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Radio frequency-H_2O plasma treatment on indium tin oxide films produced by electron beam and radio frequency magnetron sputtering methods

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ABSTRACT

Electron beam and radio frequency (RF: 13.56 MHz) magnetron sputtering methods were used to obtain a highly transparent and conductive indium tin oxide (ITO) films. The coated thin films were treated by RF-H_2O plasma in order to improve optical and electrical properties. RF-H_2O plasma characteristics were investigated by optical emission spectroscopy during surface treatments. X-ray photoelectron spectroscopy results on O 1s core levels indicated the activated oxygen species in both amorphous and crystalline ITO structures. The structural, electrical and optical properties of ITO film were characterized by scanning electron microscopy, X-ray diffraction, and four-probe techniques. After the RF-H_2O plasma treatment, the ITO films exhibited lower resistivity and better transparency due to the formation of radical species.

1. Introduction

Indium tin oxide (ITO) is a widely used semiconductor owing to its high transparency in the visible region as well as low resistivity between 10^{-3} and 10^{-4} Ω cm [1,2]. It has been used in many applications in the optoelectronic industry such as in solar cells, electrochromics, liquid crystal displays (LCDs), and organic light emitting diodes (OLEDs) [3,4]. ITO films have been deposited using a variety of techniques simply divided into solution based [5] and dry methods such as e-beam [6], pulsed laser deposition [7], and sputtering [8,9]. Among them, electron beam (e-beam) and radio frequency (RF)/direct current (DC) magnetron sputtering processes have been preferred intensively for ITO film coatings because of high-quality thin film performances. However, still some post processes are necessary to improve the properties of ITO films. Zhu and Yang investigated annealing effect on the optical and conductivity properties of ITO [10]. However, most commonly used plastic substrates have limitations to endure high temperature treatments above 200 °C. Therefore, it is important to apply modifications at low temperature. For instance, Ishibashi et al. used water vapor during DC magnetron sputtering process in order to reduce resistivity of ITO film [11]. As another approach, ITO was modified by H_2 and H_2/O_2 mixed gas plasma treatments [12]. In addition, Ohsaki et al. focused on plasma crystallization of ITO films using O_2-RF plasma without heating [13].

In this comparative study, ITO films were obtained by both RF magnetron sputtering (RFMS) and e-beam techniques. After coating ITO film by e-beam process, the annealing process has to be applied to increase the conductivity and transparency properties [14]. E-beam technique is not suitable for organic substrates due to deformation of the substrate under high temperature. On the other hand, RFMS is a low temperature process that is suitable for the deposition of ITO films on plastic substrates. It produces high performance and smooth surface morphology for applications that require flexible coatings [15]. Currently, these well-known two basic methods were compared with each other in terms of the structural, electronic and optical properties of the ITO films. The surface modification of ITO films was carried out by RF-H_2O plasma treatment at low temperature. Optical emission spectroscopy (OES) was in-situ taken during RF-H_2O plasma modification of ITO film surface. The resistivity, carrier density and optical transmittance properties of ITO film were measured and compared for two types of method.

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2. Experimental details

The same sintered ITO target disk (2 in. thickness), which is a mixture of 90 wt.% In_2O_3 and 10 wt.% SnO_2 was used as an evaporation source material for both RFMS and e-beam processes.

All glass substrates were first rinsed with liquid detergent, and then kept in diluted nitric acid for a day. These substrates were treated ultrasonically in methanol after being cleaned in distilled water, rinsed in isopropyl alcohol then dried in hot air.

2.1. ITO film coating by e-beam

A vacuum coating unit with an e-beam gun was used for the evaporation of ITO disk. The vacuum chamber was evacuated to a base pressure of 1×10^{-4} Pa. A steady-state chamber pressure was 6×10^{-4} Pa. ITO films with a thickness of 400 nm were deposited on pre-cleaned glass substrates by e-beam method. The thickness of film was controlled by using an Au coated quartz crystal thickness monitor. The deposited ITO films were annealed in a heater for 30 min at 400 °C.

2.2. ITO film coating by RFMS

In the sputtering chamber the distance between the evaporating source and the glass substrate was 5 cm and the deposition was carried out under Ar + O_2 gas mixture with a flow ratio of 9:1. The total sputtering power was set at 40 W for 40 min at 3 rpm. Before the deposition, the chamber was pumped down to 1×10^{-4} Pa base pressure. During the deposition, the working vacuum was around 0.4 Pa, the substrate stage maintained a constant rotation speed, and both cathode and anode were cooled by circulating water. The sputtering was manually terminated and the approx. 400 nm thickness of the thin film was obtained by using an Au coated quartz crystal thickness monitor controlling.

2.3. RF-H_2O plasma treatment

ITO coated substrates were loaded into a Pyrex plasma chamber and exposed to RF-H_2O plasma, at 60 W RF power and 2.6 Pa pressure for 15 min. A monochromator was used to measure the optical characteristics of the RF-H_2O plasma species (Ocean Optics HR 4000, Mikropack Halogen Light Source HL-2000-FHSA in the 200–1000 nm wavelength range). The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a SPECS EA 300 system equipped with argon ion gun and Al monochromatic anode. The specimens were analyzed at an emission angle of 45° from the surface normal. All the partial scans were done after 5 min 3 keV Ar ion bombardment. The binding energies were referenced to the neutral adventitious C 1s peak at 187.85 eV. The surface morphology of the ITO films was investigated by scanning electron microscopy (SEM, operating voltage is 7 kV) (Philips XL-30S FEG) and the crystalline structure was evaluated by using X-ray diffraction (XRD) (Philips X'Pert Pro) operating in Bragg–Brentano geometry (Cu Kα radiation, graphite monochromator, 40 kV and 40 mA) over a $10° \leq 2\theta \leq 90°$ angular range. Electrical properties were assessed by measuring the specific resistivity using a four-probe and Hall effect measurement techniques. Transmittance in the wavelength range of 400–1100 nm was examined by an optical spectrophotometer (Ocean Optics HR 4000).

3. Results and discussion

Fig. 1 shows in-situ OES study of RF-H_2O plasma processing onto ITO coated samples. As seen from spectrum, a variety of radical species and ions such as OH, O(I), O(II), N(I) were occurred onto the ITO surface [16]. The RF-H_2O plasma environment is highly oxidative and capable to defect states by ion bombardment [17]. The O(I) and O(II) lines indicate an unionized but excited oxygen atoms and ionized oxygen atom

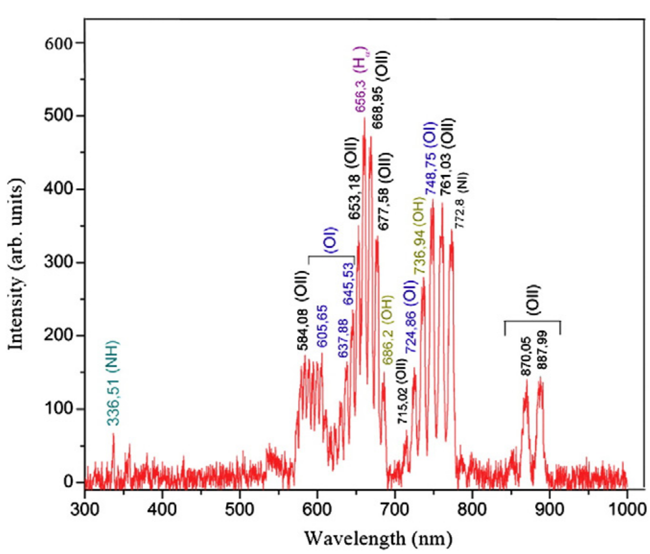

Fig. 1. Optical emission spectra of RF-H_2O plasma treatment.

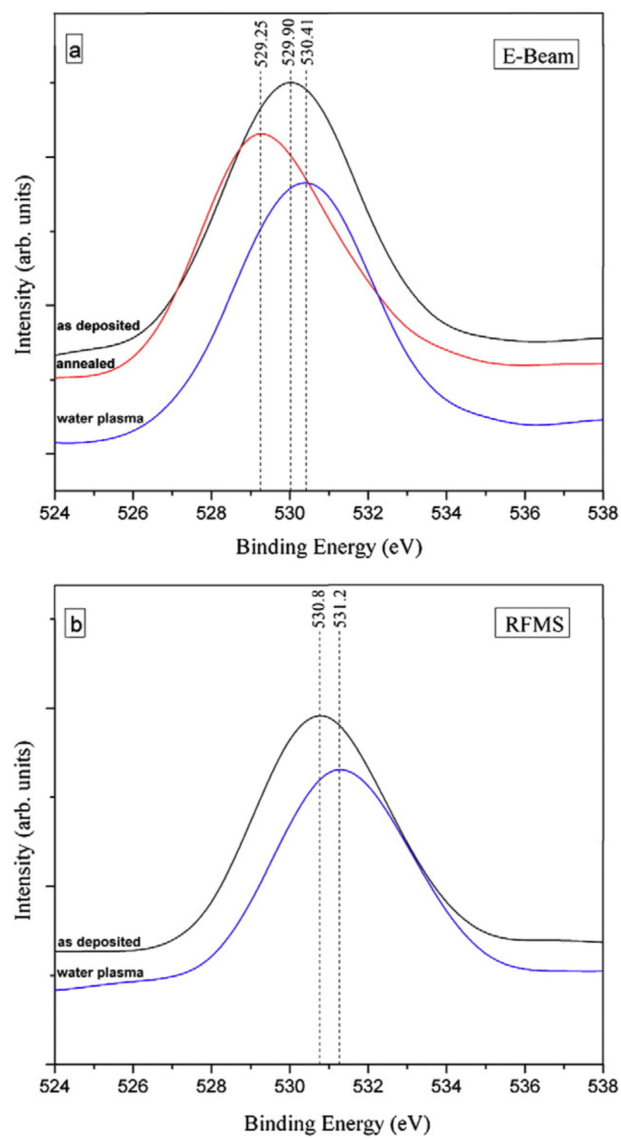

Fig. 2. XPS spectra of the O 1s region of ITO film deposited by (a) e-beam and (b) RFMS.