

High-Performance Organic Light-Emitting Diodes Using ITO Anodes Grown on Plastic by Room-Temperature Ion-Assisted Deposition**

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Organic light-emitting diodes (OLEDs) fabricated on flexible plastic substrates are the focus of increasing attention due to their broad potential applications in portable devices such as cellular phones, personal digital assistants (PDAs), and laptops, etc., which require light weight and mechanical durability.^[1,2] Heeger and co-workers first reported flexible OLEDs, fabricated from a conducting polymer electrode deposited on poly(ethylene terephthalate) (PET).^[3] It was generally thought at the time that mechanical flexibility could only be achieved with a polymeric electrode. However, Forrest and co-workers subsequently demonstrated flexible, vacuum-deposited, small-molecule OLEDs fabricated on indium tin oxide (ITO)-coated PET and having the structure PET/ITO/TPD/Alq/MgAg/Ag—analogue to those of conventional glass-based devices, and capable of repeated flexing.^[4] Subsequently, small-molecule OLEDs have been fabricated on several kinds of plastic or plastic/inorganic hybrid substrates, pre-coated with a transparent conductive oxide (TCO) such as ITO, by conventional pulsed-laser deposition or sputtering.^[2,5,6]

TCO growth on plastic remains a significant challenge for the fabrication of truly efficient flexible OLEDs, due to the poor thermal and mechanical properties of typical polymeric substrates. This is illustrated in ITO film growth on glass, where relatively high deposition and/or post-annealing temperatures (>200 °C) are typically required to achieve reasonable electrical conductivity, optical transparency, and long-term stability. Conventionally, ITO film growth on plastic has been achieved by low-temperature deposition techniques such as sputtering. However, such films are typically amorphous, leading to poor conductivity, transparency, and adhesion properties, and underscoring the need for an improved growth technique. In contrast to simple sputtering, ion-assisted

deposition (IAD) is uniquely suited for producing smooth, adherent, and microstructurally dense thin oxide films at remarkably low temperatures.^[7] IAD employs two ion beams to effect simultaneous film deposition, oxidation, and crystallization, resulting in smooth, dense, coherent films at low temperatures. In addition, the assisting ion bombardment generates fresh surfaces during the pre- and in-situ cleaning/activation process, creating strong interfacial adhesion and removal of voids that can trap loosely bound/physisorbed O₂, which may degrade OLED performance. These attractions raise the interesting question of whether IAD could be effectively employed in low-temperature ITO depositions for OLEDs, especially on plastics, because ITO's physical properties, such as work function, conductivity, morphology, and surface composition, etc., which significantly influence OLED performance, are strongly dependent on the specific deposition process and post-treatment.^[8] To date, there have been no reports of OLED fabrication with IAD-deposited ITO.^[9] We report here the growth and characteristics of high-quality ITO thin films on both glass and plastic by IAD at room temperature, and OLED response characteristics with these films as transparent electrodes. It was found that IAD-derived ITO is of high-quality with very smooth surfaces, high conductivity, and high transparency, and affords OLED performance that rivals or exceeds that of devices fabricated with commercial ITO/glass anodes.

Both conventional PET (Melinex, type 453, denoted PET) and PET with a polymeric hard coating (Kimoto Tech, Inc., denoted PET-HC) were used as substrates for ITO growth and for comparison in ion-bombardment stability. Microscope slides (Fisher Scientific, pre-cleaned, 1.0 mm thickness) were used as glass substrates. ITO films were deposited with a Veeco Ion Tech horizontal dual-gun IAD system. The Sn doping level in the IAD-ITO films grown under optimized conditions was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to be 6.0 ± 0.2% and 5.4 ± 0.4% for IAD-ITO/glass and IAD-ITO/PET-HC, respectively—somewhat lower than in the ITO target (10 %).

The electrical and optical properties of IAD-derived ITO thin films were studied as a function of growth parameters—O₂ partial pressure (P_{O_2} , Fig. 1) and ion source energy (Table 1). In the absence of O₂ or at low P_{O_2} , film mobility, carrier concentration, and conductivity are significantly lower. It is known that below specific P_{O_2} values, the constituent ITO metals are not in their highest oxidation states, leading to poor doping efficiency, carrier mobility, and long-term stability. With increased P_{O_2} , both carrier mobility and concentration increase and reach maxima at $P_{O_2} = 2 \times 10^{-4}$ torr and 1×10^{-4} torr, respectively. Four-probe electrical conductivities of as-deposited IAD-ITO films are also found to be sensitive to both substrate and assisted-ion source energies, as summarized in Table 1. Importantly, there are negligible differences in electrical properties of ITO films grown on PET-HC and on glass under optimized conditions. However, ITO films grown on PET without a HC exhibit poor conductivity, presumably reflecting ITO reaction and ion-bombardment

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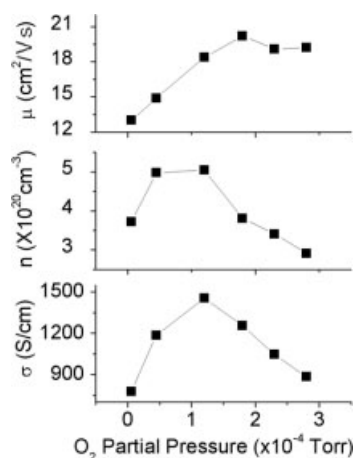


Figure 1. Carrier mobility (μ), carrier concentration (n), and conductivity (σ) of IAD-derived ITO thin films on glass substrates as a function of P_{O_2} during film growth.

Table 1. IAD-ITO thin film electrical properties' dependence on substrate and growth parameters.

Substrate	Assisted ion beam current [mA]	Assisted ion beam voltage [V]	Film thickness [nm]	Sheet resistance [Ω/\square]	Conductivity [$S\text{ cm}^{-1}$]
Glass	8	200	350	23.5	1216
Glass	23	200	297	26.1	1290
Glass	34	200	248	27.7	1456
Glass	60	200	101	90.5	1094
Glass	34	100	335	22.2	1345
Glass	34	300	155	53.7	1201
PET	34	200	200	276	181
PET-HC	34	200	200	35.2	1421

damage. ITO/PET-HC with an optimized conductivity of 1450 S cm^{-1} is obtained, with a carrier mobility (n-type) and concentration of $19\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and $5 \times 10^{20}\text{ cm}^{-3}$, respectively. Optimized sheet resistances ($35\ \Omega/\square$) are significantly below those of commercial ITO on PET, and the ITO crystallinity is far higher, as judged by X-ray diffraction.^[10] As-deposited IAD-ITO thin films are highly transparent in the visible region with an average transmittance of $\geq 85\%$, comparable to that of commercial ITO.

Generally, weak adhesion and cracking of ITO films are the two leading factors which adversely affect the stability of OLED devices fabricated on plastic.^[5] The conventional “Scotch tape”^[11] test was applied to examine the adhesion properties of IAD-ITO on PET-HC. There is no detectable change in sheet resistance and in optical microscopic images before and after the test, indicating that IAD-ITO films exhibit good adhesion properties. In addition, unlike commercial ITO on PET,^[11] the IAD-derived thin films retain integrity after sonication in organic solvents, indicating that they are sufficiently robust for solution OLED deposition processes. This confirms that the pre- and in-situ surface cleaning/activation by the assisting ion source significantly enhances interfacial bonding, hence thin film adhesion.

Smooth surface morphologies are required for ITO films used as OLED anodes both because ITO “spikes” can cause breakdown/shorting and because subsequent upper device layers will assume the irregular ITO morphology, adversely influencing stability and performance.^[12] Figure 2 shows atomic force microscopy (AFM) images of the surface morphologies of IAD-ITO/glass (Fig. 2a), IAD-ITO/PET-

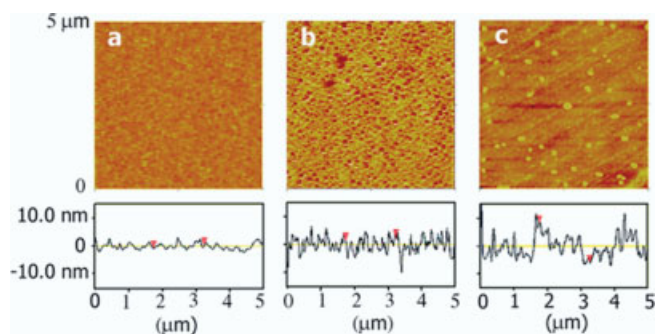


Figure 2. Contact mode AFM images and cross-sectional profiles: a) IAD-ITO/glass, b) IAD-ITO/PET-HC, and c) IAD-ITO/PET.

HC (Fig. 2b), and IAD-ITO/PET (Fig. 2c). As-deposited IAD-ITO/glass is very uniform and smooth, with a root-mean-square (RMS) roughness by contact-mode AFM of 0.9 nm over a $5\ \mu\text{m} \times 5\ \mu\text{m}$ area—even smoother than sputter-derived commercial ITO (RMS roughness = 2.5 nm). As-deposited IAD-ITO/PET-HC is also very uniform although somewhat rougher, with RMS roughness = 3.6 nm over the same area. Note that the roughness is not due to the PET-HC substrate, which is very smooth (RMS roughness = 1.0 nm). Dimple-like feathering over the entire film surface suggests traces of ion bombardment. The ITO on PET without a hard-coating exhibits a rougher morphology, with RMS roughness = 4.8 nm (Fig. 2c).

IAD-ITO thin films on PET-HC with a sheet resistance of $35\ \Omega/\square$ were then used as anodes in small-molecule OLED fabrication. Figure 3 shows light output, current–voltage characteristics (J – V), and external forward quantum efficiency for devices based on IAD-ITO/glass, IAD-ITO/PET-HC, and a control fabricated with plasma-cleaned commercial ITO/glass ($20\ \Omega/\square$). Operating characteristics are summarized in Table 2. As can be seen in Figure 3, OLEDs with IAD-ITO exhibit a turn-on voltage of 4.0 V , slightly lower than that of the commercial ITO-based control, 4.8 V .^[13] Furthermore, IAD-ITO devices exhibit higher light outputs and current densities with respect to the control. Maximum device luminance of $31\ 000\text{ cd m}^{-2}$ and $11\ 000\text{ cd m}^{-2}$ are achieved on devices with IAD-ITO/glass and IAD-ITO/PET-HC anodes, respectively—significantly greater than the $7\ 000\text{ cd m}^{-2}$ of the control device on commercial ITO. Although the external forward quantum efficiencies of 1.8% (IAD-ITO/PET-HC) and 2.2% (IAD-ITO/glass) are somewhat lower than that of the control, 2.6% , the respective operating voltages at 100 cd m^{-2} for devices on IAD-ITO/PET-HC and IAD-ITO/glass, 5.6 V

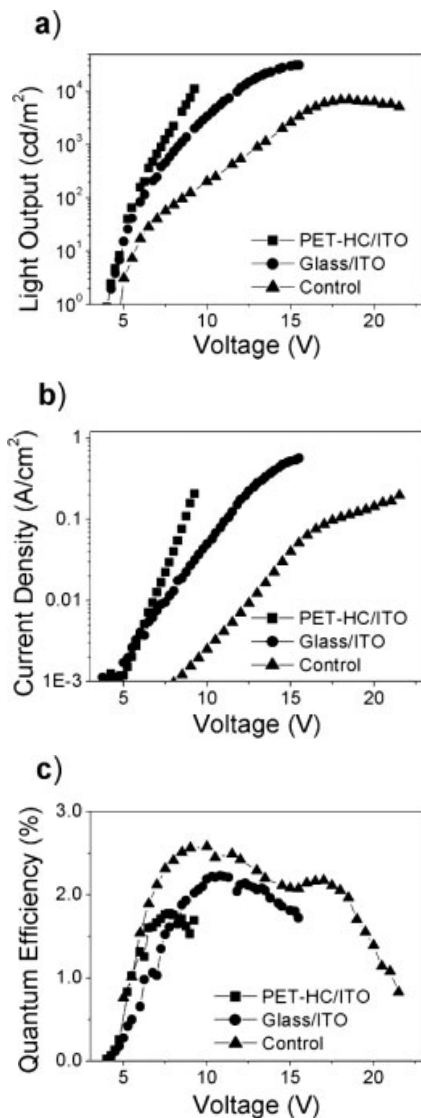


Figure 3. a) Light output, b) current density, and c) external forward quantum efficiency vs. bias for ITO/NPB/AlQ:DIQA/BCP/Li/MgAg OLEDs using IAD-ITO/glass, IAD-ITO/PET-HC, and commercial ITO/glass as anodes.

and 6.1 V, respectively, are significantly lower than that of the control, 8.5 V. Clearly IAD-derived ITO anodes afford high OLED performance, which probably reflects the specific surface chemical environment provided by IAD. Interestingly, the device on IAD-ITO/PET-HC exhibits higher light output and external quantum forward efficiency than that on IAD-

ITO/glass at identical driving voltages below 9.5 V. One possible reason is that the surface of IAD-ITO/PET-HC is somewhat rougher than that of IAD-ITO/glass, which may enhance local interfacial contact and electric fields and hence charge carrier injection, leading to lower operating voltage, higher quantum forward efficiency, and increased light output.^[14] Another possibility is that the plastic devices have a better refractive index match between the substrate and OLED components, which may enhance light extraction.^[15]

In summary, the IAD technique is demonstrated to be capable of depositing smooth, adherent, and electrically/optically high-quality ITO films on glass and plastic substrates at room temperature. ITO thin films with an RMS roughness (over a 25 μm^2 area) of 0.9 nm and 3.6 nm on glass and PET-HC, respectively, a conductivity of 1500 S cm^{-1} and optical transmittance of $\geq 85\%$ in the visible range, are obtained and implemented as anodes in small-molecule OLEDs. A maximum luminance of 31 000 cd m^{-2} , an external forward quantum efficiency of 2.2%, and a turn-on voltage of 4.0 V are achieved with an IAD-ITO/glass anode. A maximum luminance of 11 000 cd m^{-2} and an external forward quantum efficiency of 1.8% are achieved with an ITO/plastic anode at significantly lower driving voltages than for commercial ITO/glass. Importantly, this work also suggests the feasibility of employing IAD to deposit non-ITO transparent electrodes on various substrates for high performance OLEDs.

Experimental

ITO Deposition and Characterization: The ITO target ($\text{In}_2\text{O}_3/\text{SnO}_2=9:1$) was purchased from Sputtering Materials, Inc. The substrate was pre-cleaned with assisted ions ($\text{Ar} + \text{O}_2$) for 3 min prior to film deposition. Film thicknesses were measured using a Tencor P-10 surface profilometer after etching a step in the film with 20% HCl solution. Transparency measurements were carried out in the 300–3300 nm range with a Cary 500 UV-vis-NIR spectrophotometer. Composition analyses were carried out using X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). Film surface morphology was imaged with a Digital Instruments Nanoscope III atomic force microscope (AFM). Four-probe charge transport data were acquired with a Bio-Rad HL5500 Hall effect system at 25 °C.

OLED Fabrication: As-deposited IAD-ITO thin films were transferred to a glove-box/twin-evaporator facility, followed by thermal evaporation at 1×10^{-7} torr of *N,N'*-di-(1-naphthyl)-*N,N'*-diphenylbenzidine (NPB) (20 nm), Alq/1% di-isoamylquinacridone (DIQA) (50 nm), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (20 nm), Li (1 nm), and Mg/Ag (1:9, 80 nm). General details of device fabrication are described elsewhere [13]. Simultaneously, a control

Table 2. Operating characteristics of ITO/NPB/AlQ:DIQA/BCP/Li/MgAg OLEDs.

OLED anode	Sheet resistance [Ω/\square] (RMS roughness [nm])	Turn-on voltage [V] (Max. light output [cd m^{-2}])	Applied bias at 100 cd m^{-2} [V]	Power efficiency at 100 cd m^{-2} [lm/W]	Max. external forward quantum efficiency [%]
IAD-ITO/PET-HC	35 (3.6)	4.0 (11,000)	5.6	2.5	1.8
IAD-ITO/glass	28 (0.9)	4.0 (31,000)	6.1	2.2	2.2
Commercial-ITO/glass	20 (2.5)	4.8 (7,000)	8.5	3.1	2.6

device with an identical layer structure was fabricated using commercial ITO on glass (Colorado Concept Coating, LLC, cleaned in an oxygen plasma). The $0.2 \times 0.5 \text{ cm}^2$ OLED emitting areas were defined by shadow masks. Light output and J - V characteristics were measured with a Keithley 2400 source meter and IL 1700 radiometer at 25°C .

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Metallic Conductivity in a Polyoxovanadate Radical Salt of Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF): Synthesis, Structure, and Physical Characterization of β'' -(BEDT-TTF) $_5$ [H $_3$ V $_{10}$ O $_{28}$] \cdot 4H $_2$ O**

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Polyoxometalate compounds are having a large impact in many different disciplines of current interest, such as catalysis, medicine, materials science, and magnetism, due to their rich and tunable molecular and electronic properties.^[1,2] The role of polyoxometalates has been of special relevance in the field of functional molecular materials. The structural and chemical stability of these compounds has made them perfect electroactive components for the construction of materials formed by two molecular networks with the aim to combine two distinct physical properties in the same material. In this context, one of the most appealing and still challenging combinations is that of electrical conductivity, and even superconductivity, with magnetism.^[3] These hybrid materials are usually prepared as crystalline salts formed by organic electron donor molecules (tetrathiafulvalene (TTF) derivatives), responsible for the electrical conductivity, and by inorganic anions responsible for the magnetic properties. Many radical salts of polyoxometalates have been reported so far.^[4] Often they show novel organic packings and can exhibit coexistence of conducting electrons and localized magnetic moments. The finding of metallic states in this type of salts, however, is difficult because the large charges of the polyanions usually induce charge localization on the organic sublattice. In fact, most of the polyoxometalate salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) are semi-conductors, or have phase transitions to a semiconducting state at high temperatures. Only three radical salts are known to present "light" metallic regimes that disappear below 200 K.^[5]

- [1] a) *Proceeding of the U. S. Display Consortium Flexible Microelectronics and Displays Conference*, Phoenix, AZ, February 3–4, 2003, available online at: www.usdc.org/resources/resources_library.html b) H. E. A. Huitema, G. H. Gelinck, J. van der Putten, K. E. Kuijk, C. M. Hart, E. Cantatore, P. T. Herwig, A. van Breemen, D. M. de Leeuw, *Nature* **2001**, 414, 599.
- [2] a) H. Kim, J. S. Horwitz, G. P. Kushto, Z. H. Kafafi, D. B. Chrisey, *Appl. Phys. Lett.* **2001**, 79, 284. b) H. Lim, W. J. Cho, C. S. Ha, S. Ando, Y. K. Kim, C. H. Park, K. Lee, *Adv. Mater.* **2002**, 14, 1275.
- [3] G. Gustafsson, Y. Cao, G. M. Treacy, F. Klavetter, N. Colaneri, A. J. Heeger, *Nature* **1992**, 357, 477.
- [4] G. Gu, P. E. Burrows, S. Venkatesh, S. R. Forrest, M. E. Thompson, *Opt. Lett.* **1997**, 22, 172.
- [5] J. Q. Zhao, S. J. Xie, S. H. Han, Z. W. Yang, L. N. Ye, T. L. Yang, *Phys. Status Solidi A* **2001**, 184, 233.
- [6] a) M. S. Weaver, L. A. Michalski, K. Rajan, M. A. Rothman, J. A. Silvernail, J. J. Brown, P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennett, M. Zumhoff, *Appl. Phys. Lett.* **2002**, 81, 2929. b) A. N. Krasnov, *Appl. Phys. Lett.* **2002**, 80, 3853.
- [7] a) P. J. Martin, R. P. Netterfield, D. R. McKenzie, *Thin Solid Films* **1986**, 137, 207. b) J. A. Dobrowolski, F. C. Ho, D. Menagh, R. Simpson, A. Waldorf, *Appl. Opt.* **1987**, 26, 5204. c) M. Gilo, R. Dahan, N. Croitoru, *Opt. Eng.* **1999**, 38, 953. d) D. Kim, S. Kim, *Surf. Coat. Technol.* **2002**, 154, 204. e) H. Niederwald, *Thin Solid Films* **2000**, 377–378, 21.
- [8] a) Special issue on ITO, *Thin Solid Films* **2002**, 411(1). b) J. S. Kim, M. Granstrom, R. H. Friend, N. Johansson, W. R. Salaneck, R. Daik, W. J. Feast, F. Cacialli, *J. Appl. Phys.* **1998**, 84, 6859. c) F. Nuesch, L. J. Rothberg, E. W. Forsythe, Q. T. Le, Y. L. Gao, *Appl. Phys. Lett.* **1999**, 74, 880. d) J. M. Liu, P. Y. Lu, W. K. Weng, *Mater. Sci. Eng., B* **2001**, 85, 209.
- [9] There is one recent report of OLED fabrication on Zn–In–O films grown by IAD, however, the light output and quantum efficiency data suggest non-optimum TCO growth and/or device fabrication processes. W. J. Lee, Y. K. Fang, J. J. Ho, C. Y. Chen, L. H. Chiou, S. J. Wang, F. Dai, T. Hsieh, R. Y. Tsai, D. Huang, F. C. Ho, *Solid-State Electron.* **2002**, 46, 477.
- [10] Sheldahl Corp. Product Sheet G430300. Typical ITO/PET specifications (Ω/\square , %T at 550 nm): 60 ± 10 , >79 ; 80 ± 10 , >77 ; 100 ± 10 , >77 ; 200 ± 10 , >82.5 ; 300 ± 30 , >84 . (Sheldahl Corp., Northfield MN). These coatings are essentially amorphous by X-ray diffraction.
- [11] *Standard Test Methods for Measuring Adhesion by Tape Test*, ASTM, West Conshohocken, PA **1997**, D3359-3397.
- [12] Y. H. Tak, K. B. Kim, H. G. Park, K. H. Lee, J. R. Lee, *Thin Solid Films* **2002**, 411, 12.
- [13] Q. Huang, J. Cui, J. G. C. Veinot, H. Yan, T. J. Marks, *Appl. Phys. Lett.* **2003**, 82, 331.
- [14] Y. Yang, E. Westerweele, C. Zhang, P. Smith, A. J. Heeger, *J. Appl. Phys.* **1995**, 77, 694.
- [15] P. E. Burrows, G. L. Graff, M. E. Gross, P. M. Martin, M. Hall, E. Mast, C. Bonham, W. Bennett, L. Michalski, M. Weaver, J. J. Brown, D. Fogarty, L. S. Sapochak, *Proc. SPIE-Int. Soc. Opt. Eng.* **2000**, 4105, 75.

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