



Deposition of low sheet resistance indium tin oxide directly onto functional small molecules



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ABSTRACT

We outline a methodology for depositing tin-doped indium oxide (ITO) directly onto semiconducting organic small molecule films for use as a transparent conducting oxide top-electrode. ITO films were grown using pulsed laser deposition onto copper(II)phthalocyanine (CuPc):buckminsterfullerene (C₆₀) coated substrates. The ITO was deposited at a substrate temperature of 150 °C over a wide range of background oxygen pressures (P_d) (0.67–10 Pa). Deposition at 0.67 ≤ P_d ≤ 4.7 Pa led to delamination of the organic films owing to damage induced by the high energy ablated particles, at intermediate 4.7 ≤ P_d < 6.7 Pa pressures macroscopic cracking is observed in the ITO. Increasing P_d further, ≥ 6.7 Pa, supports the deposition of continuous, polycrystalline and highly transparent ITO films without damage to the CuPc:C₆₀. The free carrier concentration of ITO is strongly influenced by P_d; hence growth at >6.7 Pa induces a significant decrease in conductivity; with a minimum sheet resistance (R_s) of 145 Ω/□ achieved for 300 nm thick ITO films. To reduce the R_s a multi-pressure deposition was implemented, resulting in the formation of polycrystalline, highly transparent ITO with an R_s of ~20 Ω/□ whilst maintaining the inherent functionality and integrity of the small molecule substrate.

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1. Introduction

Recently, there has been tremendous effort to integrate organic electronic materials into optoelectronic devices—owing to the possibility of producing low-cost, lightweight flexible products [1–4]. In devices that require the absorption or emission of photons, a vast amount of research has been directed towards transparent conducting electrodes (TCOs) [5–7]. Although there has been increased interests in flexible materials, such as metallic nanowires [8,9], the most widely implemented materials are metal oxides, particularly indium tin oxide (ITO) [10]. Currently light absorbing or emitting devices *i.e.* photovoltaics (PVs) or light emitting diodes (LEDs) have the structure shown in Fig. 1a, where the functional organic thin films (<100 nm) are deposited onto mechanically supported ITO (*e.g.* glass or polyethylene terephthalate (PET) [11,12]) and device completion is by means of an evaporated metallic electrode.

To overcome the low thermal stability of typical polymer substrates/supports, such as PET, metal oxide deposition is usually carried out by sputtering processes [11,13] where high energy particles are directed toward the substrate during deposition, thus negating the requirement

for high substrate temperatures [14]. However it has been demonstrated that sputtering techniques can result in sub-surface damage of the PET, with penetration depths up to 10 nm [15]. This is deemed to be acceptable as the functionality of these substrates is transparency and mechanical support, neither of which is affected by this damage. However for the case of the thin organic layers which play an active role in the device such damage is unacceptable, as their functionality is dependent on molecular structure, ordering or orientation (*e.g.* small molecules) and the integrity of the organic/metal oxide interface must be maintained to preserve functionality (*e.g.* charge transfer). For many organic optoelectronic devices *e.g.* PVs or LEDs it has become common to deposit the functional organic materials onto a TCO electrode and subsequently evaporate a metallic electrode (Fig. 1a). This configuration results in limitations to the available processing routes and device architectures achievable for developing organic devices.

The direct deposition of low sheet resistance (R_s < 50 Ω/□) ITO onto functional organic substrates, whilst maintaining the integral properties of the organic layer and the continuity of the organic-oxide interface, remains a challenge, and as such, has not previously been demonstrated. The ability to directly deposit TCO top contacts opens a pathway to *i)* device fabrication from the metal electrode up (Fig. 1b), where the TCO may also act as an encapsulant [16], and *ii)* create semi-transparent devices if used in conjunction with a transparent bottom contact (Fig. 1c). Previously we have described the deposition of ZnO [17] and Al-doped ZnO [18] onto the well-studied conjugated polymer poly(3-hexylthiophene-2,5-diyl) (P3HT), using a modified pulsed laser deposition (PLD) technique. PLD allows highly crystalline films

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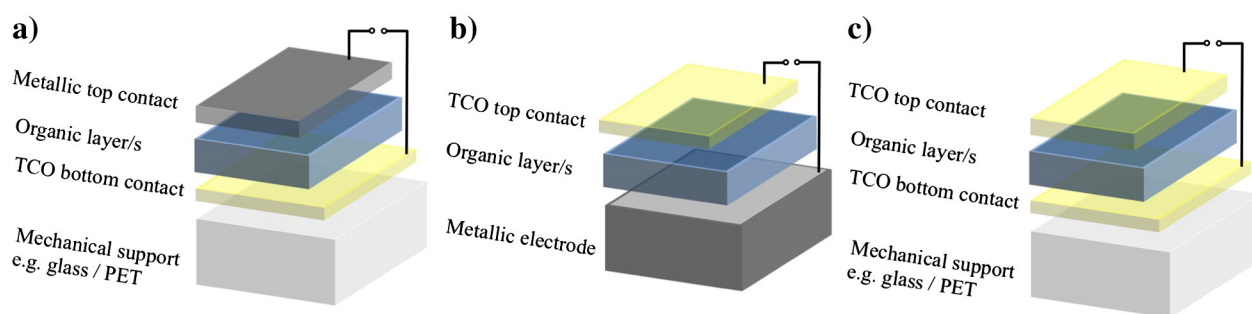


Fig. 1. Schematic illustration of various device architectures. a) Conventional device structure with metallic top contact, and b) non-typical device structure with TCO top contact and c) a semi-transparent device with an active organic layer sandwiched between two transparent electrodes.

to be deposited at low temperatures, owing to the high energy ablated particles created as the laser interacts with the target material [19]; however, these energetic species usually render PLD an inappropriate technique for oxide deposition on *soft* organic films [20]. In our modified method, background oxygen in the deposition chamber is used to control the energy of the incident particles from the PLD plume *and* the resulting oxygen content of the film, which in turn affects the electrical properties. It was found in the case of ZnO that there is a narrow deposition window in which highly crystalline, transparent films can be deposited with damage to the underlying substrate [17] and when appropriately doped with aluminum, these films are highly conducting [18]. In this work, we extend this methodology to the deposition of the widely implemented material, ITO, onto an archetypal small molecule blend of copper phthalocyanine (CuPc) and Buckminsterfullerene (C₆₀) coated onto rigid transparent substrates [21]. Despite the relatively high cost of indium, ITO remains the most common choice of TCO, owing to its favourable electronic properties. Additionally CuPc and C₆₀ have been extensively studied as electronic materials [22,23] and are well reported as small molecule solar cells [24,25]. Here, we consider this as a “*standard*” small molecule thin film system [21], analogous to other small molecule systems, such as other fullerenes [26], porphyrins & phthalocyanines [27], polyacenes [28], perylene derivatives [29] and oligothiophenes [30]—thus highlighting the wider applicability of our deposition method.

2. Experimental details

Glass substrates (12 × 12 mm) were cleaned by sequentially washing, with the aid of ultrasonics, in acetone, isopropanol and de-ionized water before drying in flowing nitrogen. CuPc and C₆₀ were evaporated in a Kurt J Lesker Spectros evaporation chamber using a typical recipe optimized for of photovoltaic device structures optimized for our organic molecular beam deposition (OMBD) system [24,31]. CuPc (97.99% Sigma Aldrich) and C₆₀ (99.0% Alfa Aesar) powders were heated to 350 °C and 480 °C respectively in alumina crucibles at a chamber pressure of $\sim 7 \times 10^{-5}$ Pa; the resultant deposition rate was ~ 1 Å/s. In this work, 3 nm of CuPc was initially evaporated followed by the co-evaporation of 25 nm of CuPc:C₆₀ (1:1 blend) followed by 5 nm C₆₀.

The ITO targets were prepared by adding 10 wt.% SnO₂ powder to 90 wt.% In₂O₃ (99.99% Sigma Aldrich). The In₂O₃ and SnO₂ powders were ball milled overnight in methanol before drying and uniaxial pressing. Green pressed targets were then sintered at 1000 °C for 10 h in air; the targets had a measured density >90%.

The CuPc:C₆₀ coated glass substrates were mounted onto a resistive heater using silver paint with the ITO targets mounted opposite at a distance of 50 mm. The chamber was evacuated to a base pressure of 3×10^{-5} Torr (4×10^{-3} Pa) and the substrates were heated to 150 °C. The temperature of the substrate heater was measured using a thermocouple embedded within it and was controlled by a Eurotherm unit maintaining set temperature ± 0.5 °C. The KrF laser (248 nm) had a pulse duration of 25 ns, and the laser energy density and

repetition rate were fixed at 1.25 J/cm² and 8 Hz respectively for all depositions. The background oxygen pressure (P_d) was then set between 0.667 Pa and 10.00 Pa (5–75 mTorr); full details can be found elsewhere [17]. In this work, the ITO target was typically exposed to 5000 pulses for thin film deposition. After the deposition the chamber was backfilled with 80 Pa oxygen and the samples were allowed to cool to room temperature.

Film morphology was assessed using a LEO Gemini 1525 field emission gun scanning electron microscope (FEG-SEM), operating at 5 kV. Cross-sections were prepared using a FEI Helios dual-beam FIB-SEM with the FIB operating at 30 kV, 5 kV and 2 kV in succession, and the SEM operating at 5 kV. Subsequent transmission electron microscope (TEM) images using a JEOL 2010 FX TEM operated at 200 kV. X-ray diffraction (XRD) measurements were performed using a PANalytical X’Pert pro MPD diffractometer equipped with an X’celerator detector using CuK α radiation ($\lambda = 1.5418$ Å), operating at 40 kV and 40 mA in conventional reflection mode. For grain size analysis the Scherrer method was used, the $K_{\alpha 2}$ contribution to full width half maximum (FWHM) was removed using X’Pert software prior to calculation. UV-Vis spectroscopy was carried out using a monochromated white light source (300–900 nm) and controlled by BenWin + software. Thickness measurements were made using a Dektak 150 stylus profilometer with a working accuracy of 0.6 nm, with measurements averaged over 5 scans.

3. Results

3.1. Fixed oxygen pressure ITO deposition

Initially, ITO was deposited onto glass substrates to study the microstructure and electrical properties. At low pressures ($0.67 < P_d < 4.7$ Pa) the films deposited were continuous and showed the characteristic surface morphology of ITO (Fig. 2a). When CuPc:C₆₀ thin films were used as substrates under these same conditions, significant delamination occurred (Fig. 2b) and the characteristic blue/green color of the organic species was missing in large areas (inset). As the pressure is increased ($4.7 < P_d < 6.67$ Pa) deposition of ITO is supported and the organic layer is preserved; however, cracking of the ITO layer is observed—which does not occur on bare glass substrates. Further increasing the pressure ($P_d > 6.67$ Pa) supports the deposition of crack free, Fig. 2c continuous ITO films on both substrates across the entire 12 × 12 mm substrate area (inset).

Whilst the initial energy of ablated species may be in the region of 100 eV, [20] collisions with molecular oxygen in the chamber result in a reduction in the energy. Increasing P_d results in increased interaction between the ablated species and the background gas; consequently the energy of the ablated species incident on the substrate is reduced [17,32]. On rigid substrates (e.g. glass), it is this high particle energy, which permits the deposition of highly crystalline films at low substrate temperature. However for easily damaged organic substrates such as small molecules described here, further consideration must be made.

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