

## Indium tin oxide modified transparent nanotube thin films as effective anodes for flexible organic light-emitting diodes

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Sn-doped In<sub>2</sub>O<sub>3</sub> (ITO) modified single-walled carbon nanotube (SW-CNT) transparent electrodes are fabricated on flexible polyethyleneterephthalate (PET) substrates by stamp printing SW-CNT films, followed by room temperature ion-assisted deposition of ITO. Polymer light-emitting diodes (PLEDs) using such film as anodes exhibit superior performance versus CNT-only controls. Flexible PLEDs with the following structure: PET/CNT(30 nm)-ITO(45 nm)/poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)/[poly(9,9-dioctyl-fluorene-co-N-(4-butylphenyl)diphenylamine)]+[4,4'-bis[(p-trichlorosilyl propylphenyl)-phenylamino]biphenyl]/[poly(9,9-dioctylfluorene-co-benzothiadiazole)]/CsF/Al, achieve a maximum light output of 8900 cd/m<sup>2</sup> with a current efficiency of 4.5 cd/A. Bending test comparisons with ITO/PET show the ITO modified CNT/PET electrodes to be far more mechanically flexible. © 2008 American Institute of Physics. [DOI: 10.1063/1.2970049]

Small-molecule organic and polymer light-emitting diodes (OLEDs/PLEDs) are creating great interest due to their applicability in flat panel displays and solid-state lighting.<sup>1</sup> It is known that OLED/PLED performance, lifetime, and durability are strongly influenced by the anode charge injection characteristics.<sup>2</sup> Tin-doped indium oxide (ITO), with electrical conductivity and visible range transparency of  $(3-5) \times 10^3$  S/cm and 85%–90%, respectively, is currently the most widely used OLED anode material. However, rising In costs and other limitations present challenges for next-generation optoelectronics.<sup>3,4</sup>

Recently, thin film electronic materials based on random carbon nanotube (CNT) networks having excellent optical transparency and electrical conductivity have been explored<sup>5</sup> for applications requiring low sheet resistance ( $R_s$ ) and high optical transparency ( $T$ ). These films are fabricated by solution processing and are mechanically flexible. Moreover, their intrinsic work function (4.5–5.2 eV)<sup>6</sup> is similar to that of ITO (4.4–4.9 eV).<sup>7</sup> CNT films have been used as anodes for OLEDs<sup>8–10</sup> and organic photovoltaics (OPVs).<sup>11,12</sup> In OPVs, CNT anodes exhibit superior mechanical performance with comparable energy conversion efficiency versus devices using ITO anodes.<sup>12</sup> However, in OLEDs, CNT-based devices exhibit less than optimum performance versus ITO. The maximum OLED light output with CNT-only anodes is <10% of those with ITO anodes,<sup>8,10</sup> probably reflecting higher CNT film sheet resistance, poor CNT surface wetting by the active organic layers, and nonuniform charge injection from the rough CNT surfaces. The conducting polymer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT-PSS)<sup>8</sup> with a parylene-C<sup>9</sup> buffer layer, partially addresses these issues, leading to somewhat improved OLED/PLED performance.

To achieve greater conductivity, transparency, and multifunctionality, electrode modification with another layer is sometimes used in optoelectronics. For example, Au modified ITO electrodes facilitate Ohmic contact and decrease

OLED turn-on voltages.<sup>13</sup> For CNT electrodes, ITO is an attractive choice for modification due to perfect work function matching. Here we report a simple, efficient strategy for ITO/CNT thin film growth. Attractions include: (1) lower sheet resistance with great optical transparency, (2) smoother surface morphology, (3) greater mechanical flexibility, (4) better wettability and charge injection uniformity, (5) greater environmental stability, (6) lower materials cost, and (7) simple growth process applicable to other transparent conducting oxide/CNT structures.

To avoid damaging the CNT films on flexible polyethyleneterephthalate (PET) substrates, a low-temperature ITO growth technique was employed. Ion-assisted deposition (IAD) employs two ion beams for simultaneous film deposition, oxidation, and crystallization, resulting in smooth, adherent, microstructurally dense film growth on a variety of substrates at room temperature.<sup>14</sup> ITO film microstructural, electrical, and optical properties can be finely tuned via the IAD O<sub>2</sub> pressure and ion beam power. We report here the first growth, electrical, and optical properties of double-layer ITO/CNT thin films, and their implementation in PLEDs. The lower sheet resistance, smoother surface, and higher figure-of-merit<sup>15</sup> ( $\Phi = T^{10}/R_{\text{sheet}}$ , where  $T$  = average transmittance from 400–700 nm) than that of CNT-only films, yield PLED performance far superior to CNT-only devices, and rivaling commercial ITO-based devices. The mechanical flexibility is far superior to that of ITO/PET anodes.

The fabrication of transparent, conducting SWNT films on PET substrates is described elsewhere.<sup>16</sup> These films have highly nanoporous structures, with specific surface areas of  $\sim 1500$  m<sup>2</sup>/g. Scanning electron microscopy of a PET/SWNT thin film reveals uniform NT distribution, while voids illustrate the three-dimensional nature of the film. The rms roughness is  $\sim 12$  nm by atomic force microscopy (AFM) [Fig. 1(a)]. The as-deposited SWNT films were next transferred to the IAD for ITO overcoating using an In<sub>2</sub>O<sub>3</sub>:SnO<sub>2</sub>=9:1 target. During ITO deposition,  $P_{\text{O}_2}$  and the growth rate were optimized at  $1.1 \times 10^{-4}$  Torr and 1.8 nm min<sup>-1</sup>, respectively.<sup>14</sup> ITO film thickness was monitored *in situ*.

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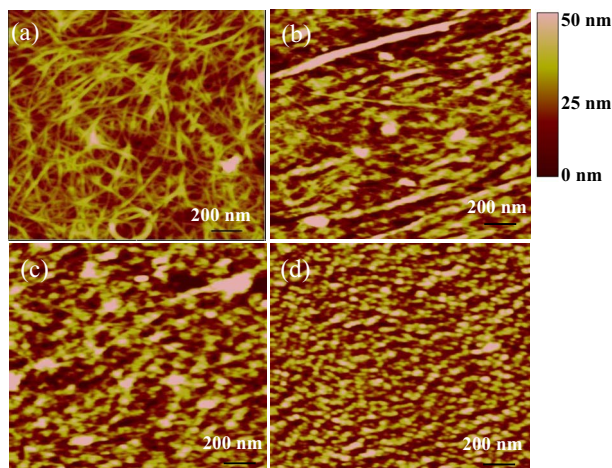


FIG. 1. (Color online) AFM images of: (a) a pristine CNT film, (b) 14 nm ITO modified CNT (anode A), (c) 30 nm ITO modified CNT (anode B), and (d) 45 nm ITO modified CNT (anode C).

Smooth surface morphologies are required for OLED anodes both because “spikes” can cause breakdown/shorting and because subsequent upper device layers assume any irregular anode morphology, adversely influencing performance.<sup>17</sup> Figure 1 shows contact mode AFM images of CNT (30 nm), 14 nm ITO modified CNT (anode A), 30 nm ITO modified CNT (anode B), and 45 nm ITO modified CNT (anode C) films. The rms roughnesses of these ITO modified CNT surfaces decrease with increased ITO film thickness; e.g., the rms roughness of anode C is  $\sim 7$  nm, less than anode A,  $\sim 11$  nm. This reflects the marked tendency of IAD-derived ITO to planarize the SWNT films, as summarized in Table I.

Figure 2 shows optical transmittance spectra of CNT and anodes A–C. The average transmittance of ITO modified CNT films decreases slightly as the ITO thickness increases, while the sheet resistance decreases significantly. Optical transmittance, sheet resistance, and figure of merit ( $\Phi = T^{10}/R_{\text{sheet}}$ ) data are summarized in Table I. Note that anode A samples exhibit almost the same sheet resistance as the CNT films, suggesting that the 14 nm ITO film is not sufficient to form a continuous coverage on the relatively rough CNT surface. Note that the anode C films exhibit the highest figure of merit among all the modified CNT films.

PLEDs having the structure, PET/CNT or anodes A–C /PEDOT-PSS/poly(9,9-dioctyl-fluorene-co-N-(4-butylphenyl)diphenylamine] (TFB)+4,4'-bis[p-trichlorosilyl

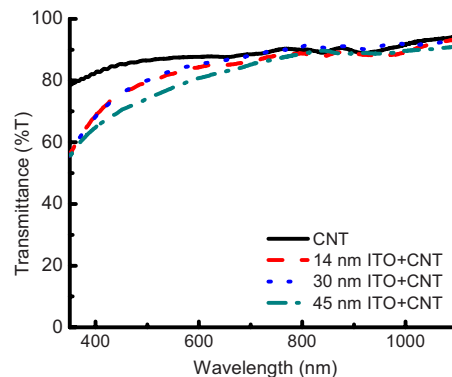


FIG. 2. (Color online) Optical transmittance spectra of CNT (30 nm), anode A (14 nm ITO on 30 nm CNT), anode B (30 nm ITO on 30 nm CNT), and anode C (45 nm ITO on 30 nm CNT) films.

propylphenyl)-phenylamino]biphenyl (TPDSi<sub>2</sub>)/ poly(9,9-dioctylfluorene-co-benzothiadiazole) (BT)/CsF/Al were next fabricated.<sup>17</sup> Here the PEDOT-PSS hole-injection/hole transport layer (HTL), which also planarizes the anode was first spin-coated onto the anodes and cured at 120 °C overnight under vacuum. Next, a crosslinkable, HTL/electron-blocking layer (EBL) consisting of TPD-Si<sub>2</sub> blended with the hole-transporting polymer TFB (1:1 mass ratio) was spin-coated onto the PEDOT-PSS-coated anodes, followed by thermal crosslinking to afford a robust, insoluble film. A third layer of the emissive polymer BT was then spin-coated onto the HTL/EBL to form a multilayer heterostructure. Finally, CsF and Al were thermally evaporated onto the emissive layer at  $<10^{-6}$  Torr using a shadow mask to define  $2 \times 5$  mm<sup>2</sup> electrode areas.<sup>18</sup>

In parallel, PLEDs with identical structures were fabricated using CNT-only and commercial PET/ITO films (sheet resistance=200  $\Omega/\square$ ,  $\sim 3$  nm rms roughness) for comparison. Steady-state light output and  $J$ - $V$  characteristics were measured under ambient atmosphere using instrumentation described elsewhere.<sup>18</sup> Luminance, and current efficiency versus bias responses for the present PLEDs are compared in Fig. 3. Differences between various ITO modified CNT films and CNT-only control devices are attributable to differences in anode characteristics. As seen in Fig. 3, Anode C PLEDs exhibit a turn-on voltage of 3.7 V, lower than for anode B and CNT-based devices, 4.0 and 4.3 V, respectively, presumably reflecting the low anode C sheet resistance—150  $\Omega/\square$ , lower than that of anode B and CNT films. The anode C-derived PLED exhibits maximum luminance

TABLE I. Properties of single-layered CNT and double-layered CNT/IAD-derived ITO thin films, and operating characteristics of PLEDs having the structure: PET/CNT or PET/CNT/ITO double-layered anode/PEDOT-PSS/TFB+TPDSi<sub>2</sub>/BT/CsF/Al.

Sample	Thickness (nm)	Sheet resistance ( $\Omega/\square$ )	Average transmittance in 400–700 nm (%)	Figure of merit $\Phi = T^{10}/R_{\text{sheet}}$ ( $10^{14} \Omega^{-1}$ )	Surface roughness (nm)	Turn-on voltage (V)	Maximum light output (cd/m <sup>2</sup> )	Maximum current efficiency (cd/A) [voltage (V)]
PET/CNT	30	350	86.2	6.3	11–13	4.3	3050	1.6 (11.0)
PET/CNT/ITO Anode A	30/14	345	83.1	4.5	$\sim 11$	4.7	2430	0.97 (11.5)
PET/CNT/ITO Anode B	30/30	215	82.7	6.5	$\sim 8$	4.0	4380	2.1 (10.8)
PET/CNT/ITO Anode C	30/45	150	80.5	8.1	$\sim 7$	3.7	8900	4.5 (10.5)

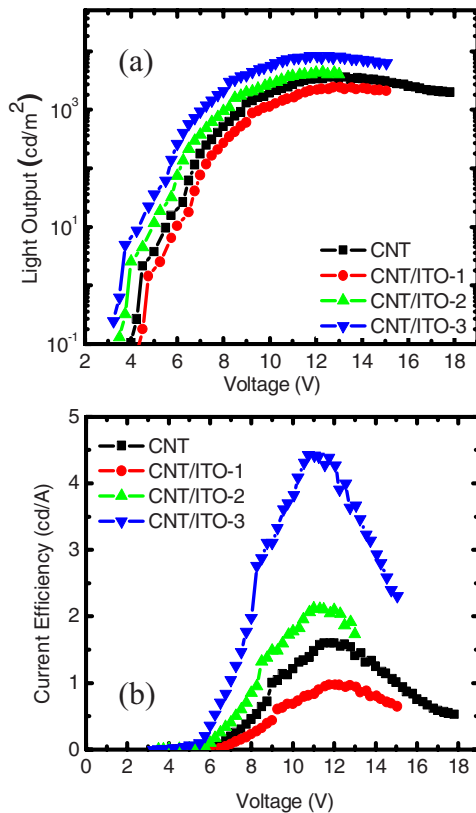


FIG. 3. (Color online) Response characteristics of PLEDs having the structures: CNT(30 nm) or IAD-derived ITO modified CNT/PEDOT-PSS (30 nm)/TFB+TPDSi<sub>2</sub>(25nm)/BT(70nm)/CsF(1.8nm)/Al(110nm). (a) luminance vs voltage; (b) current efficiency vs voltage. Lines through the data points are drawn as a guide to the eye.

=8900 cd/m<sup>2</sup>, and current efficiency=4.5 cd/A at 10.5 V—threefold increases versus a CNT-only control. This enhancement in metrics likely reflects: (1) PEDOT-PSS wettability and adhesion on hydrophilic ITO surface are much greater than on the hydrophobic CNT surface. PEDOT-PSS, as a hole transport/injection layer, straddles the SWNT/ITO and TFB-TPDSi<sub>2</sub> work functions, facilitating hole injection. (2) IAD-derived ITO planarizes the CNT surface, affording more uniform hole injection from the anode. CNTs with 45 nm ITO films exhibit the lowest rms roughness of 7 nm. (3) IAD-derived ITO improves the CNT film conductivity. Anode C has a sheet resistance of 150 Ω/□, ~60% lower than that of for the CNT film. Note that the anode C-based device performance rivals that of a commercial PET/ITO-based control having maximum light output=13000 cd/m<sup>2</sup> and current efficiency=5.5 cd/A.

The performance of the anode-A-derived PLED is comparable to or inferior in performance to devices having CNT-only anodes. As seen in the scanning electron microscopy the presence of voids in the CNT three-dimensional network suggests that 14 nm of IAD ITO cannot form a continuous, conductive lattice on the relatively rough surface, while optical transmittance decreases with 14 nm ITO. Thus, PLED performance with ITO modified CNTs is enhanced with increased IAD-derived ITO thickness. The mechanical flexibility of the ITO/CNT films on PET substrates was investigated in bending tests and found to be much greater than that of ITO-only films of the same thickness on PET (Table II). Thus, 30 nm ITO modified CNT films can be bent to radii of

TABLE II. Properties of single-layered CNT, 30 nm IAD-derived ITO, and double-layered CNT (30 nm)/IAD-derived ITO (30 nm) thin films, and sheet resistances after mechanical bending tests.

Sample	Sheet resistance (Ω/□)	Average transmittance in 400–700 nm (%)	After R=4.0 mm bending test (Ω/□)	After R=2.0 mm bending test (Ω/□)
PET/CNT (30 nm)	460	87.5	470	500
PET/ITO (30 nm)	350	93.6	2000	8000
PET/CNT/ITO	380	85.8	400	800

curvature of ~4 mm with a 5% increase in sheet resistance. In marked contrast, ITO/PET films show a ~600% increase in sheet resistance on bending to radii of 4 mm, and cracks are obvious in the SEM. This increased ITO/CNT film mechanical flexibility is attributed to the ITO/CNT interpenetrating network microstructure, ITO adhesion to the CNTs, and intrinsic CNT mechanical flexibility.

In summary, ITO modified transparent, conducting, mechanically flexible CNT films are used as PLED anodes. The overall film figure of merit with 30 nm CNT and 45 nm IAD-derived ITO (anode C) is significantly greater than that of CNT-only films. Anode C-based PLEDs exhibit superior performance to that of CNT-only controls and rival that of a commercial ITO devices while being far more flexible. Note that the CNT/ITO films have lower In content than ITO/PET, rendering them promising for large-area optoelectronics.

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