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Effect of cerium doping on the electrical properties of ultrathin indium tin oxide films for application in touch sensors

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ABSTRACT

The electrical and microstructure properties of cerium doped indium tin oxide (ITO:Ce) ultrathin films were evaluated to assess their potential application in touch sensors. 10 to 150-nm ITO and ITO:Ce films were deposited on glass substrates (200 °C) by DC magnetron sputtering using different ITO targets (doped with CeO_2: 0, 1, 3, 5 wt.%). ITO:Ce (doped with CeO_2: 3 wt.%) films with thickness <25 nm showed lower resistivity than ITO. This lower resistivity was accompanied by a significant increase in the Hall mobility despite a decrease in crystallinity. In addition, the surface morphology and wetting properties improved with increasing Ce concentration. This is related to an earlier transition from an island structure to continuous film formation caused by an increase in the initial nucleation density.

1. Introduction

Tin-doped indium oxide (ITO) films are highly degenerate n-type semiconductors with a wide band gap that are used as transparent electrodes in flat panel displays (FPDs), such as liquid crystal displays, plasma display panels and organic light emitting diodes, on account of their high conductivity and transmittance in the visible light range [1–3]. Recently, the touch display industry has expressed major interest in the development of FPDs for applications in areas, such as smart phones and tablet PCs. With the recent demand for high resolution properties in touch sensors, the deposited ITO films need to be as thin as possible to improve the transmittance over the entire visible light range.

The transmittance of ITO films increases with decreasing film thickness but there is a concomitant decrease in electrical conductivity due to the deteriorated film crystallinity [4,5]. In the case of an ultrathin film, the film properties are affected not only by high energy neutrals (Ar^0) and ions (O^-), but also by the initial film growth mode. The growth of ITO films involves different stages: tunneling, percolation and linear Ohmic growth. Isolated small islands grow gradually and coalesce, leading to the formation of continuous conduction paths at the percolation stage [6]. Therefore, a study of the electrical behavior and microstructure in the very thin region is very important for improving the electrical conductivity and transmittance.

For several decades, several studies have examined the characteristics of ITO films according to the film thickness and Sn doping efficiency [7–12]. In particular, the electrical properties of very thin ITO films were found to depend on the nucleation site and deposition temperature [13]. In addition, the onset thickness for achieving conductivity in ITO films was reported to be affected by the initial film formation stages, reflecting the nucleation density, surface morphology and wetting properties [14]. Therefore, a key point for the electrical conductivity in ultrathin ITO films could be determined by the relationship between the initial stages of film formation and the nucleation density, whose value is also affected by the bond enthalpy. In this respect, Ce insertion into ITO was chosen to explain the key factors dominating the initial stages of ultrathin film growth because of its much higher bond enthalpy (Ce–O: 795 ± 8 kJ/mol) than the other atoms (In–O: 320.1 ± 41.8 kJ/mol, Sn–O: 531.8 ± 12.6 kJ/mol), meaning that it can easily cause nucleation with strong bonds.

In this study, the electrical properties and microstructure of ultrathin ITO:Ce films were examined in terms of the Ce concentration, which can affect the properties of very thin films due to the change in nucleation density.

2. Experimental details

The electrical behavior of ITO ultrathin films with different Ce concentrations was analyzed. For this, 10 nm thick ITO and ITO:Ce films were deposited on non-alkali glass (Corning E2000) by DC magnetron sputtering using an ITO target (10 wt.% SnO_2, Samsung Corning Co., LTD) containing 0, 1, 3 and 5 wt.% Ce (Multi-sputtering system, Dae Ki Hi-Tech Co. Ltd.). In addition, ITO and ITO:Ce films with various thicknesses (10–150 nm) were deposited using ITO targets containing 0 and 3 wt.% Ce. The substrate temperature was 200 °C, which is above the crystallization temperature (170 °C) of ITO. The total gas pressure and substrate to target distance were 0.7 Pa and 70 mm, respectively. In addition, the total sputtering power was 70 W, which was optimized

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in a previous study [15]. Prior to deposition, all targets were pre-sputtered for 5 min to sustain the plasma stability and obtain reproducible films. The film thickness and microstructure were examined using a spectral reflectometer (ST-2000 DLXn, K-Mac) and X-ray diffraction (XRD, CuKα radiation at 40 kV–40 mA, θ–2θ mode, GADDS, BRUKER). The electrical properties of the ITO films were determined by Hall Effect measurements (HMS-3000, ECOPIA). The surface morphology of the films was analyzed by atomic force microscopy in non-contact mode (AFM, L-Trace, Nano Navi). The contact angle of a water droplet on the film was measured using a contact angle meter (KRUSS Easy Drop) using the sessile drop method.

3. Result and discussion

Fig. 1 shows the electrical properties [(a) sheet resistance, (b) resistivity, (c) carrier concentration, (d) Hall mobility] of ITO and ITO:Ce films deposited using ITO targets (doped with CeO_2: 1, 3, 5 wt.%) as a function of the film thicknesses 10 to 150-nm at a substrate temperature (T_s) of 200 °C. The sheet resistance of both ITO and ITO:Ce films decreased with increasing film thickness, but the resistivity showed a different trend. These changes in resistivity might be related to the carrier density and Hall mobility. In contrast, the undoped ITO films showed a decrease in resistivity with increasing film thickness, which is in good agreement with other reports [5–8]. This was attributed to an increase in carrier concentration, which was generated by Sn^{4+} ions substituted into the In^{3+} sites with increasing film crystallinity [15–17]. The decrease in Hall mobility with increasing carrier concentration was attributed to the increase in ionized impurity scattering based on substitutional Sn^{4+} ions [17]. On the other hand, the resistivity of ITO:Ce films thicker than 25 nm increased with increasing film thickness with a concomitant decrease in Hall mobility but there was no significant change in carrier concentration. This suggests that the decrease in Hall mobility is influenced by the increase in neutral impurity scattering with the formation of a neutral Sn–Ce oxide defect complex, causing a decrease in the Sn doping efficiency and film crystallinity with the introduction of Ce atoms.

As a result, the ITO films (2.26×10^{-4} to 2.34×10^{-4} $\Omega\cdot$cm) had a relatively lower resistivity than the ITO:Ce films (4.43×10^{-4} to 6.96×10^{-4} $\Omega\cdot$cm) over the thickness range, 80 to 150-nm. On the other hand, over the thickness range 10 to 25-nm, the electrical conductivity of the ITO and ITO:Ce films showed a different tendency due to the introduction of Ce. In this thickness (<25 nm) range, the ITO:Ce films showed lower resistivity than the undoped ITO film due to an obvious increase in Hall mobility, even though the carrier concentration decreased slightly. This means that the Hall mobility dominates the electrical conductivity in very thin films (<25 nm). The growth of ITO films is generally classified into 3 modes: nucleation, island formation and coalescence. These growth modes are due to the initial nucleation density. Therefore, the Hall mobility is strongly affected by an earlier transition from an island structure to continuous film formation due to an increase in the initial nucleation density with the introduction of Ce atoms. This might be due to the promotion of strong bonds to the nucleus because the Ce–O bond enthalpy (795 ± 8 kJ/mol) is higher than that of other atoms (In–O: 320.1 ± 41.8 kJ/mol, Sn–O: 531.8 ± 12.6 kJ/mol) [18]. This can also be explained by the suppressed surface migration of sputtered atoms because the crystallization temperature of ITO:Ce is higher than that of un-doped ITO [19].

Fig. 2 shows the (a) resistivity, (b) carrier concentration and (c) Hall mobility of ultrathin (10 nm) ITO:Ce (doped with CeO_2: 1, 3, 5 wt.%) films deposited at T_s = 200 °C as a function of the Ce concentration. The resistivity of the ITO films decreased with increasing Ce concentration up to 3 wt.% due to an increase in Hall mobility, whereas the carrier concentration decreased slightly due to a decrease in Sn doping

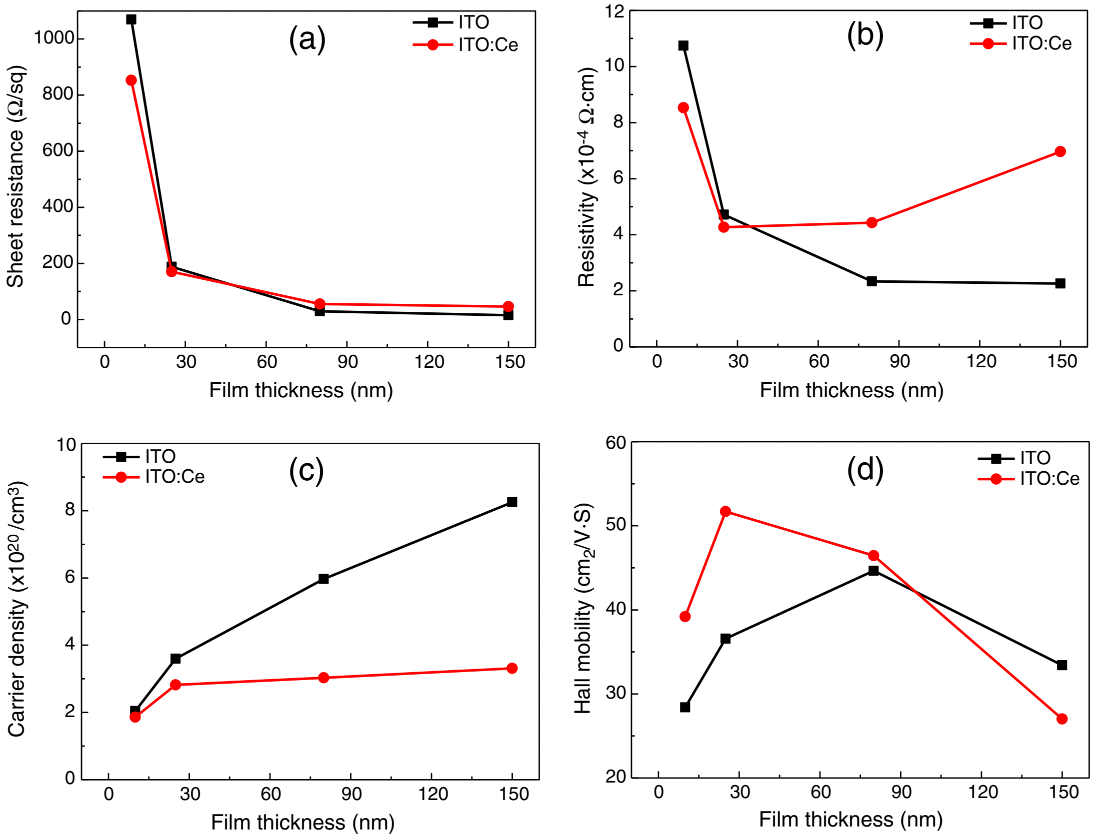

Fig. 1. Electrical properties [(a) sheet resistance, (b) resistivity, (c) carrier density, (d) Hall mobility] of ITO and ITO:Ce (doped with CeO_2: 3 wt.%) film with various film thicknesses 10–150 nm.