Materials Research Bulletin 47 (2012) 2800–2803

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Room temperature deposition of IZTO transparent anode films for organic light-emitting diodes

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ARTICLE INFO

Article history:
Available online 25 April 2012

Keywords:
A. Organic compounds
B. Sputtering
D. Electrical properties
D. Optical properties
D. Surface properties

ABSTRACT

This study was to investigate anodic electrode IZTO films deposited by pulsed DC magnetron sputter at room temperature with various oxygen partial pressures onto glass substrate and to analyze the structural, electrical, and optical properties, as well as the relationship between the chemical binding state of the surface and the characteristics of IZTO films. In addition, the prepared IZTO films were used to fabricate the organic light emitting diodes (OLEDs) as an anode layer to study the device performances. The IZTO film deposited at optimal oxygen partial pressure of 2.0% in sputtering process showed the best properties, such as a low electrical resistivity and high optical transmittance of $<5.1 \times 10^{-4}\ \Omega$ cm and >80% in the visible wavelength of 400–800 nm, respectively. The OLED characteristics with the optimum condition showed good brightness and the lowest turn-on voltage of >10,000 cd/m^2 and 4.67 V. These results indicate that IZTO films can be a promising candidate as an alternative TCO electrode material for flexible and OLED devices.

1. Introduction

Transparent conducting oxide (TCO) films have been widely used as transparent electrodes of various optoelectronic devices such as FPD (flat-panel display), solar cell and TSP (touch screen panel) [1–3]. In particular, indium tin oxide (ITO) is one of the most commonly used TCOs in display applications due to its good optical and electrical properties. However, indium has become increasingly expensive and rare because of its limited resources. In addition, ITO thin films physically have some problems for OLED and flexible displays, such as imperfect work function, chemical instability and high deposition temperature [4]. Therefore, multi-component TCO materials have been reported as anode materials. Among the various materials, IZTO films have gained much attention as anode materials due to their high work function, good conductivity, high transparency, and low deposition temperature [5]. In previous studies, Kim et al. reported that transparent conductive IZTO films deposited at optimum oxygen partial pressures could be obtained using facing targets sputtering system [6]. However, the effect of the oxygen partial pressure on the properties of IZTO films for their potential use as an anode material for OLED devices has not been reported. In this study, we prepared IZTO films on glass substrate at room temperature using a pulsed DC magnetron sputtering system with different oxygen partial pressure. The structural, electrical, and optical properties of IZTO films were examined. In addition, the effect of the IZTO anode electrode on the performance of OLED devices in terms of the optical transmittance and electrical resistance of the devices was characterized.

2. Experimental

IZTO thin films with a thickness of 200 nm were deposited on Corning 1737 glass substrate at room temperature by pulsed DC magnetron sputtering with a sintered ceramic target of IZTO (In_2O_3 80 wt.%, ZnO 10 wt.%, SnO_2 10 wt.%). The plasma power and working pressure were 125 W and 6 mTorr, respectively. During film deposition, the sputtering gas was a mixture of argon and oxygen, and the oxygen partial pressures ($O_2/(Ar + O_2)$) varied from 0.0% to 3.0%. The film structure was observed by X-ray diffraction system, and the surface morphology and thickness were analyzed using a field emission scanning electron microscope. The resistivity, carrier density and mobility of the IZTO thin films were measured by four-point probe and Hall measurement system. The transmittance was investigated in the wavelength range of 200–1100 nm using a UV–visible spectrometer. X-ray photoelectron spectroscopy (XPS) was used to confirm the surface chemical state of the IZTO films. We used the IZTO films as anodes for the OLED

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http://dx.doi.org/10.1016/j.materresbull.2012.04.089

devices using a standard vacuum evaporation process. The OLED structures were aluminum (Al), lithium fluoride (LiF), tris-(8-hydroxyquinoline) aluminum (Alq_3), N,N′-diphenyl-N,N′-bis(3-methylphenyl)-1,1′-diphenyl-4,4′-diamine (TPD), and anode electrode (IZTO), which were used as the top cathode, cathode buffer layer (CBL), emitting layer (EML), hole transport layer (HTL), and bottom anode, respectively. The current density–voltage (*I–V*) of the OLED devices with IZTO and conventional ITO anode films was measured by a Keithley 2400 electrometer. The brightness–voltage (*B–V*) of the OLED devices was evaluated by measuring the photocurrent induced during light emission with a Keithley 485 picoammeter.

3. Results and discussion

Fig. 1 shows XRD plots of the reference ITO and IZTO films deposited by pulsed DC magnetron sputtering at various oxygen partial pressures. In order to compare the crystallization properties of IZTO films, the reference ITO film deposited at room temperature was prepared at the same process conditions [7]. All XRD plots, regardless of the oxygen partial pressures, showed weak and broad peaks representing amorphous glass ($\theta = \sim 23^\circ$) and amorphous IZTO structure ($\theta = \sim 31^\circ$) due to the low substrate temperature. All IZTO films showed stable amorphous structures. Bae et al. reported that the crystallization of Sn-doped In_2O_3 film occurs rapidly at low temperature ($\leq 150^\circ$) due to low amorphous/crystalline transition temperature [8]. Conversely, IZO films have a stable amorphous structure below 500 °C due to high amorphous/crystalline transition temperature [9]. Due to the immiscibility of ZnO and SnO_2 in In_2O_3, the IZTO films could also maintain a stable amorphous structure. Therefore, phase separation of ZnO and SnO_2 from In_2O_3 is necessary for obtaining crystallized IZTO films. As a result, the IZTO films can maintain a more stable amorphous structure than ITO films. This structural stability of the amorphous IZTO films is beneficial for the stable performance of OLEDs and flexible OLEDs.

Fig. 2 shows the resistivity, mobility and carrier density of IZTO anode films at different oxygen partial pressures. These results show that the electrical properties of IZTO films are sensitive to the oxygen partial pressures in the sputtering process. As the oxygen partial pressure increased to 2.0%, the resistivity of IZTO films decreased. However, the resistivity of the IZTO films increased slightly from 2.5% to 3.0% oxygen partial pressure. As a result, the lowest resistivity of the IZTO films was obtained at 2.0% oxygen partial pressure.

To understand this tendency, the sources of electrical charge carriers in the films should be considered. In general, the electrical

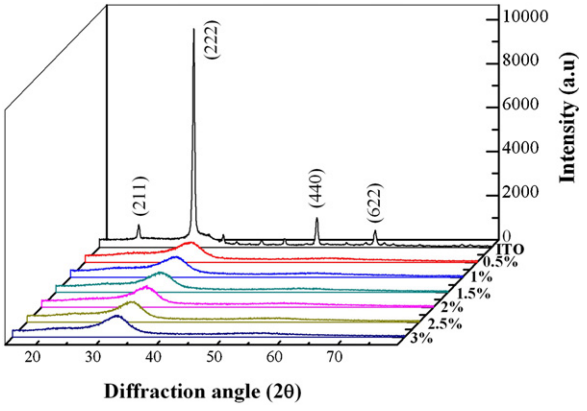

Fig. 1. X-ray diffraction patterns of reference ITO and IZTO films deposited at various oxygen partial pressures on glass substrate.

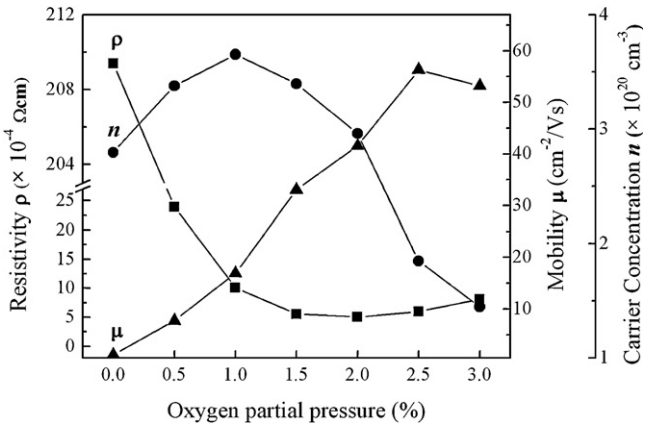

Fig. 2. Variations of the resistivity, mobility and carrier density of IZTO films with different oxygen partial pressures.

charge generation of amorphous IZTO films is possibly related to the following two explanations. First, the substitution of Sn^{4+} ion for the site of In^{3+} caused by locally ordered region in amorphous matrix could be the effective dopant even in amorphous IZTO films [10]. Another is that unintentionally Sn-doped In_2O_3 with a high deficiency of oxygen gives rise to doubly charged oxygen vacancies [11]. In this study, the doping concentration of Sn was fixed, but only oxygen partial pressures were varied to optimize their resistivity. Therefore, it can be said that the introduction of oxygen gas during the sputtering process contributes to the carrier generation, such as oxygen vacancies.

The IZTO film deposited without oxygen gas shows extremely high resistivity ($\sim 2.1 \times 10^{-2}\ \Omega$ cm), even though it has relatively high carrier density. This may be due to the fact that the oxygen deficiencies deteriorate the structure properties, and the scatter centers exist in the form of Sn–O complexes without proper oxygen partial pressure, and consequently reduce the carrier mobility [12,13]. Up to 1.0% oxygen partial pressure, the carrier density and mobility increased due to the introduction of oxygen gas; consequently, the resistivity of the IZTO films decreased sharply. However, the carrier density decreased from 1.5% oxygen partial pressure, as the incorporation of excess oxygen ions (O^{2-}) would eliminate oxygen vacancies. The available mobile electronic charge density would decrease, but the increase in charge carrier Hall mobility would compensate due to the removal of scatter centers. As a result, the IZTO film deposited at 2.0% oxygen partial pressure showed enhanced electrical properties, such as low electrical resistivity of $5.1 \times 10^{-4}\ \Omega$ cm. The resistivity of IZTO films prepared at room temperature is comparable to that of conventional ITO films deposited at high temperatures above 300 °C.

Fig. 3 shows the optical transmittance of the IZTO films at various oxygen partial pressures. It can be seen that the optical transmittance of the IZTO films significantly increased from 1.5%, obviously exhibiting that adding a proper amount of oxygen gas significantly improved the transmittance and electrical properties of the IZTO films. The IZTO films at 2.0–3.0% oxygen partial pressure exhibited high optical transmittance, higher than 80% with glass substrate in the UV visible range (400–800 nm), suggesting that the served oxygen gas improved the optical transmittance of IZTO anode films due to the reduction of the doped metallic Sn and Zn oxide complexes in the IZTO films. The transmittance of the IZTO anode films deposited at optimized oxygen partial pressure is fairly high compared to conventional ITO films.

Fig. 4 shows the XPS core level spectra for O 1s, In 3d, Zn 2p, and Sn 3d on the surface of the IZTO films. As oxygen partial pressure is