Pulsed Laser Deposition of Nanostructured Indium-Tin-Oxide Film

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ABSTRACT

Effects of O_2, N_2, Ar and He on the formation of micro- and nanostructured indium tin oxide (ITO) thin films were investigated in pulsed Nd:YAG laser deposition on glass substrate. For O_2 and Ar, ITO resistivity of $\leq 4 \times 10^{-4}$ Ωcm and optical transmittance of > 90% were obtained with substrate temperature of 250 °C. For N_2 and He, low ITO resisitivity could be obtained but with poor optical transmittance. SEM images show nano-structured ITO thin films for all gases, where dense, larger and highly oriented, microcrystalline structures were obtained for deposition in O_2 and He, as revealed from the XRD lines. EDX results indicated the inclusion of Ar and N_2 at the expense of reduced tin (Sn) content. When the ITO films were applied for fabrication of organic light emitting devices (OLED), only those deposited in Ar and O_2 produced comparable performance to single-layer OLED fabricated on the commercial ITO.

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Keywords: Indium-tin-oxide (ITO), pulsed laser deposition (PLD), organic light emitting diode (OLED), nanostructures, nanorod, transparent conducting oxide.

1. INTRODUCTION

Indium tin oxide (ITO) has been used the hole-injection anode [1] in the organic light emitting device (OLED). These are commonly coated on glass substrate by the magnetron sputtering [2-3], spray pyrolysis [4], electron beam evaporation [5] and the pulsed laser deposition (PLD) [6-12]. The PLD deposition usually employs either a KrF or ArF excimer laser. For example, Kim et al. [7-8] reported a low resistivity of 2.0×10^{-4} Ωcm with a maximum optical transmission of 92% in the visible region, which was used for the fabrication of OLED. The OLED performance was comparable to that fabricated using the commercial ITO.

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The ITO deposition was also prepared by pulsed Nd:YAG laser deposition at 355 nm [9-11] with resistivity (ρ) ~ 1×10^{-4} Ωcm but on heated substrates. There was also report on ITO deposition in the inert gas in order to avoid substrate oxidation. Morales-Paliza et al. [12] employed N_2 as the background gas for the KrF-laser deposition of ITO and obtained a film resistivity ρ of ~ 8×10^{-4} Ωcm and an optical transmittance (T) ~ 85 %, as compared to a lower ρ ~ 4×10^{-4} Ωcm and T ~ 90 %. For other gases such as neon, argon and xenon, Thestrup et al. [13] obtained ρ ~ (1×10^{-2} - 4×10^{-3}) Ωcm and T ~ (70 – 80) % by using a pulsed Nd:YAG laser with heated glass substrate at 200 °C. In our report [11], ITO with $\rho > 5 \times 10^{-4}$ Ωcm could not be used for OLED. It is generally understood that the surface roughness plays an important role in the OLED stability but there are also reports that surface roughness due to etching of ITO surface could enhance the OLED efficiency [14-15]. In this work, ITO with different surface nano-structures were prepared in Ar and N_2 and tested for OLED performance.

2. EXPERIMENTAL

The basic setup for pulsed Nd:YAG laser deposition (PLD) of ITO films was reported previously [11]. The deposition chamber was first evacuated to a base pressure of 6.7×10^{-4} Pa and the O_2, Ar, N_2 or He were admitted at different flow rates to vary the working pressure. The ablation target was a sintered, 2-inch diameter disk of ITO target with a composition of 90 wt% In_2O_3 and 10 wt% SnO_2 (Target Materials, Inc., USA). The laser beam was focused to < 1 mm^2 but was scanned over 5×5 mm^2 on the ITO target by a x-y motorized mirror. The deposition distance was fixed at 8 cm, and the deposition rate was estimated to be 0.5 nm/second.

The ITO films were 150 nm thick, as measured by a stylus profilometer (Perthometer S2, Mahr) and also by the Zygo optical interferometer. The ITO film resistivity was measured with the four-point probe technique and the van der Pauw Hall Effect technique (Hall-effect, Lake Shore Model 7507 HMS with EM7). The optical transmittance was measured by an UV-Vis-NIR spectrophotometry. The microstructure of the ITO films was obtained with a field-emission scanning electron microscopy (SEM; LEO1560) at 5 kV.

OLEDs were fabricated in a N_2-filled glove box inside a cleanroom. The light emitting layer of OLED consisted of poly(N-vinylcarbazole) (PVK) as host, doped with the electron-transport tris(8-hydroxyquinoline) aluminum (III) (Alq_3) and the hole-transport N,N'-bis (3-methylphenyl)-N,N'-bis-(phenyl)-benzidine (TPD). The host and dopants were dissolved in chloroform at 10 mg/ml concentration. The ITO samples were patterned into parallel strips by wet etching using diluted aquaregia solution of (HNO_3 (69%):HCl (37%):H_2O of 1:3:4). A 65 - 75 nm thick layer of (PVK + TPD + Alq_3) was spin-coated on top of the patterned ITO. Cross strips of 50-nm aluminum (Al) as the cathode were thermally evaporated on top of (PVK + TPD + Alq_3) layer at 5.3×10^{-4} Pa. The mutually orthogonal overlap between ITO and Al strips formed the OLED, of 0.075 cm^2. A control sample of OLED was fabricated using the commercial ITO (ρ ~ 28 Ω/sq, T~ 90 %). The current–voltage (I-V) characteristic and the electroluminescence or brightness of OLEDs was measured, respectively, using a source-meter (Keithley 238 I-V) and an optical power meter with a silicon photo-detector (Oriel Instruments, model 70260)

3. PROPERTIES OF ITO AND OLED PERFORMANCE

Figure 1 shows different nanostructures for ITO samples deposited in O_2, Ar, N_2 and He. The ITO film was usually polycrystalline if deposited in O_2 and He, the former was fine (< 100 nm) and fairly uniform in size while the latter was coarse (>200 nm), cramped together and with some degrees of disorientation. For ITO deposited in Ar, the nano-grains were ultrafine (< 50 nm), highly uniform in size, but randomly oriented and also highly compact. For ITO deposited in N_2, the nanostructure was totally different, as it shows a porous network of nano-rods of about 30 nm in diameter and 300 nm in length, similar to those reported by others [16]. The elemental analysis of ITO films by the EDX method

(Table 1) shows that Ar and N_2 were incorporated in the ITO, while the presence of He could not be determined due to the EDX limitation.

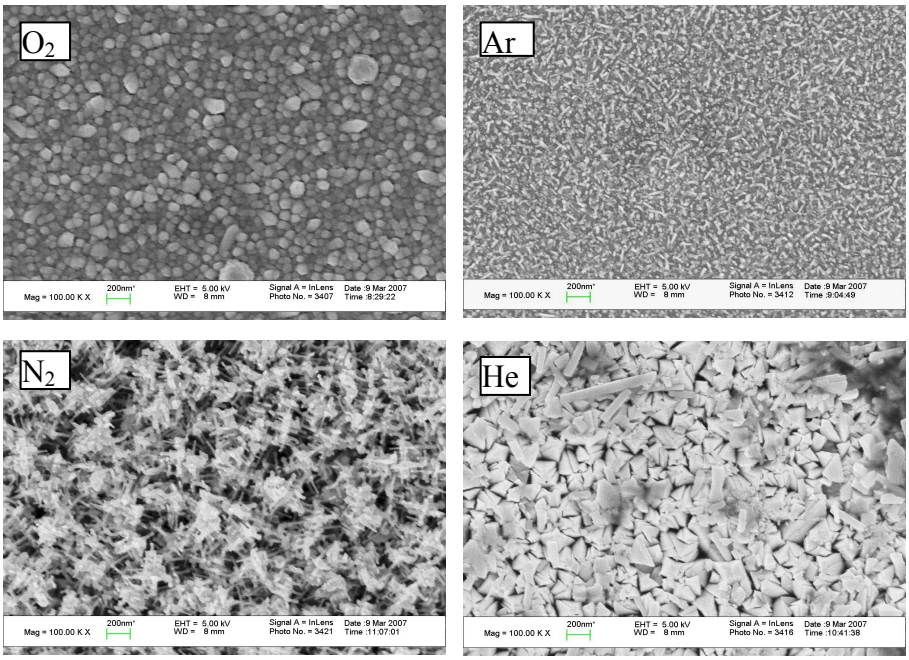

Figure 1. Effect of the background gas on the ITO microstructures. a) O_2, b) Ar, c) N_2 and d) He.

Table 1. Elemental analysis (EDX) of ITO films deposited in different gases.

	Element					
Background Gases	He (wt %)	N (wt %)	O (wt %)	Ar (wt %)	In (wt %)	Sn (wt %)
Ar	-	-	23.749	1.566	72.102	2.583
O_2	-	-	26.058	-	66.874	7.668
N_2	-	9.163	16.456	-	70.168	4.273
He	0.000	-	28.126	-	68.446	3.428

The X-ray diffraction patterns for ITO deposited in O_2, Ar, and He show similar peaks at (222), (400), (440) and (622) but different intensities. For the case of O_2, there were double peaks because of internal reflections as the ITO layer [15] was found to consist of a polycrystalline layer at the top, and amorphous layer beneath it. The grain size of ITO deposited in He may explain why its XRD pattern shows much sharper lines and higher intensity. For the case of N_2, however, the nano-rods were found to be highly amorphous.

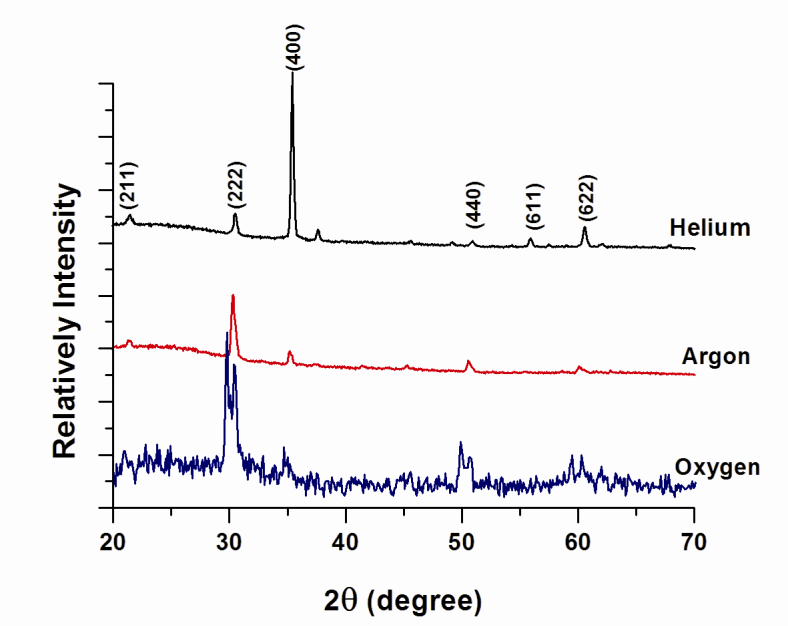

Figure 2. XRD spectra of ITO films deposited in O_2, Ar, and He background gases.

Figure 3 compares the optical transmittance (%) for ITO films deposited in Ar, O_2, N_2 and He as the background gas. The optical transmittance for ITO films deposited in N_2 and He are relatively poor, of < 65 % and < 17 % respectively. These may be explained by severe light scattering due to the grain arrangement for the case of He, and highly porous network of nano-rods for the case of N_2. In comparison, the highly compact or knitted formation of nanostructured ITO for the case of Ar had better T~ 91.4% as compared to 90.7% for ITO.

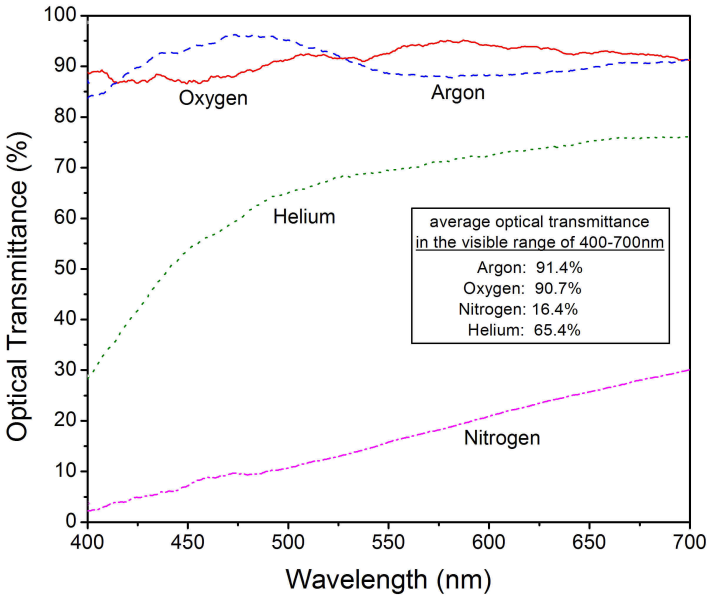

Figure 3. Comparison of optical transmittance (%) of ITO films.

Table 2 Compares operation characteristics and performance of three OLEDs using ITO deposited in O_2 and Ar by PLD and that of commercial ITO. These results were the average values for 3 to 5 individual OLEDs fabricated on the same ITO sample. For ITO deposited in Ar and O_2 at 8 cm, their OLEDs' threshold voltage and maximum brightness are 10 % lower and 13 % lower respectively, as compared to OLED on the commercial ITO"

Table 2. Comparison of OLED performance using ITO deposited in O_2 and Ar, with reference to that based on the commercial ITO

	OLED-1	OLED-2	OLED-3
ITO Type	O2 / 8 cm	Ar / 8cm	Commercial
ITO Resistivity ($\times 10^{-4}$ ¤cm)	3.5	2.8	~2.0
ITO RMS surface roughness (nm)	4.3 nm	~ 4 nm	1.6 nm
OLED Threshold Voltage (V)	16.4	15.8	15.2
OLED Max Voltage / Range (V)	23 / 6.6	22 / 6.2	22 / 6.8
OLED Max Brightness (a.u.)	~ 21,000	~ 20,000	~ 23,000

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