Journal of Industrial and Engineering Chemistry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Improved performance of flexible polymer light emitting diodes with an indium-zinc-tin-oxide transparent anode by controlling the thermal treatment temperature

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ARTICLE INFO

Article history:
Received 17 January 2017
Received in revised form 20 March 2017
Accepted 25 March 2017
Available online xxx

Keywords:
Flexible transparent electrode
Flexible polymer light emitting diodes
IZTO transparent electrode

ABSTRACT

The indium-zinc-tin-oxide (IZTO) target, which consisted of 70 at.% In_2O_3, 15 at.% ZnO, 15 at.% SnO_2, was manufactured to replace indium-tin-oxide (ITO). The flexible IZTO (FIZTO) transparent electrodes were deposited on polyimide (PI) films at temperatures ranging from room temperature to 300 °C. The mechanical, optical and electrical properties of the FIZTO films and the flexible polymer light emitting diodes (FPLEDs) were characterized. Amorphous FIZTO prepared at 50 °C showed the best performance. The optimized FPLEDs exhibited 31% and 9% enhanced maximum brightness and luminance efficiency, respectively, as compared to PLEDs with an ITO glass. In addition, the FPLEDs worked normally in the stretching and twisting state at 3.2% and 58°, respectively.

Introduction

Optoelectronic devices such as organic (polymer) light emitting diodes (OLEDs and PLEDs) [1–4], touch screen panels (TSPs) [5], quantum dot solar cells (QDSCs) [6,7], and organic photovoltaic cells (OPVs) [8–11] have attracted significant attention as the next-generation flexible electronic devices (FEDs) that can enhance productivity by continuous processing. For high-efficiency FEDs, it is necessary to increase the performance of the active matrix and enhance its chemical and mechanical stability. In addition, advanced encapsulation technology is required to protect the active matrix. Recently, a number of studies have also been conducted on the development of transparent conducting electrodes (TCEs) which maintain a high level of transmittance, conductivity, and flexibility for the commercialization of FEDs. In general, ITO is the most common choice for a transparent conducting electrode (TCE) material, owing to its advantages of low resistivity and high transparency in the visible wavelength region [12–14]. Demand for ITO as an essential component in a wide range of industrial applications including flat panel displays, solid-state lighting, solar cells, and e-paper is rapidly increasing.

However, ITO has major drawbacks with respect to its properties and costs [15]. It is a ceramic material that cracks and fractures at low strains (2–3%) [16]. In addition, salt, acid, or device adhesives that are commonly found in nature corrode the ITO electrode and reduce the lifetime of the devices [17,18]. Further, the high-cost ingredient of the ITO, 'indium' and the deposition process are the biggest obstacles in using ITO as the TCE for FEDs. Because of the high deposition temperature and the low glass transition temperature (T_g) of the plastic substrate, it is difficult to apply the ITO to the flexible device [19]. Therefore, it is necessary to reduce the processing-temperature, the low-resistance, and high-transparency indium, or develop technologies for indium-free transparent electrodes [20–23].

TCEs can be developed into one-dimensional structures such as CNTs, graphene nanoribbons, metal nanowires, and nanowires of oxides. However, they have the disadvantage of low flexibility [24–26]. In addition, continuous structure films such as fluorine-doped tin oxide including ITO, novel oxide, metal thin films, large-area graphene, and conducting polymer require complicated and high processing temperatures. Among these oxide continuous films, indium zinc tin oxide (IZTO) with a reduced indium content,

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http://dx.doi.org/10.1016/j.jiec.2017.03.050
1226-086X/

containing ZnO has emerged as a leading alternative to ITO [27–29]. In spite of low deposition temperatures, the IZTO maintains a high work function, low resistivity, low sheet resistance and a high transmittance. Therefore, it can be applied onto the plastic substrate, making the fabrication of flexible devices possible [30].

Oxide continuous film TCEs are usually fabricated using the magnetron sputtering system. Because properties of them are sensitive to the deposition conditions, which are deposition power, gas pressure, composition of gas contents and processing temperature of the sputtering system, the optimization of deposition conditions is highly important. In our previous study, we had discussed the effects of oxygen partial pressure on electrical resistivity, optical transmittance of the IZTO and the PLED fabricated on the IZTO using a glass substrate [30]. However, studies have not been conducted to investigate the electrical, optical, and structural properties of the IZTO thin film prepared on a plastic substrate under variations in processing temperature.

In this study, therefore, IZTO TCEs comprising of In_2O_3 (70 at.%), ZnO (15 at.%) and SnO_2 (15 at.%) were fabricated as the IZTO target. After fixing the oxygen flow rate at 3%, the IZTO TCEs were fabricated under diverse deposition temperature conditions ranging from room temperature (RT) to 250 °C, and then their properties were analysed. To check the behaviour of IZTO at high thermal treatment conditions, colourless polyimide (PI) with a high thermal resistance was used as the plastic substrate. Then, the chemical binding state and the work function of the surface, that have a major effect on the characteristics of the FEDs and the optimum deposition conditions were measured through X-ray photoelectron spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). In addition, optimized IZTO thin films were introduced as flexible TCE, and flexible PLEDs that have generated attention as the next-generation FEDs, were fabricated and characterized.

Experimental section

Deposition and characterization of IZTO thin films on a polyimide (PI) substrate

By using pulsed DC magnetron sputter at an oxygen flow rate of 3% with deposition temperature range of room temperature ~200 °C, the IZTO films were deposited on a PI film (Mitsubishi gas chemical, 100 μm, Japan). The target were of the composition 70 at.% In_2O_3 15 at.% ZnO^- 15 at.% SnO_2. The PI substrate was washed by ultrasonication with detergent (10 wt% in water), acetone, isopropyl alcohol, and de-ionized water in sequence. The substrates were dried by blowing N_2 gas and baked at 120 °C hot plate. The cleaned PI substrates were loaded in the sputtering chamber. Sputtering was carried out with 125 W input power, 30 kHz frequency and 6 mTorr oxygen partial pressure whose flow ratio was 3% [O_2/(O_2 + Ar)]. The thickness of the deposited IZTO films was 200 nm.

The X-ray diffraction (XRD) patterns of IZTO films were analysed by Rigaku D/MAX 2200 diffractometre with Cu Kα radiation. Focused ion beam (FIB; NOVA600 NanoLab, FEI, Holland) through STEM (JEM-2100(HR) + Cs corrector, JEOL/CEOS, Japan) technic was processed for sample preparation and crystal phase was reviewed. Atomic force microscopy (AFM; XE-100, Park systems, Korea) and field emission scanning electron microscopy (FESEM; S-4800, HITACHI, Japan) were used to characterize surface morphology of IZTO films. The thickness of all prepared films was measured by an Alpha step 500 surface profiler (KLA-Tencor, USA). The electrical properties which are the resistivity, carrier concentration, and the mobility of the IZTO films were characterized by using the van der Pauw method with a Hall measurement system (HMS-3000, ECOPIA, Korea). The transmittance of the transparent anodes was measured by a UV-visible spectrometre (HP Agilent 8453, USA). The surface chemical state and work function of films were analysed by X-ray photoelectron spectroscopy (XPS; ESCA 2000, VG Microtech, UK) and UPS (He I, $h\nu$ = 21.22 eV, AXIS-NOVA, Kratos Inc., UK).

Fabrication and characterization of the flexible PLEDs with an IZTO transparent anode

To clean the surface of IZTO/PI, ultrasonification was performed in detergent (Alconox© in deionized water, 10 wt%), isopropyl alcohol (IPA), and deionized water for 1 min in sequence. After cleaning, moisture was completely removed by blowing N_2 gas and baking at 110 °C hot plate for 10 min. The IZTO transparent electrodes were ultra-violet ozone (UVO) treated for 10 min. For emitting layer, SPG-01T (green emitting polymer, Merck, Germany) was dissolved in chlorobenzene with concentration of 0.5 mg/ml and filtered through a 0.45 μm PTFE syringe filter. The emitting layer was coated to an 80 nm thickness and annealed at 90 °C for 30 min to remove the residual solvents. The electron transport layer and cathode were deposited thermally in a high vacuum chamber ($<1 \times 10^{-6}$ Torr) in the order of BaF_2 (0.1 Å/s, 2 nm), Ba (0.2 Å/s, 2 nm), and Al (5 Å/s, 200 nm). The performance of the PLEDs was characterized by using a Keithley 2400 source metre unit (Keithley, USA) and a PR 670 spectra scan (Photo Research, USA).

Results and discussion

Fig. 1 shows the XRD patterns of the FIZTO film deposited by pulsed DC magnetron sputtering. The films were deposited at various temperatures from RT to 300 °C with an oxygen partial pressure of 3%. The sample exhibited an amorphous structure with a weak and broad peak (2θ = ~31°) in the temperature range RT–150 °C. However, when the deposition temperature was 200 °C or higher, crystallization occurred. In case of SnO_2-doped In_2O_3 (ITO) thin films, in general, low amorphous and crystalline transition temperatures are found. Therefore, rapid crystallization takes place even at low substrate temperatures (RT–150 °C). In case of ZnO-doped In_2O_3 (IZO) thin films, however, higher amorphous and crystalline transition temperatures are found. Therefore, the amorphous structure remains stable until approximately 500 °C [31]. The FIZTO films have a stable amorphous structure similar to the IZO film because of the immiscibility of SnO_2 and ZnO in In_2O_3. ITO thin films fabricated at room temperature normally exhibit (222) orientations of crystalline structure because of surface heating caused by plasma irradiation during sputtering. In this

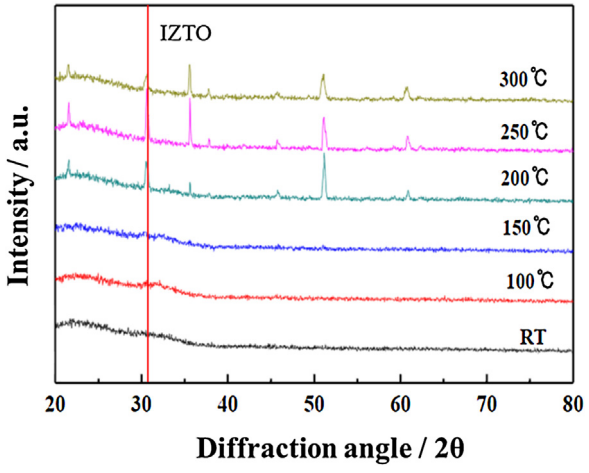

Fig. 1. X-ray diffraction patterns of IZTO films with various deposition temperatures on a PI substrate.

Please cite this article in press as: S.W. Heo, et al., Improved performance of flexible polymer light emitting diodes with an indium-zinc-tin-oxide transparent anode by controlling the thermal treatment temperature, J. Ind. Eng. Chem. (2017), http://dx.doi.org/10.1016/j.jiec.2017.03.050