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Preparation of indium tin oxide anodes using energy filtrating technique for top-emitting organic light-emitting diode

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ABSTRACT

Indium tin oxide (ITO) anodes were deposited by an improved magnetron sputtering technique (energy filtrating magnetron sputtering technique, EFMS) for top-emitting organic light-emitting diodes (TOLEDs). The phases, surface morphologies and optical properties were examined by X-ray diffraction (XRD), scanning electron microscope (SEM), atomic force microscopy (AFM) and spectroscopic ellipsometer. The sheet resistances were measured by the sheet resistance meter. The electrical properties were tested by the Hall measurement system. The electro-optic characteristics were examined by a special home-made measurement system. Results indicated that ITO anode deposited by EFMS had a more uniform and smoother surface with smaller grains. ITO film was prepared with the electrical property of the lowest resistivity ($4.56 \times 10^{-4}\ \Omega$ cm), highest carrier density (6.48×10^{20} cm^{-3}) and highest carrier mobility (21.1 cm^2/V/s). The average transmissivity of the ITO film was 87.0% in the wavelength range of 400–800 nm. The TOLEDs based on this ITO anode had a lower turn-on voltage of 2 V (>0.02 mA/cm^2), higher current density of 58.4 mA/cm^2 at 30 V, higher current efficiency of 1.374 cd/A and higher luminous efficiency of 0.175 lm/W. The possible mechanism of the technique was discussed in detail.

1. Introduction

The new generation of top-emitting organic light-emitting diodes (TOLEDs) [1,2] has caused considerable interests in recent years. Compared with the traditional bottom-emitting organic light-emitting diodes (BOLEDs) in which the anode was deposited directly on the glass, TOLEDs had higher brightness, wider visual angle, smaller power, faster response and lower cost [3]. In the TOLEDs, indium tin oxide (ITO) film was used commonly as the transparent top anode for its special characteristics, such as high transparence in the visible wave range, low resistance and relatively high work function [4,5]. Direct current reactive magnetron sputtering (DMS) is a traditional method to prepare the ITO film [6,7]. However, the bombardment of the energetic anions particles in the process of DMS will generate great damages in the organic layer of the TOLEDs, which lower the luminance and efficiencies and shorten the life-time of the TOLEDs. A buffer layer such as Mg–Ag [8], perylene-tetracarboxylic dianhydride (PTCDA) [9] or pentacene [10] between the organic layer and the ITO anode have been used to prevent the damages in the organic layer. But this buffer layer decreased the transparence of the TOLEDs. Other methods such as typical mirror target sputtering [11] and kinetic energy controlled sputter-deposition (KECD) with r.f. power source [12] focused on the reduction of the energy of the sputtering particles in DMS have been investigated and some improvements have been obtained. However, continuous efforts are still in need to prevent the damages in the organic layer.

In this paper we reported an improved DMS named as energy filtrating magnetron sputtering technique (EFMS) to deposit ITO film as the TOLEDs anode. This technique could efficiently filter most energetic anions and prepare ITO film with better quality. As a result, the TOLEDs with such deposited ITO anode had a much higher current density and current efficiency as well as a higher luminous efficiency.

2. Experiments

2.1. Films preparation

The structure of the TOLEDs is shown in Fig. 1. The flat glass substrate was sequentially rinsed in detergent solution and de-ionized water, and then was ultrasonic cleaned sequentially with acetone, isopropyl alcohol and de-ionized water. Finally the substrate was dried in the oven.

At first, a 100 nm Al layer acted as the cathode was deposited on the glass substrate. Second a 50 nm tris-(8-hydroxyquinoline)

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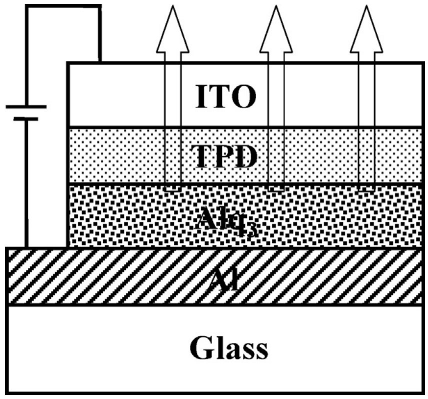

Fig. 1. Structure of the TOLEDs.

aluminum (Alq_3) layer acted as the electron conduction and light emitting material was grown on the Al layer. Then a 45 nm *N*,*N*′-dipheny1-*N*,*N*′-bis(3-methylpheny1)-1,1′bipheny1-4,4′-diamine (TPD) layer acted as the hole-transporting layer (HTL) was grown on the Alq_3 layer. All the films mentioned above were deposited by a conventional thermal evaporation in a high vacuum evaporation system (CS-450). These films were transferred immediately into a CS-300 DMS system to deposit the ITO film on the TPD layer. An ITO bulk (purity 99.99%) containing In_2O_3 (90 wt%) and SnO_2 (10 wt%) in size of $180 \times 80 \times 4\,mm^3$ was used as the sputtering target. All the films were deposited at room temperature. The sputtering pressure was 0.75 Pa, with the Ar and O_2 flux regulated at 44.20 and 0.62 sccm by mass flow controllers, respectively. The sputtering power was maintained at 150 W.

Fig. 2 illustrates the principle of the EFMS. A stainless metal grid served for the filtering electrode was set in front of the substrate with a distance of 6 mm. 100 μm thick square grids with different mesh area (grid 1 and grid 2) were investigated. The mesh area of grid 1 was $0.238\,mm^2$ with the open area rate of 55%. The mesh area of grid 2 was $0.016\,mm^2$ with the open area rate of 20%. Three different kinds of TOLEDs with ITO anodes named as D1 (deposited without grid), D2 (deposited with grid 1) and D3 (deposited with grid 2) were fabricated. In order to study the properties of the ITO film separately, ITO films were deposited on glass substrates additionally with the preparation of the TOLEDs simultaneously, which were named as (A) (deposited without grid), (B) (deposited with grid 1) and (C) (deposited with grid 2). According to the accomplished experiments, the deposition rates of ITO films were 42 nm/min (without grid), 18 nm/min (with grid 1) and 6 nm/min (with grid 2). A number of 80 nm-thick ITO films were deposited to investigate the effect of the structural and surface morphologies on the efficiency of the TOLEDs.

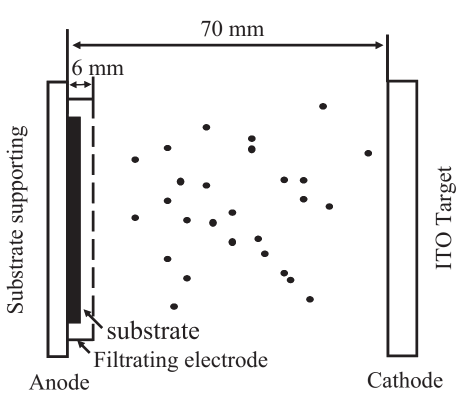

Fig. 2. Schematic diagram of EFMS.

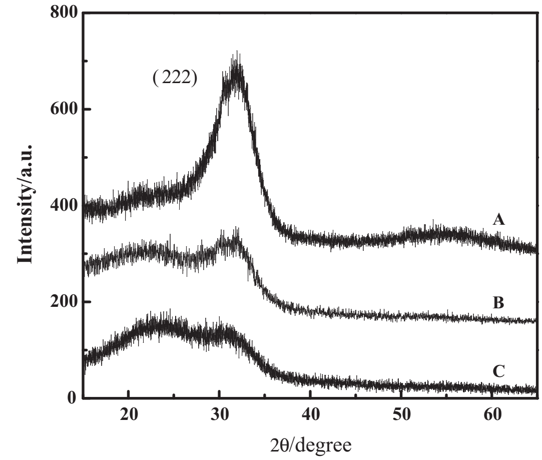

Fig. 3. XRD spectra of the ITO films.

2.2. Film characterization

The phases of the ITO films were examined by X-ray diffraction (XRD, Philips X'Pert Pro). The surface and section morphologies of the TOLEDs were examined by field emission scanning electron microscope (FESEM, JSM-6700F) and atomic force microscopy (AFM, Park Ins.) in tapping mode. The sheet resistances were examined by the sheet resistance meter (Escort EDM-2347). The electrical properties were measured by the HMS-3000 Hall tested system. The thickness and optical properties of the films were obtained by V-Vase spectroscopic ellipsometer (Vase 32). The *J–V–L* characteristics of the TOLEDs were measured by a special home-made measurement system.

3. Results and discussion

3.1. Phases, morphologies, electric and optical properties of ITO films

Fig. 3 shows the XRD patterns of the ITO films A, B and C deposited on glass substrates. It can be observed that sample A exhibits a broad diffraction peak at ($2\theta = 30.6°$) peculiar to the ITO (2 2 2) diffraction peak, indicating that micro-crystalline may be embedded in the amorphous matrix in this sample [13]. The formation of the micro-crystalline may be attributed to the higher substrate temperature due to the bombardment of the energetic particles in the plasma [14]. As contrast, the XRD pattern of sample B and sample C show weaker and broader peaks, which indicate the reduction of the bombardment of the energetic particles on the substrates owing to the filtrating metal grids. Especially sample C do not show any crystalline peaks in accurate X-ray, which means an amorphous structure or the crystal structure with very fine crystallites. This fact suggests that the smaller mesh grid can filter the energetic particles more effectively.

Fig. 4 shows the AFM images of these samples. The roughness average, R_a, is calculated from the AFM images by using a high-pass filter to remove swelling components on the substrate. A rougher surface ($R_a = 2.137$ nm) of sample A composed of grains is observed. The R_a of samples B and C are obtained of 1.170 and 0.961 nm, respectively. The smoothest surface of sample C is achieved. It is suggested that the R_a of the film decreased with the decreasing of the open area rate of the metal grid.

Table 1 gives the electrical properties of the samples. All samples have small resistivity. Sample C has the lowest resistivity of $4.56 \times 10^{-4}\,\Omega\,cm$ and sample A has the highest resistivity of $6.25 \times 10^{-4}\,\Omega\,cm$. The carrier densities of samples B and C are