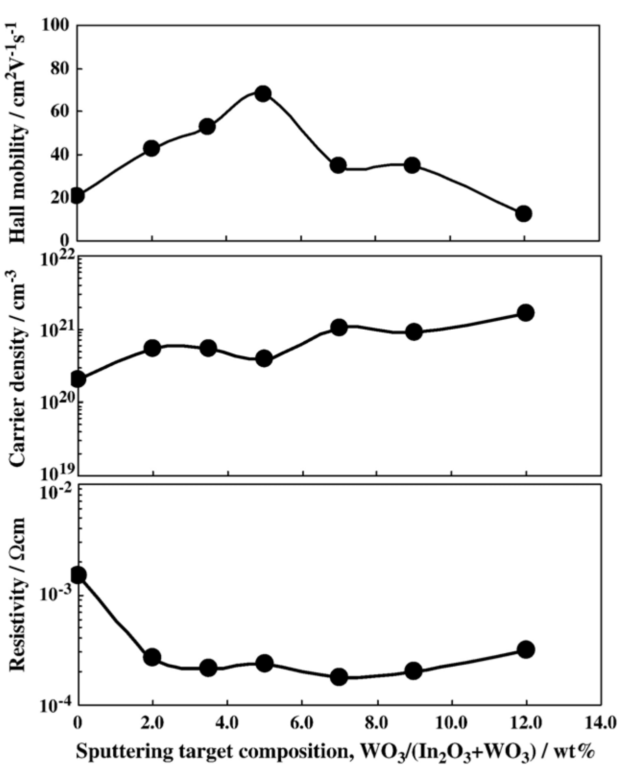

Fig. 2. Resistivity, carrier density and Hall mobility of polycrystalline IWO films as a function of composition of sputtering target. These films were deposited at T_s of 300 °C under the total sputtering gas pressure of 0.6 Pa and oxygen gas content of 0.5 vol.% in sputtering gas. Film thickness: 400 nm.

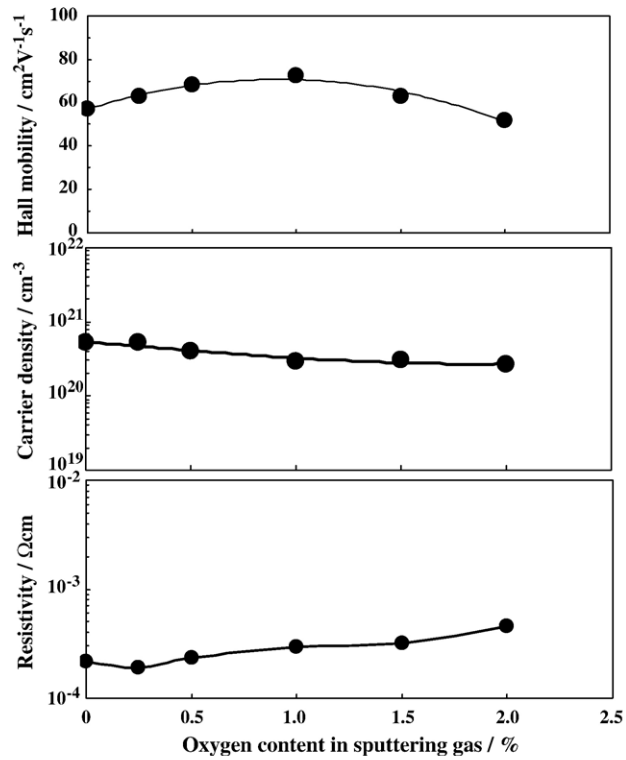

Fig. 3. Resistivity, the carrier density and the Hall mobility of IWO(5.0) films deposited at 300 °C under the various oxygen concentrations. Film thickness: 400 nm.

3. Results and discussion

Fig. 1 shows $\theta/2\theta$ scans for IWO(5.0) film prepared at T_s of 300 °C using the ceramic target of In_2O_3 containing 5.0 wt.% WO_3. As shown in this figure, peaks corresponding to the cubic phase of bixbyite-type In_2O_3 can be easily identified. The surface morphology of IWO(5.0) films was observed using SEM. The surface of IWO(5.0) films deposited at 300 °C revealed the polycrystalline structure showing small subgrain regions within larger columnar grains. Such subgrain microstructure was similar to that shown in sputter-deposited ITO films [13].

Fig. 2 shows the resistivity, the carrier density and the Hall mobility of IWO films as a function of the target composition. These films were deposited under the oxygen content of 0.5 vol.% in the sputtering gas and T_s of 300 °C and had a bixbyite-type polycrystalline monophase. With increasing WO_3 content in target, the carrier density increased from 2.0×10^{20} cm^{-3} of IO (IWO(0)) film to 1.0×10^{21} cm^{-3} of IWO(7.0) film.

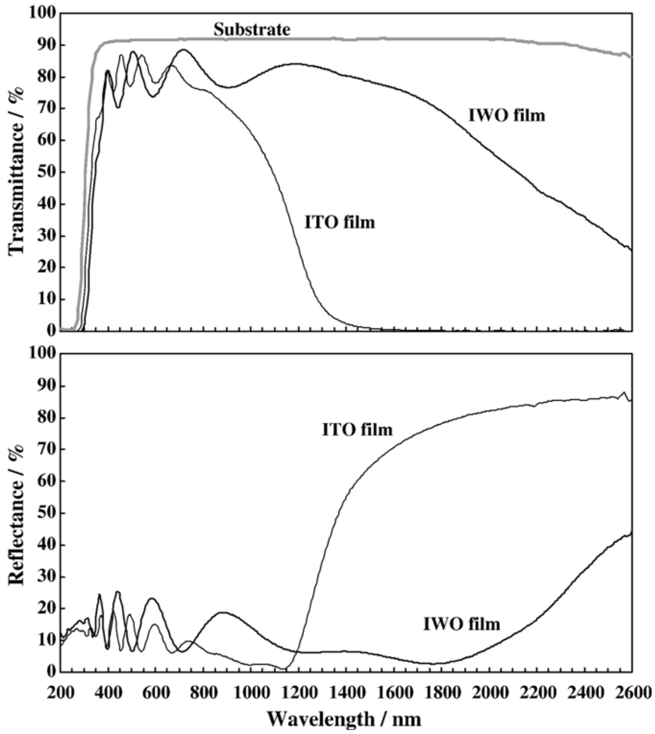

Fig. 4. Transmittance and the reflectance of IWO(5.0) film and conventional ITO film in the wavelength range from 200 to 2600 nm. IWO(5.0) film was deposited at T_s of 300 °C under the total sputtering gas pressure of 0.6 Pa and oxygen gas content of 1.0 vol.% in the sputtering gas. ITO film was deposited at T_s of 300 °C under the total sputtering gas pressure of 0.6 Pa and oxygen gas content of 1.5 vol.% in the sputtering gas. Film thickness: IWO film, 400 nm; ITO film, 600 nm.

The Hall mobilities increased with increasing of the WO_3 content in target up to 5 wt.% but decreased above 7 wt.%. IWO(5.0) film showed the large Hall mobility of 68 cm^2/V s. The composition of this film was 2.2 at.% W content [W/(In+W)]. The lowest resistivity of 1.8×10^{-4} Ω cm was obtained in IWO(7.0) film whose composition was 3.3 at.% W content. Therefore, these results revealed that W element was a useful dopant for the improvement of conductivity of sputter-deposited indium oxide films.

Kanai [11] reported the electrical properties of 5 at.% W-doped In_2O_3 single crystal prepared by flux method, but failed in the improvement of the conductivity. The single crystal preparation by the flux method does not use plasma energy and is not done in vacuum, which is different from the film preparation using the sputtering method. Thus the conditions of doping impurity and formation of oxygen vacancy in preparation of single crystal by flux method were different from those in preparation of film by sputtering method, leading to such different results.

It is noteworthy that W-doping increased the Hall mobility and IWO (5.0) film showed large Hall mobility. Next, we investigated the electrical properties of IWO(5.0) films at various oxygen concentrations in the sputtering gas. Fig. 3 shows the resistivity, the carrier density and the Hall mobility of IWO(5.0) films under the conditions of substrate temperature of 300 °C and the various oxygen concentrations in the sputtering gas. The carrier densities decreased monotonically with an increase of the oxygen concentrations and the Hall mobilities showed a maximum (73 cm^2/V s) at oxygen concentration of 1.0 vol.%. This film showed a relatively low carrier density of 2.9×10^{20} cm^{-3} and low resistivity of 3.0×10^{-4} Ω cm. For comparison non-doped In_2O_3 (IO, IWO(0)) films were deposited under the same conditions. The largest Hall mobility of IO films at optimum oxygen concentration was 49 cm^2/V s which was much lower than that of IWO(5.0) films. Weiher [14] reported that the mobility of non-doped In_2O_3 single crystals was approximately 160 cm^2/V s. The mobilities of sputter-deposited IO films in this study were much lower than this value. This may be attributed to the grain boundary scattering or the charged impurity scattering due to the oxygen vacancy which was introduced in the sputter-deposited IO films. The results of Figs. 2 and 3 revealed that a small amount of W-dopant (2.2 at.%) improved the damaged mobility of sputter-deposited IO films effectively.

Fig. 4 shows the transmittance and the reflectance of IWO(5.0) film and conventional ITO film in the wavelength range from 200 to 2600 nm. The IWO(5.0) film was deposited under 1.0 vol.% oxygen concentration in the sputtering gas and showed the novel properties, that is, the carrier density of 2.9×10^{20} cm^{-3}, the Hall mobility of 73 cm^2/V s and resistivity of 3.0×10^{-4} Ω cm (Fig. 3). ITO film was deposited under 1.5 vol.% oxygen concentration in the sputtering gas and T_s of 300 °C and showed typical electrical properties that is, the carrier density of 1.3×10^{21} cm^{-3}, the Hall mobility of 35 cm^2/V s and resistivity of 1.4×10^{-4} Ω cm. Both of these films exhibited the average transmittance of over 89% in the visible range (wavelength of 400–800 nm). Such high transmittance should be sufficiently high for most applications. However, comparing the transmittance properties of IWO film and ITO film, the transparency window was entirely different. ITO film showed the smaller wavelength of the absorption edge at the wavelength of 250–300 nm than IWO(5.0) film. Since ITO film had a larger carrier density than IWO(5.0) film, ITO film showed a large band-gap shift due to the Burnstein–Moss effect. Moreover, the transparency of IWO(5.0) film in the near-infrared region was much higher than that of ITO film. Generally, the end of the transparency window in the near-infrared region is defined by the plasma-absorption frequency, which depends on the carrier density and the effective mass of the carrier. Since IWO(5.0) film had the lower carrier density than that of ITO film, the end of the transparency window in the near-infrared region was much higher than that of ITO films.

The films having both high conductivity and high transparency in visible region and near-infrared region, like IWO(5.0) film, are useful as transparent electrodes of solar cells [6] or optical communication devices [15] controlling the light of 1310 nm or 1550 nm, e.g. optical modulators, optical attenuators, optical switches, emitters and detectors.

4. Conclusions

In this study, the polycrystalline films of W-doped indium oxide were prepared by d.c. magnetron sputtering at the substrate temperature of 300 °C using ceramic targets. It was revealed that W-doping effectively lowered the resistivity of the indium oxide films. The lowest resistivity of 1.8×10^{-4} Ω cm was obtained in the 3.3 at.% W-doped film. The 2.2 at.% W-doped film exhibited high mobility and relatively low carrier density, resulting in novel characteristics of high conductivity and high transparency in the near-infrared wavelength region.

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