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Laser processing of indium tin oxide thin film to enhance electrical conductivity and flexibility

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ABSTRACT

This work reports a method that uses a KrF excimer laser to enhance the electrical and mechanical properties of amorphous indium tin oxide (ITO) thin films on flexible substrates. Irradiation with nanosecond laser pulses induces thermal crystallization of ITO, and thereby increases the electrical conductivity and flexibility of film deposited on polyethylene terephthalate substrates. The shallow optical (~45 nm) and thermal penetration (~100 nm) of the laser beam confines the thermal effect to within the ITO layer without damaging the substrate. The laser treatment changed the crystallinity of ITO film from amorphous to poly-crystalline; as a result, its electrical-conductivity increased by 20–25%. Moreover, the treatment decreased the critical bending radius to avoid loss of electrical property from 8 mm to 5 mm. The adhesion strength and transparency of the ITO film were not affected significantly by the laser treatment. This work suggests that laser treatment can be an effective tool to enhance the crystallinity, of sputtered ITO thin film, and its electrical and mechanical properties on flexible substrate.

1. Introduction

Transparent conductive oxides (TCOs) have high optical transmittance *OT* in the visible range, low electrical resistivity, and chemical stability [1], and are therefore widely used for electrical devices, solar cells, displays, and flexible electronics [2]. Among various TCOs, indium tin oxide (ITO) is used in various fields [3] and therefore intensive investigations have been performed regarding its fabrication [4,5], applications [6–8], and modification of its properties [9]. Interest in ITO is rapidly increasing because of a growing interest in flexible devices [10]. However, the brittleness of ITO hinders its application in flexible devices [11]. TCO materials including ITO are generally brittle and thus cannot withstand excessive or repeated compression and stretch strain of bending [12]. The critical bending radius r_{CRIT} is defined as the minimum radius of bending curvature above which the electrical conductivity is not impaired by bending. When ITO films are bent to a radius of curvature $< r_{CRIT}$, they develop cracks, which degrade the electrical or mechanical properties seriously [13].

Because cracking is an importance issue in ITO applications, several investigations were performed to reveal the mechanisms of crack initiation and propagation in ITO thin films [14–18]. It has been shown that poly crystalline-ITO (c-ITO) thin film can withstand up to three times larger strain than the amorphous ITO (a-ITO) thin film of same thickness and roughness [16,17]. It has been shown that a-ITO is less resistant to crack initiation than c-ITO mainly because of the free volume in the amorphous microstructure [15–18]. A larger amount of free volume in the amorphous material induces concentrated strain near the free volume [19]. Under high level of stress, deformation is localized near the zone and it leads to crack initiation [20]. Also, cracks can propagate more easily along the free volume, leading to easy creation of fracture surfaces when free volume is large [20,21]. Various attempts have been made to increase the crystallinity of TCO; methods include development of a new deposition [22], optimization of deposition parameters [23], performing post-thermal [24,25] and laser treatments [26]. However, c-ITO thin film is difficult to deposit on a flexible polymer substrate because an interlayer distortion at the ITO-polymer interface induces lattice distortion of the ITO film [25]. Crystallization by post-treatment is widely used for various devices, but this method cannot be used with flexible polymer substrates because the heat degrades them. If a-ITO film on PET substrate can be crystallized into c-ITO, the crack initiation problem can be solved, and electrical conductivity can be improved. The metallic property of ITO is improved [24] when a-ITO is crystallized, and its conductivity can be increased by increasing its crystallinity.

Here we propose a method in which amorphous ITO film is crystallized to enhance the electrical and mechanical properties of a-ITO thin film deposited on flexible substrates. The method uses a nanosecond KrF excimer laser to exploit its spatially confined thermal effect

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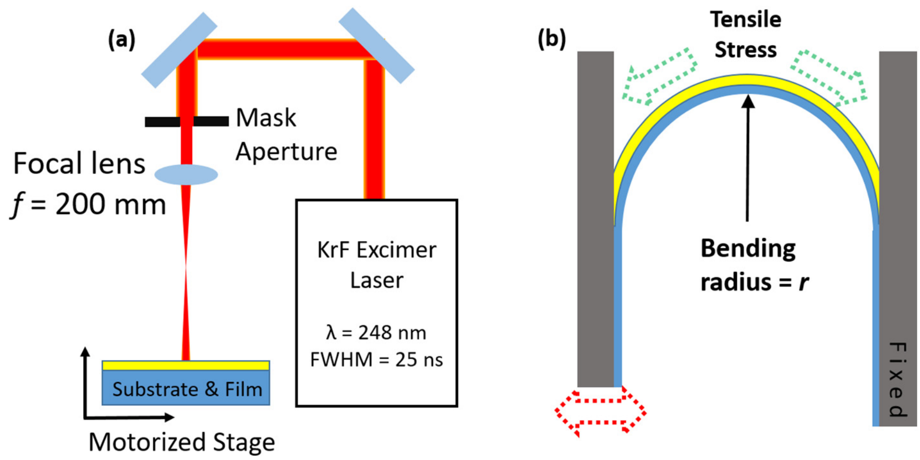

Fig. 1. Schematic diagram of experimental set-up: (a) laser set-up (b) bending test with tensile stress.

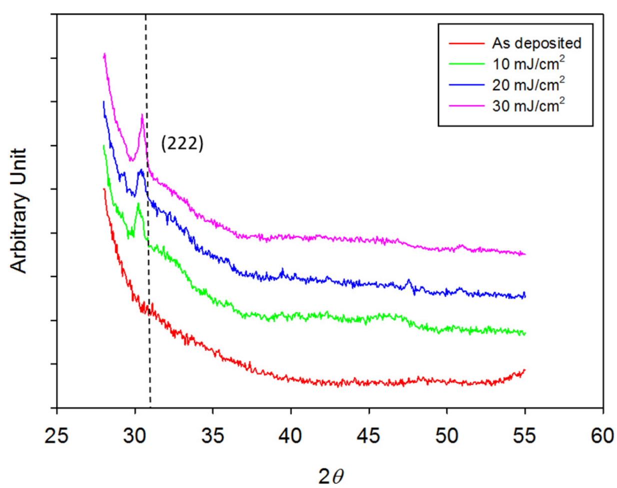

Fig. 2. X-ray diffraction spectra of ITO thin films (T_{ITO} = 130 nm). in as-deposited films, and after laser irradiance at various fluences.

Table 1
Structural parameters of as-deposited and laser treated ITO thin films (T_{ITO} = 130 nm).

Parameter	As-deposited	Laser treated		
		10 mJ/cm^2	20 mJ/cm^2	30 mJ/cm^2
a_0 (Å)	10.248	10.236	10.195	10.156
$\Delta d/d_0$ (%)	1.19	1.07	0.67	0.29
CS (nm)	–	13.23	17.92	28.68

due to short pulse width. The laser pulse induced thermal reaction only within the ITO layer without thermally affecting the polyethylene terephthalate (PET) substrate. Various diagnostic methods were used to examine the structural changes due to laser treatment. The optimized process significantly enhanced the electrical conductivity and flexibility of the ITO film.

2. Experiments

Two commercially-available a-ITO coated PET films (Sigma Aldrich, sample 1: thickness T_{ITO} of ITO = 70 nm, thickness T_{PET} of PET = 150 μm, sheet resistance R_S = 100 Ω/□; sample 2: T_{ITO} = 130 nm, T_{PET} = 150 μm, R_S = 60 Ω/□) were used in the experiment. A KrF excimer laser (wavelength λ = 248 nm, full width at half maximum FWHM = 25 ns) was used as a laser source for the thermal treatment. Although ITO is transparent in the visible spectrum ($OT \geq 90\%$ at $\lambda \geq 300$ nm), the absorption coefficient at λ = 248 nm is 2.2×10^5 cm^{-1} [27], which corresponds to an optical penetration depth of 45 nm [27]. The pulse duration of 25 ns corresponds to thermal penetration of ~100 nm in ITO material, as calculated using the equation that thermal penetration = $\sqrt{\alpha\tau}$ [2] where $\alpha = 2.2 \times 10^5$ cm^{-1} is absorption coefficient of ITO at λ = 248 nm and τ is the pulse duration of laser. Therefore, the laser pulse is partially absorbed by the PET substrate when T_{ITO} = 70 nm.

The excimer laser beam was incident on the surface from the normal direction (Fig. 1a). A square mask with a 3 mm × 3 mm aperture was used to transmit the center part of the excimer laser beam; as a result, the energy distribution on the sample surface was spatially uniform. The laser beam was scanned over the surface by moving the sample on a motorized stage; the laser-treated sample was 4 cm × 4 cm in size. The laser fluence was $10 \leq F \leq 40$ mJ/cm^2 and the pulse number N_P was ≤200.

Crystallization of the ITO thin film by excimer laser irradiation was analyzed by optical microscopy, field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM). The electrical resistance, adhesion strength and *OT* of the ITO film were measured before and after the laser treatment. The surface resistance was measured using the four-wire sensing technique. The adhesion strength between the ITO film and the PET substrate was measured using the standard 3M™ tape test method (ASTM D3359 B: 100 cross-cut tape test) [28]. The flexibility of the sample was assessed by measuring the changes in the surface conductivity after different bending cycles (Fig. 1b) [15–18]. A thin-film sample was inserted between two flat parallel plates to form a U shape. Bending cycles were then applied by moving a plate with a motorized stage. The radius of the U-shape semicircular region of the sample becomes the bending radius *r* when the gap distance is 2*r*. The critical bending radius r_{CRIT} is defined as the bending radius at which the resistivity increase exceeds 10% after 100 bending cycles have been applied.

3. Results and discussion

Structural changes in the ITO film (T_{ITO} = 130 nm) after laser irradiation was examined by XRD measurements (Fig. 2). After laser irradiation, new XRD peaks were generated from a-ITO which has no crystalline peak. The 2θ peak position at ~30.5° corresponds to the (222) orientation in the ITO lattice. This orientation is related to the metallic characteristic and thus the electrical conductivity of ITO [29]. The peak appears when a-ITO is heated to > 300 °C, and forms c-ITO [24]. The generated peaks were shifted to smaller 2θ angles than that