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Amorphous indium tungsten oxide films prepared by DC magnetron sputtering

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Indium-tungsten-oxide (IWO) films were prepared by dc magnetron sputtering at ambient substrate temperature (T_s). Characteristics of the films were compared with those of In_2O_3–SnO_2 (ITO) thin films prepared under the same condition. The sputter-deposited IWO films have entirely amorphous structure with an average transmittance of over 85% in the visible range and exhibit a minimum resistivity of 3.2×10^{-4} Ωcm at W content [$W/(\mathrm{In} + W)$] of 0.57 at.%. An in-situ heating X-ray diffraction measurement have shown that the crystallization temperature of IWO films is higher than those of ITO films (150–160°C) and increases with increasing W content. This enabled a smooth amorphous surface of IWO films as compared with a rough surface of partially crystallized ITO films as revealed by an atomic force microscopy. IWO films are useful for transparent electrode of organic light emitting diode and polymer LCDs because of the low resistivity, high transparency and smooth surface obtainable by the conventional dc magnetron sputtering at room temperature.

1. Introduction

It is well-known that tin-doped indium oxide (ITO, In_2O_3:Sn) films have characteristics of low electrical resistivity and high optical transparency [1]. They have been utilized widely as transparent electrodes of flat panel displays (FPD) such as liquid crystal display (LCD) [2], plasma display panel (PDP) and organic light-emitting diode (OLED) display [3]. When depositing ITO on polymer color filter substrates in LCDs, substrate temperature (T_s) should be kept low in order to prevent substrate deformation [4]. Amorphous ITO films are often used for the transparent electrode of FPDs because of their superior patterning characteristics for micro-lithography [5]. The stability and efficiency of OLED are reported to depend on the smoothness of surface morphology of electrodes [6]. For elongating its OLED with long lifetime, transparent electrodes with very smooth surface such as a-ITO is useful. The a-ITO films are also required in most applications to have the characteristics of low resistivity and high transparency.

Crystallinity of ITO films depends on the deposition technique and deposition condition. By using electron-beam (EB) evaporation, amorphous ITO films can be prepared at T_s below the crystallization temperature (T_c). T_c of ITO is reported as 150–160°C [5, 7]. On the other hand, ITO films prepared by sputtering method are apt to form a polycrystalline structure even when they are deposited at T_s as low as room temperature (RT) [8]. These results have been explained in terms of the relativily high kinetic energy of sputtered particles reaching the substrate surface when sputtered under low pressure. It is reported that H_2O addition in the sputtering gas results in obtaining amorphous ITO films when sputtered at RT [9]. However, resistivity of the amorphous ITO has not been made below 7×10^{-4} Ωcm, although lower resistivity is required for a practical use in FPDs.

There are some reports concerning amorphous In_2O_3–based films other than ITO. It is known that In_2O_3–ZnO (IZO) films are easy to form an amorphous structure even when they were sputter-deposited at temperatures between RT and 300°C. By making use of rf magnetron sputtering resistivity of IZO films can be reportedly brought down to 4.5×10^{-4} Ωcm [10]. F-doping is reported [11] to degrade the crystallinity of In_2O_3 thin film. Amorphous films of F-doped In_2O_3 could be obtained by sputtering at ambient T_s and low gas pressure, but their resistivity was not lower than those of ITO films.

In this paper, we present a new amorphous transparent conductive film of indium-tungsten-oxide (In–W–O, IWO). IWO films have been prepared by using dc magnetron sputtering method and their electrical and optical properties were investigated.

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2. Experimental

IWO films were prepared by dc magnetron sputtering method using ceramic targets (6 inchϕ × 5 mmt, Sumitomo Metal Mining Co., Ltd.) that were fabricated by sintering the powder compact of mixture of In_2O_3 (purity, 99.99%) and WO_3 (purity, 99.99%). The sputtering gas was a mixture of Ar and O_2 gases and the total gas pressure at deposition was 0.6 Pa. Vacuum pressure of chamber attained before deposition was 2×10^{-4} Pa or below. Dc power of 160 W was input between substrate and target to perform the deposition. The target was pre-sputtered for 20 min and the sputtering time for deposition was 5–10 min. IWO films with the thickness of 350–400 nm were deposited on the fused silica glass substrate at RT. These films are herein abbreviated 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 and ITO films were also prepared using the ceramic targets of In_2O_3 and ITO (10 wt% SnO_2) under the same condition as above.

Characterizations of the prepared films were made as follows. Resistivity (ρ) was measured by the four-point probe method. Optical properties such as transmittance and reflectance in the wavelengths of 200–2600 nm were measured by using a double-beam spectrophotometer Hitachi H-800. Tungsten content in films was analyzed by inductively-coupled plasma (ICP) emission spectroscopy and electron probe microanalysis (EPMA). X-ray diffraction (XRD) analysis with Cu-K_α radiation and transmission electron microscopy (TEM) were used for an estimation of the crystallinity of the films. Surface morphology was recorded by scanning an area of 1 × 1 μm using an atomic force microscope (AFM).

3. Results and discussion

First, we investigated a relation between electrical property of IWO films and sputtering target composition. Fig. 1 shows the carrier density, the Hall mobility and electrical resistivity of IWO films with varying WO_3 contents in the sputtering targets. These films were deposited at T_s of RT under the total sputtering gas pressure of 0.6 Pa, and the oxygen content of 1 vol% in the sputtering gas. As shown in Fig. 1, the carrier density increased from 1.4×10^{20} cm^{-3} of non-impurity-content to 8.2–10.5×10^{20} cm^{-3} of tungsten-content which were obtained from the ceramic target containing 0.5–5.0 wt% WO_3. Such increase of the carrier density contributed toward the decrease of the resistivity from 2.2×10^{-3} Ωcm to 5.6×10^{-4} Ωcm and below. On the contrary, as the tungsten content was increased, the Hall mobility of the films slightly decreased. The minimum electrical resistivity could be obtained by using the ceramic target containing 1 wt% WO_3. The composition of this film was 0.57 at.% W content [$W/(In + W)$].

In general, the electrical and optical properties of the sputtered In_2O_3-based films depend on the oxygen content in the sputtering gas. This is because the carrier density and the mobility largely depend on the oxygen deficiency in the films. So, the oxygen content in the sputtering gas was taken as a variable in plotting the carrier density, Hall mobility and electrical resistivity of IWO films as shown in Fig. 2. Regarding IWO (1.0), the lowest electrical resistivity of 3.2×10^{-4} Ωcm is obtained at oxygen content of 1%. This is lower than those of ITO and IO, 4.6×10^{-4} and 1.8×10^{-3} Ωcm, respectively, both being obtained at oxygen content of

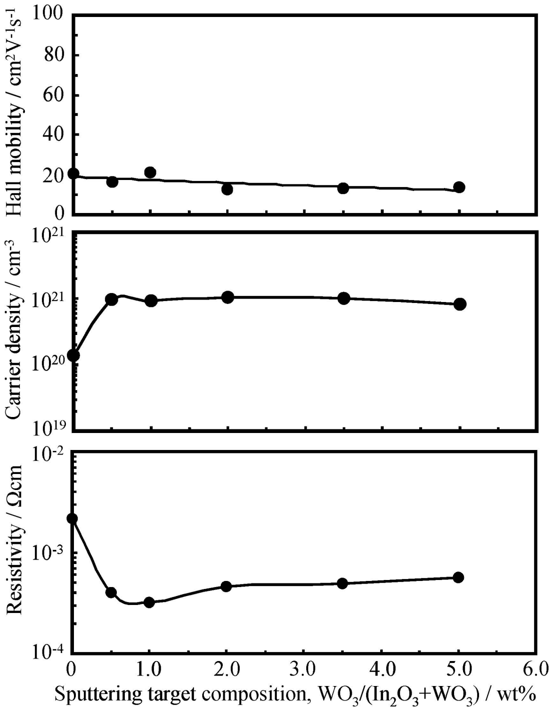

Figure 1 Hall mobility, carrier density and electrical resistivity of IWO films as a function of composition of sputtering target. These films were deposited at T_s of RT under the total sputtering gas pressure of 0.6 Pa and the oxygen content of 1 vol% in the sputtering gas.

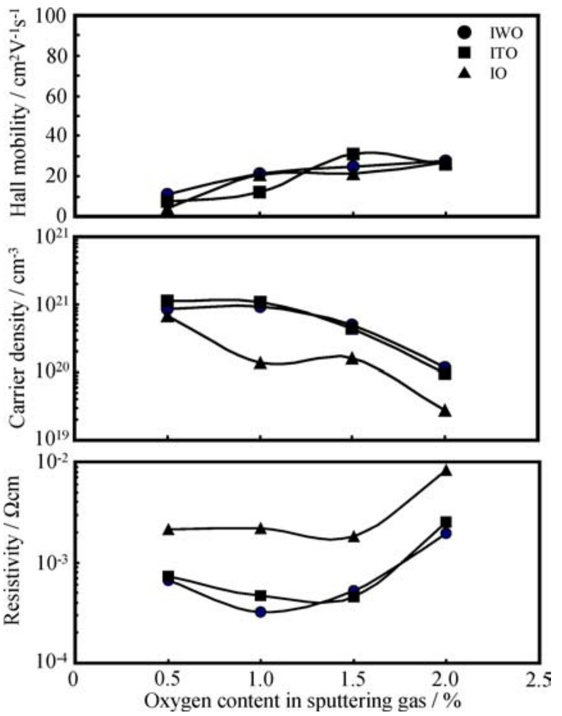

Figure 2 Hall mobility, carrier density and electrical resistivity of IWO (1.0) (●), ITO (■) and IO (▲) films as a function of oxygen content in sputtering gas. These films were deposited at T_s of RT under the total sputtering gas pressure of 0.6 Pa.

1.5 vol%. The difference in the optimum oxygen content in the sputtering gas may be due to the difference of oxygen content in the ceramic target. It was noteworthy that the lowest resistivity of IWO (1.0) films is lower than that of conventional ITO films. The Hall-effect measurement showed that this IWO (1.0) film had the carrier concentration of 9.2×10^{20} cm^{-3} and Hall mobility of 21 cm^2/Vs.

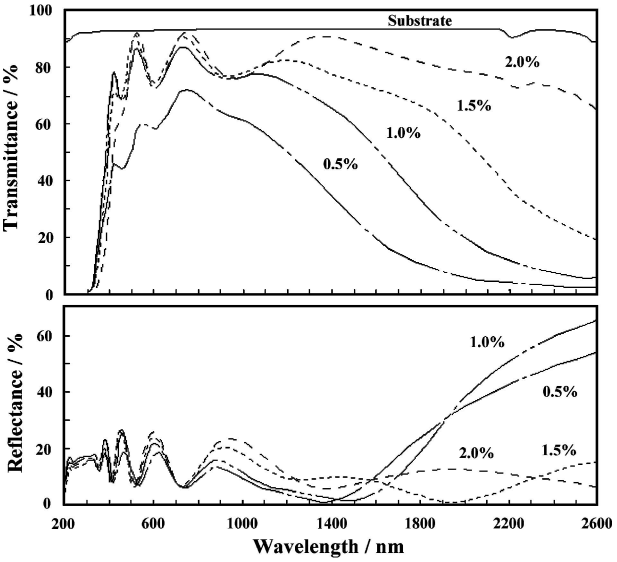

Figure 3 Transmittance and reflectance of IWO (1.0) films deposited under different oxygen content in sputtering gas, total gas pressure of 0.6 Pa and T_s of RT.

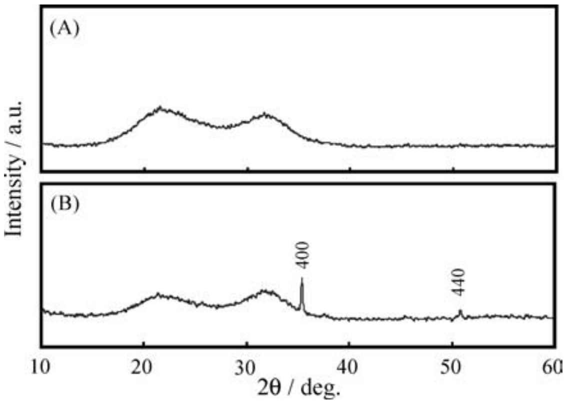

Figure 4 X-ray diffraction (θ-2θ) patterns of IWO (1.0) film (A) and ITO film (B) deposited at T_s of RT. Total sputtering gas pressure was 0.6 Pa and oxygen content in sputtering gas was 1% for IWO (1.0) film and 1.5% for ITO film.

Fig. 3 shows the optical transmittance and reflectance as a function of wavelength for IWO (1.0) films deposited under the various oxygen contents in the sputtering gas. The transmittance in the visible wavelength region increased with increasing the oxygen content in the sputtering gas. IWO (1.0) film deposited under 1 vol% oxygen content in the sputtering gas, which showed the lowest resistivity, exhibited the average transmittance of 85% in the visible range. This transmittance should be sufficiently high for most applications. Fig. 3 also shows a decrease in transmittance and an accompanied increase in the reflectance in near-infrared wavelength with decreasing oxygen content. These changes in the optical properties are consistent with the change in the carrier density.

Fig. 4 shows XRD patterns for $2\theta = 10$–$60°$ of IWO (1.0) film (A) and the ITO film (B). Both of them were deposited under the total gas pressure of 0.6 Pa and T_s of RT. The oxygen contents in the sputtering gas were 1% for IWO (1.0) film and 1.5% for ITO film. As shown in Fig. 4B, weak peaks are observed in the pattern of ITO film, which implies that the film contains polycrystalline phases. On the contrary, as shown in Fig. 4A the XRD pattern of IWO (1.0) film shows only a halo pattern, indicating that the film is an amorphous structure. An electron diffraction pattern was taken for IWO film and ITO film. Fig. 5A shows a diffuse ring pattern, which indicates that IWO film was entirely amorphous. On the other hand, Fig. 5B shows both the diffuse ring and diffraction spots, indicating the mixture of the amorphous and crystalline phases.

Fig. 6 shows AFM surface images of IWO (1.0) film (A) and the ITO film (B). Many protruded regions are observed in the flat surface of ITO films, which are considered to correspond to the crystallite phases. The crystallite phases increased the average roughness (R_a) up to 5.06 nm. It is known that ITO films prepared by sputtering under low gas pressure tend to have a polycrystalline structure even when they are deposited at T_s of RT [8]. When the sputtering deposition is performed under low sputtering gas pressure, the kinetic energy of sputtered particles arriving at the substrate surface is so large as to heat up the microregions in the substrate surface above the crystallization temperature (T_c) of

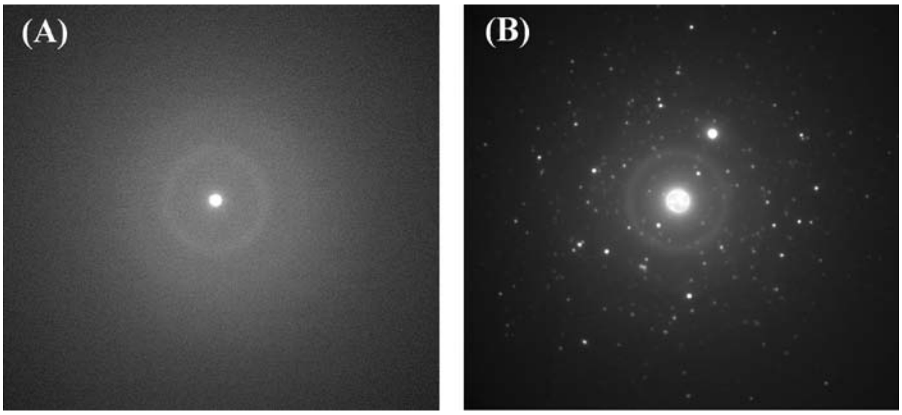

Figure 5 An electron diffraction pattern of IWO (1.0) film (A) and ITO film (B) deposited at T_s of RT. Total sputtering gas pressure was 0.6 Pa and oxygen content in sputtering gas was 1% for IWO (1.0) film and 1.5% for ITO film.

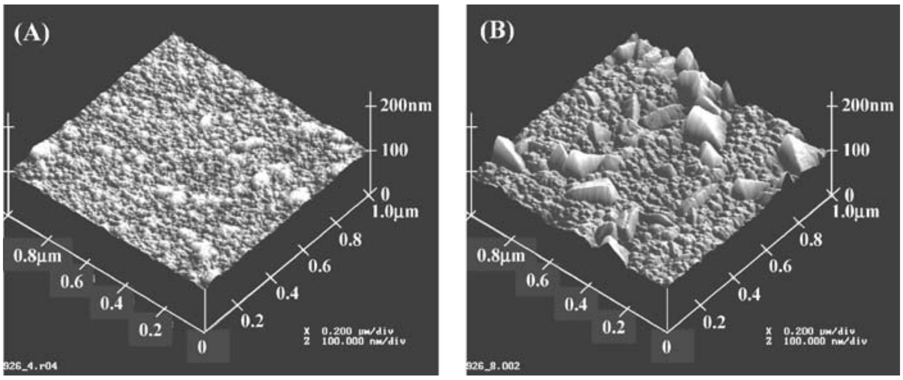

Figure 6 AFM surface images of IWO (1.0) film (A) and ITO film (B) deposited at T_s of RT. Total sputtering gas pressure was 0.6 Pa and oxygen content in sputtering gas was 1% for IWO (1.0) film and 1.5% for ITO film.

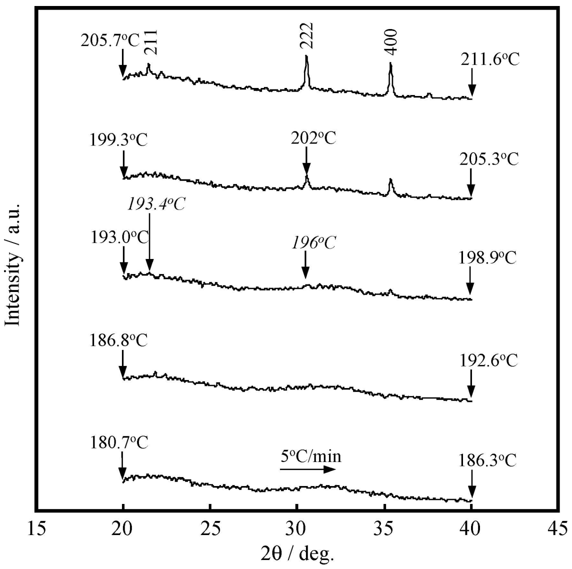

Figure 7 In-situ heating X-ray diffraction (θ-2θ) patterns of IWO (1.0) film with heating at the rate of 5°C a minute.

ITO (150–160°C) [5, 7]. This situation results in the formation of crystallite phases in films. The crystallite phases observed in Fig. 6B are considered to be formed by this mechanism. On the other hand, the surface morphology of IWO films shows no major protrusions but forms a very flat surface. Small R_a of 1.29 nm were obtained in the surface of IWO (1.0) films.

The crystallization temperatures of the amorphous IWO (1.0) films have been estimated by XRD measurement. Fig. 7 shows the XRD patterns of IWO (1.0) film taken while heating from RT to 220°C at the heating rate of 5°C per minute. A diffraction peak observed first was that of 222 diffraction at 2θ of 30.5° when the temperature of the film was 196°C. When the temperature of the film was 193.4°C, the pattern did not show the 211 diffraction peak at the diffraction angle of 21.5° which could be shown at 206.1°C. These results suggests that the T_c of IWO (1.0) film with W content of 0.57 at.% was around 193–196°C. This value of T_c is higher than that of the ITO films reported in references [5, 8]. The T_c of IWO films with various W content was estimated in the same way. The T_c was 200–203°C for IWO (2.0), 209–211°C for IWO (3.5), and 238–240°C for IWO (5.0). Thus the little addition of W acts effectively to raise the crystallization temperature of In_2O_3. Those high T_c is considered to assist the formation of the entirely amorphous films easily even when they are prepared by sputtering under the low gas pressure.

4. Conclusions

In this study, amorphous films of Indium-tungsten-oxide (IWO) were prepared by dc magnetron sputtering without heating the substrate. With an increase of W content in the films the crystallization temperature was raised, which enables the preparation of the amorphous films by conventional sputtering easily. IWO films had low resistivity, high transparency and a smooth roughness of the surface. Therefore the amorphous IWO films are useful for transparent electrode of OLEDs or plastic LCDs.

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