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Roll-to-Roll fabrication of ITO thin film for flexible optoelectronics applications: The role of post-annealing

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ABSTRACT

We have developed and examined new and cost effective methods for fabrication indium tin oxide (ITO) film on flexible substrate. The ITO film is deposited to polyethylene terephthalate film using roll-to-roll (RTR) sputtering advanced technology. The film's properties are evaluated before and after heat treatment. Effect of post annealing time on the electrical, optical, structural and surface properties of RTR sputtered ITO films is estimated. In addition, mechanical flexibility of as-sputtered amorphous ITO and annealed crystalline ITO films are compared. It is estimated that post-annealing at 150 °C reduces sheet resistance and increase the optical transmittance of the ITO films. The best results are observed when annealing time is 60 min. In this case the sheet resistance of ITO is measured to be 125 Ω/sq. and optical transmittance is 87.3% at wavelength range from 380 nm to 780 nm. It is demonstrated successful operation of touch screen panels fabricated on annealed ITO film. It is estimated that post-annealing significantly improves ITO performance as compare of that as-deposited film. Based on Hall measurement and transmittance electron microscopy examinations, possible mechanism to explain the effect of post-annealing time on RTR sputtered ITO films is manifested.

1. Introduction

Rapid development of the optoelectronic industry such as solar cells, displays, opto-electrical interfaces and circuitries requires new and challenging properties for structure and functional components. This triggers to extensive research on high-performance transparent conductive oxide (TCO) which is essential component of optoelectronics [1]. Requirements for the TCO are different and strongly depend on applications; however two main properties i.e. high conductivity and high transparency is the most important parameters [2]. Nowadays the most important TCO considered to be tin doped indium oxide, typically called indium-tin-oxide or ITO. The ITO is a solid solution of indium (III) oxide (In_2O_3) and tin (IV) oxide (SnO_2), with typically 90%wt In_2O_3, 10%wt SnO_2 ratio. The ITO is used as a transparent electrode almost in all flat panel displays (FPDs) [2]. Very early fabrication of ITO dates back to 1950s where In/Sn metal film is sputtered then oxidized at 400–500 °C [3].

Latter on for fabrication ITO thin film several methods such as ion assisted plasma evaporation [4], electron beam evaporation, magnetron sputtering [5,6], etc. have been developed. Recently, T. Ito et al. suggest a novel wet coating process for preparing indium tin oxide (ITO) films [7]. This method involves high temperature step (up to 800 °C) and produces film with low sheet and volume resistivities of 188 Ω $sq.^{-1}$ and 4.23×10^{-3} Ω cm, respectively. In the [8] atomic layer deposition method is also used for fabricating ITO layer. Although formed film possess low resistivity (3×10^{-4} Ω cm) and high optical transparency (92%) the composition was different from expectation. Huge efforts for fabrication high-performance ITO thin film is mainly directed for deposition the ITO to a glass substrate. Today, ITO sheets with approximately 1.2×10^{-4} Ω-cm are the best reproducible resistivity reported. However this can be fabricated only by involving high temperature steps. Typical low temperature process yields amorphous ITO with resistivity approximately $> 5 \times 10^{-4}$ Ω cm, whereas high-temperature (> 200 °C) deposition processes produce polycrystalline ITO with a resistivity $\sim 2 \times 10^{-4}$ Ω cm. In general amorphous ITO has lower performance compare of that crystalline phase [9–19]. Recently huge interest is focused on development of flexible displays and electronics. This triggers extensive research for development TCO including ITO on

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plastic film. However caused by limited temperature, performance of ITO is lower. In addition, cracking issue must be addressed when flexible substrate is used [20]. High resistivity is a serious problem for many flexible displays and electronics where a low sheet resistance TCO transparent electrode is required. For instance, roll-to-roll (RTR) sputtering of ITO film on polyethylene terephthalate (PET) substrate is easy for mass production and formed film possesses high transparency; however caused by flexible substrate the process temperature is limited and in most cases sputtered ITO film has an amorphous structure. Although amorphous ITO film shows a fairly high optical transmittance and a low resistivity, the sheet resistance is higher than requirement and can't be used for capacitive-type TSPs. Thus, high-performance TCO is needed for high-quality touch screen panels (TSPs) with multi-touch function and high touch speed [21–23]. In order to reduce sheet resistance the RTR sputtered ITO films are generally undergo to the post-annealing step [24]. Although extensive research is performed to estimate annealing effect on the properties of sputtered ITO films, the effect of post annealing time on the RTR sputtered amorphous ITO films is still lacking.

The main goal of this work is fabrication ITO film on flexible substrate using cost-effective RTR method. To improve film's performance post-annealing step is involved and effect of the post annealing time on the electrical, optical, structural, and surface properties are examined. The annealing temperature adjusted to be 150 °C and phase and microstructure transformation is monitored. Next attempt is correlating electrical and optical properties of ITO with the microstructure. Using flexible substrate prospect of using optimized ITO for flexible electronics is explored. Finally, effectiveness of post-annealing step is confirmed by fabricating high-end TSPs.

2. Experimental

In order to manufacture high performance and low cost flexible ITO film for touch screen panel a specially designed pilot-scale roll to roll sputter system is implemented. The ITO film was continuously deposited on flexible PET (Higashiyama Co., Ltd., Japan) substrate at room temperature. Fig. 1(a) and (b) show a schematic illustration and photo of the roll to roll sputtering system, respectively. The RTR sputtering system is composed of the degassing and process chamber. The degassing chamber equipped with unwinds roller, rewind roller, and halogen heater to remove the contaminations and the moisture of PET surface. Table 1 shows the degassing conditions of PET substrate in degassing chamber. The PET substrate (1250 mm width, 0.125 mm thickness) was subjected to degassing process in degassing chamber then installed on unwind and rewind roller in process chamber. The process chamber equipped with a unwind roller, rewind roller, cooling drum, tension controller, two ITO target, and halogen lamp heater. The ITO (In_2O_3: SnO_2 = 95: 5, Mitsui & Co., Ltd., Japan) target with surface of 1300 mm × 100 mm were placed at a distance of 80 mm from a PET substrate. To remove surface contamination and improve the adhesion between the ITO and PET substrate, the surface of the PET substrate was passed repeatedly over the cooling drum by motion of unwind and rewind rollers during the continuous RTR process with halogen lamp heater temperature of 200 °C. After the substrate pre-heat treatment, the ITO electrode were continuously sputtered on the rolling PET substrate, which is mechanically attached on cooling drum to maintain the substrate temperature below 50 °C, using two ITO target at a constant dc power of 7.5 kW, working pressure of 3 mTorr, Ar/O_2 flow rate of 1050/15 sccm and rolling speed of 3.4 m/min. To investigate the effect of the post annealing process on the characteristics of flexible ITO electrode, the large ITO/PET sample was cut in to six pieces with 10 cm × 10 cm in size. Sampled pieces were annealed in high temperature chamber (TS295S) at 150 °C. Processing time was varied from 10 min to 60 min. The sputtering rate and thickness of the ITO films were obtained by means of a stylus profilometer (Tenco Alpha-step 250). The electrical properties of the ITO films were measured by the

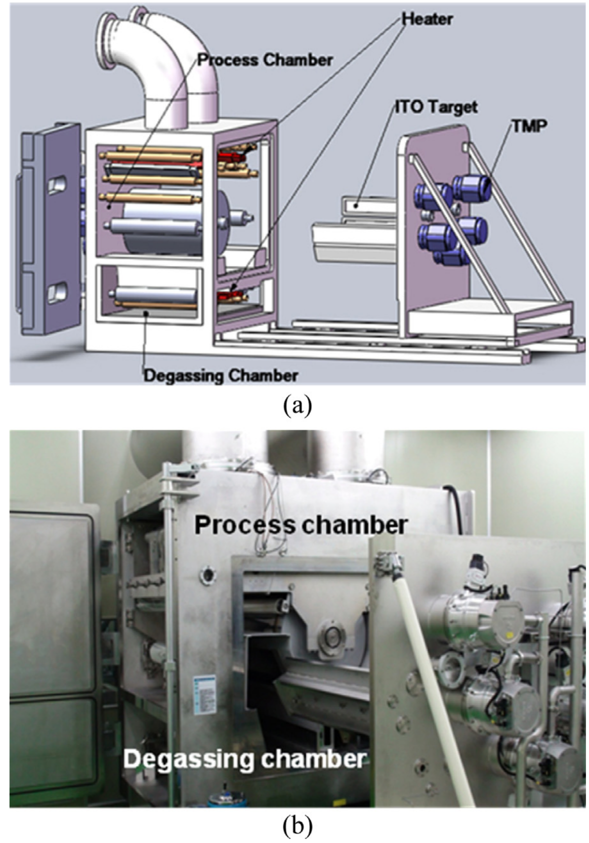

Fig. 1. Schematics (a) and picture (b) of the RTR sputtering system used for the continuous deposition of the ITO electrode on the roll-type PET substrate at room temperature.

Table 1
The degassing conditions of PET substrate in degassing chamber.

Parameters	Degassing conditions
Working pressure	1.0×10^{-3} Torr
Rolling speed	4 m/min
Heater temperature	160 °C
Tension	280 N

Hall measurements (HL5500PC, Accent Optical Technology) at room temperature. The optical transmittance of the ITO films was investigated by UV/Visible spectrometer (Lambda 35) in a range of 220–800 nm. The structural properties of the ITO films were studied by X-ray diffraction (XRD, D/Max 2500) with Cu K_α (λ = 1.54059 Å) radiation. The surface of the ITO films were analyzed by field emission scanning electron microscopy (Hitachi-S4800: FESEM) with operating voltage of 5 kV and atomic force microscopy (AFM: VEECO D-3100). Furthermore, the flexibility of the flexible ITO film was estimated using Bending tester system (ZB-100, Z-tec). The samples were clamped between two Cu plates. To avoid the formation of cracks in the clamped region two Cu tilted plates were used. One Cu plate was connected to the motor for repeated motion, while the other was fixed to a rigid support. The bending radius and frequency was 8 mm and 1 Hz, respectively. During the bending test, the resistance of the samples was measured using a multi-meter.

To investigate the feasibility of the ITO film as a transparent electrode for capacitive-type TSPs, a simple capacitive-type TSPs was fabricated using the optimized ITO films. The ITO film with 25 nm thickness was directly deposited onto the PET substrate, and the ITO electrode was then patterned by a conventional photolithograph and wet-etching process. After patterning of the ITO electrode, the Mo/Al/