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Titanium-doped indium oxide films prepared by d.c. magnetron sputtering using ceramic target

Yoshiyuki Abe · Noriko Ishiyama

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Abstract Polycrystalline thin films of Ti-doped indium oxide (indium–titanium-oxide, ITiO) were prepared by d.c. magnetron sputtering and their electrical and optical properties were investigated. Doping of Ti was effective in improvement of the electroconductivity of the indium oxide: the electrical resistivity of 1.7×10^{-3} Ω cm of non-doping decreased to minimum value of 1.8×10^{-4} Ω cm at 2.4 at.% Ti-doping when the films were deposited at 300 °C. The polycrystalline ITiO films of 0.8–1.6 at. % Ti-doping showed the high Hall mobilitiy (82–90 $cm^2 V^{-1} s^{-1}$) and the relatively low carrier density ($2.4–3.5 \times 10^{20}$ cm^{-3}) resulting in characteristics of both low resistivity ($2.1–3.0 \times 10^{-4}$ Ω cm) and high transmittance in the near-infrared region (over 80% at 1550 nm), which cannot be shown in the conventional Sn-doped indium oxide (ITO) films.

Introduction

Indium oxide (IO) doped with oxygen deficiency, $In_2O_{3-\delta}$, are well-known as an n-type semiconducting material with wide band-gap (3.75 eV) [1, 2]. Sn-doping in IO effectively increases its carrier density without decreasing wide band-gap, which results in the low resistivity ($1–3 \times 10^{-4}$ Ω cm) with high optical transparency in visible region [2]. Thus the films of Sn-doped indium oxide (indium–tin-oxide, ITO), $In_2O_{3-\delta}$:Sn, have been utilized widely as transparent electrodes of many devices such as liquid crystal displays (LCDs) [3], plasma displays or solar cells [4]. The characteristics and the preparation technique of ITO films have been studied well [5–7].

This paper is concerned with Ti-doped indium oxide film. There have been few reports concerning Ti-doping in IO material. Vossen [8] tried to prepare the Ti-doped indium oxide films by r.f. sputtering method using the target of In_2O_3 containing 20 mol% TiO_2 (6.7 wt.% TiO_2). However, this film exhibited the useless low conductivity (7.5×10^{-1} Ω cm). Kanai [9] examined the effect of dopants such as Ti, Zr, Hf, Nb, Ta, or W on the electrical resistivity and the carrier density of In_2O_3 single crystal. However, only Hf and Zr were the effective dopant on improvement of conductivity while the other elements including Ti were not effective.

We previously reported that conductivity of sputter-deposited indium oxide films were improved by small amount of Ti-doping [10]. This paper presents in detail the electric properties and the optical properties of the Ti-doped indium oxide (indium–titanium-oxide, ITiO) films prepared by d.c. magnetron sputtering method using the ceramic targets of In_2O_3 containing 1–5 wt.% TiO_2.

Experimental procedure

Films of ITiO were prepared by d.c. magnetron sputtering using the ceramic targets (6 inchϕ × 5 mmt, purity of 99.99%, Sumitomo Metal Mining Co., Ltd.). The conditions of film preparation were

Y. Abe (✉) · N. Ishiyama
Ichikawa Research Laboratory, Sumitomo Metal Mining Co., Ltd., Nakakokubun, Ichikawa-shi, Chiba 272-8588, Japan
e-mail: AbeYoshiyuki@adch.smm.co.jp

as follows. The sputtering gas was the 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 following to the sputtering deposition for 2–10 min. ITiO films were deposited on the quartz glass substrate or fused silica glass substrate. The substrate temperatures (T_s) were varied from room temperature (RT) to 300 °C.

As a reference, the IO films and the conventional ITO films were also prepared using the ceramic target (6inch$\phi \times 5$ mmt, 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 preparation of the ITO films.

The characterizations of the prepared thin films were as follows. Film thickness was measured with a surface texture-measuring instrument. The resitivity (ρ), the carrier density (n) and the Hall mobility (μ_H) were measured by the four-point probe method and Hall-effect measurement using van der Pauw method. 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. X-ray diffraction analysis with Ni filtered CuKα radiation was used for qualitative analysis of the crystallinity and the phase of the films.

Results and discussion

Figure 1 shows the ITiO film composition (Ti/(In + Ti), at.%) as a function of TiO_2 content in ITiO sputtering targets. Content of Ti in films monotonically increased as increasing TiO_2 content in targets. Figure 2 shows the resistivity, the carrier density and the Hall mobility of ITiO films as a function of the film composition. These films were prepared under the oxygen content of 1 vol.% in the sputtering gas and T_s of 300 °C and had a bixbyite-type polycrystalline monophase. With increasing the concentration of Ti, the carrier density increased from 8.9×10^{19} cm^{-3} of non-doping to 7.9×10^{20} cm^{-3} of 5.5 at.% Ti-doping. The Hall mobilities increased with increasing the Ti concentration up to 0.8 at.% but decreased above 1.6 at.%. The large Hall mobility of 89.5 cm^2/V s was obtained at 0.8 at.% Ti-doping. The lowest resistivity of 1.8×10^{-4} Ω cm was obtained at 2.4 at.% Ti-doping, which was remarkably decreased as compared with that of non-doped film (1.8×10^{-3} Ω cm). It can be said, therefore, that Ti was useful dopant for improvement of conductivity of sputter-deposited indium oxide films.

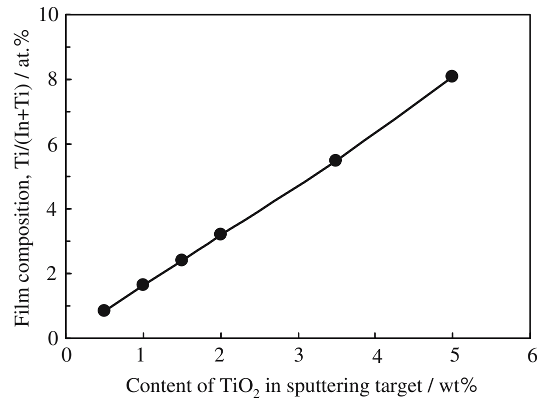

Fig. 1 Composition (Ti/(In + Ti), at.%) of ITiO films as a function of TiO_2 content ($TiO_2/(In_2O_3 + TiO_2)$, wt.%) in sputtering targets

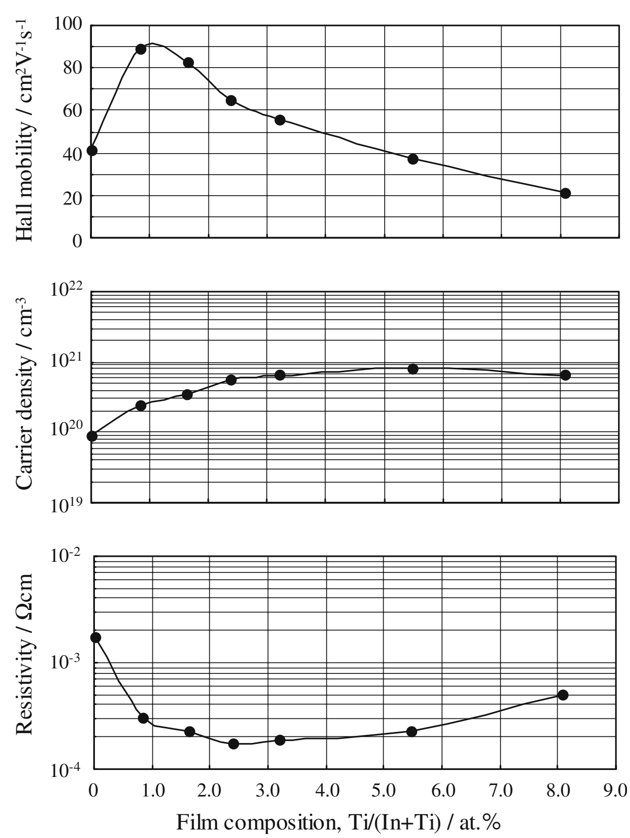

Fig. 2 Resistivity, carrier density and Hall mobility of ITiO films as a function of film composition. Total gas pressure: 0.6 Pa, oxygen content in sputtering gas: 1 vol.%, substrate temperature: 300 °C. Film thickness: 500 nm

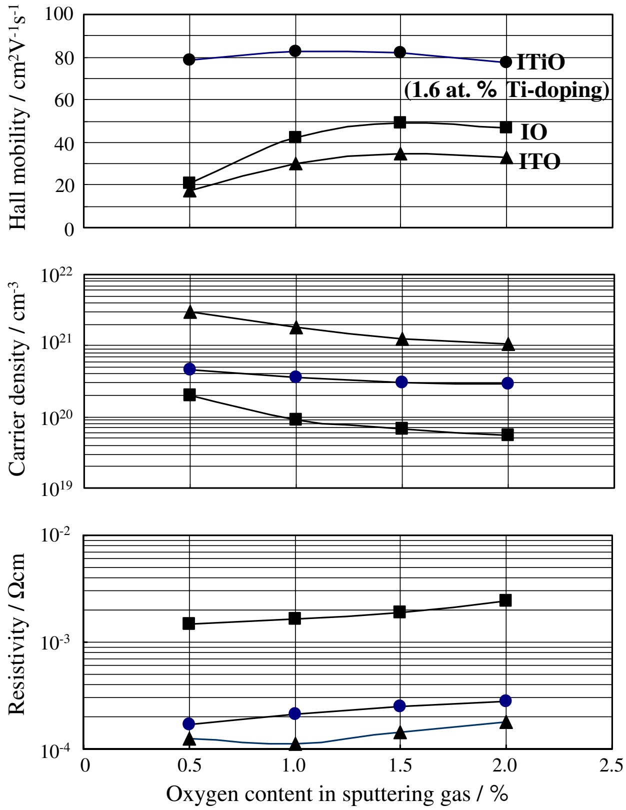

Fig. 3 Resistivity, carrier density and Hall mobility of ITiO films of 1.6 at.% Ti-doping, IO films and ITO films deposited at 300 °C under the various oxygen concentrations. Film thickness: 500 nm

Vossen [8] tried to prepare the Ti-doped indium oxide films by r.f. sputtering method but obtained the only films with high resistivity (7.5×10^{-1} Ω cm). Although, this paper did not show detail conditions of film preparation, it can be inferred that one of the reasons for this failure was too much Ti dopant (20 mol% TiO_2) in the films. Kanai [9] prepared about 5 at.% Ti doped In_2O_3 single crystal by flux method, but failed in an improvement of the conductivity of In_2O_3 single crystal. The single crystal preparation by flux method does not use plasma energy and is not done in vacuum, which is different from the film preparation by sputtering method. Thus conditions of carrier formation by Ti-doping and formation oxygen vacancy in preparation of single crystals by flux method were different from those in preparation of film by sputtering method, leading to different results.

It is known that the electrical properties of sputter-deposited-films of IO and ITO have highly dependent on the oxygen concentration in the sputtering gas. We investigated the electrical properties of ITiO films at various oxygen concentrations in the sputtering gas. Figure 3 shows the resistivity, the carrier density and the Hall mobility of ITiO films of 1.6 at.% Ti-doping prepared from the ITiO target containing 1 wt.% TiO_2 under the conditions of substrate temperature of 300 °C and the various oxygen concentrations in the sputtering gas. This figure also showed the properties of IO film and conventional ITO film prepared by the same conditions for comparison. In every film, the carrier densities decreased monotonically with an increase of the oxygen concentrations and the Hall mobilities showed a maximum at certain oxygen concentration. However, the Hall mobilities of ITiO films had small dependence on oxygen concentration and showed high value (77.3–82.6 cm^2/V s) in the wide range of oxygen concentration, which were not shown in IO film and ITO film. The mobilities of ITO films were smaller than those of IO films. The reason for this may be explained in terms of the effects of charged and neutral impurity scattering formed by Sn-dopant in ITO films [11]. Weiher [1] reported that the mobility of IO 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 small amount of Ti-dopant (0.8–1.6 at.%) improved the damaged mobility of sputter-deposited IO films effectively.

Figure 4 shows the substrate temperature dependency of the resistivity, the carrier density and the Hall mobility of ITiO films of 1.6 at.% Ti-doping. These films were deposited on the condition of 1.0 vol.% oxygen concentration in the sputtering gas. As shown in Fig. 4, with increasing T_s, the resistivity decreased monotonically. The characteristic of high mobility was obtained in the films deposited at T_s of 150–300 °C and the value increased with increasing T_s.

Figure 5 shows the transmittance and the reflectance of ITiO films of 0.8 at.% Ti-doping and 1.6 at.% Ti-doping in the range from 200 to 2600 nm. This figure also showed the data of the conventional ITO film for comparison. These films were deposited under 1.0 vol.% oxygen concentration in the sputtering gas and T_s of 300 °C. Comparing the transmittance properties of ITiO films and ITO film, the transparency window was quite different. ITO film showed the smaller wavelength of the absorption edge at the wavelength of 250–300 nm than ITiO film. Since ITO film had a larger carrier density than ITiO film (Fig. 3), ITO film showed a large band-gap

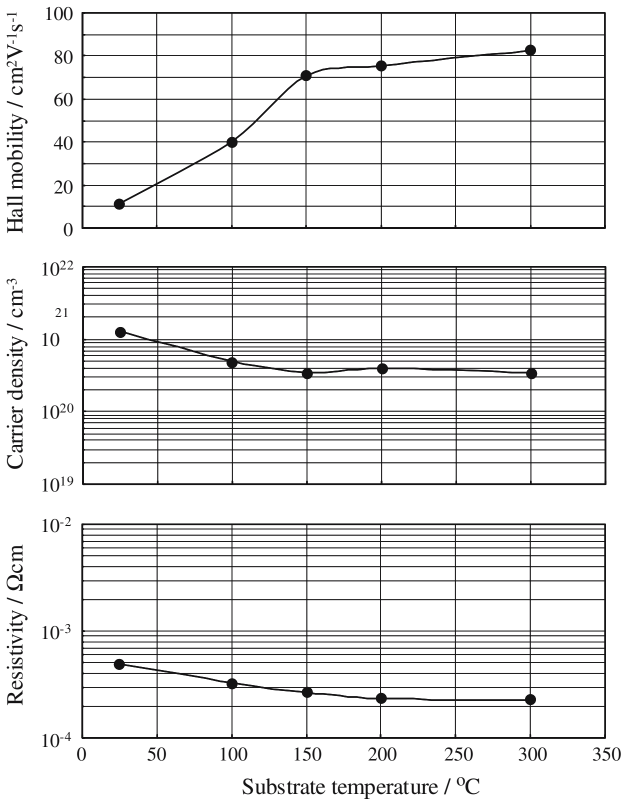

Fig. 4 Substrate temperature dependency of resistivity, carrier density and Hall mobility of ITiO films of 1.6 at.% Ti-doping. Total gas pressure: 0.6 Pa, oxygen content in sputtering gas: 1 vol.%. Film thickness: 500 nm

shift due to Burnstein–Moss effect. The transparency window of ITiO films in the near-infrared region was much higher than that of ITO films. In general, 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 ITiO film had the lower carrier density than that in ITO films (Fig. 3), the end of the transparency window in the near-infrared region was much higher than that of ITO films.

ITO films were tried to be used as electrode of optical communication devices which control near-infrared rays (wavelength of 1310 or 1550 nm) [12, 13] because of their lower absorption loss than that of conventional metal electrodes. Spectroscopic ellipsometry measurement was performed for estimation of optical constants of the films in the near-infrared region. The extinction coefficient (k) at the wavelength of 1550 nm for ITiO film of 0.8 at.% Ti-doping was 0.060 and that for ITiO film of 1.6 at.% Ti-doping was 0.087. These values were much lower than that of conventional ITO film (0.955) indicating that ITiO films had lower absorption loss of the near-infrared ray. Therefore, it can be said that ITiO films are useful for the electrodes of optical communication devices such as optical modulators, optical attenuators, optical switches, emitters (LD, LED), detectors and so on.

Conclusions

In this study, the polycrystalline films of Ti-doped indium oxide were prepared by d.c. magnetron sputtering. It was revealed that Ti-doping effectively lowered the resistivity of the indium oxide films. The lowest resistivity of 1.8×10^{-4} Ω cm was obtained for the film of 2.4 at.% Ti-doping prepared at 300 °C. The 0.8–1.6 at.% Ti-doped films deposited over 150 °C exhibited high mobility and relatively low carrier density, showing the high transparency in near-infrared region and the high conductivity.

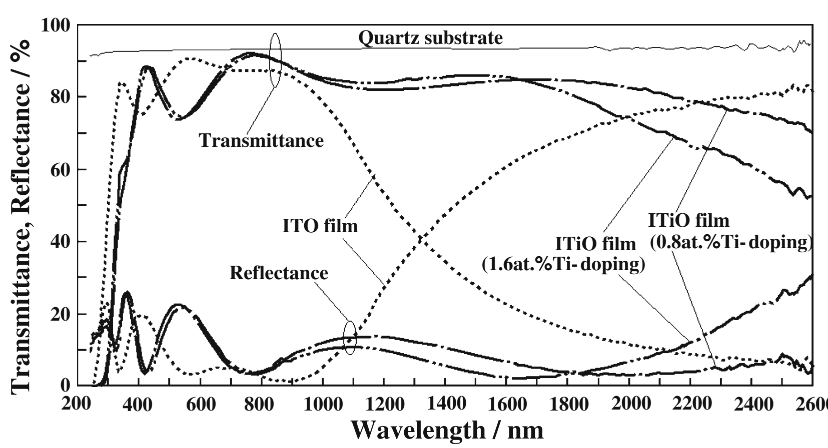

Fig. 5 Transmittance and reflectance of ITiO films of 0.8 at. % Ti-doping and 1.6 at. % Ti-doping and conventional ITO film in the range from 200 to 2600 nm. Total gas pressure: 0.6 Pa, oxygen content in sputtering gas: 1 vol. %, substrate temperature: 300 °C. Film thickness: ITiO film of 0.8 at.% Ti-doping; 204 nm, ITiO film of 1.6 at.% Ti-doping; 212 nm, ITO film 158 nm

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