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Utilising solution processed zirconium acetylacetonate as an electron extracting layer in both regular and inverted small molecule organic photovoltaic cells

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ABSTRACT

Interfacial layers are commonly employed in organic photovoltaic (OPV) cells in order to improve device performance. These layers must be transparent, stable, be compatible with the photo-active materials and provide efficient charge extraction with a good energetic match to the relevant organic material. In this report we demonstrate the compatibility of zirconium acetylacetonate (ZrAcac) electron extracting layers in both regular and inverted small molecule OPV cells. When the ZrAcac was processed in both air and under N_2, low work function (3.9 and 3.7 eV respectively), highly transparent layers were formed, with good energetic alignment to both C_{60} and hexachlorinated boron subphthalocyanine chloride (Cl_6-SubPc) acceptors. Initial measurements indicate similar stabilities when using the ZrAcac in either device architecture. These results indicate that the ZrAcac layer can be used as a direct replacement for the commonly used bathocuproine (BCP) in small molecule OPV cells.

1. Introduction

Organic photovoltaic (OPV) cells show great promise as a source of cheap and flexible renewable energy [1]. In recent years the performance of laboratory scale OPV cells have begun to reach the efficiencies required to consider commercialisation [2]. The incremental improvements in cell performance have been achieved through the use of new photo-active materials, cell architectures and electrodes [3–9]. However, in order to achieve the optimum cell performance for a specific photo-active system a judicious choice of the interfacial hole and electron extracting layers is also required [10,11]. The desired polarity of the cell, method and conditions of fabrication, photo-active material class and properties, and the electrodes all impact on the choice of interfacial layer. In some cases, the method of interfacial layer preparation will dictate the elected cell polarity. The requirement of high temperature annealing for some electron extracting layers is one such example, forcing the use of inverted cells to avoid damaging the organic layers [12]. Thus, a wide choice of interfacial layers are necessary to allow OPV manufacturers to match the properties required for the specific photo-active materials used in OPV cells.

A number of electron extracting materials have been employed in both polymer and small molecule based OPV cells. Reese et al. showed that low work function metals such as Ca and Ba provided a suitable contact in bulk heterojunction polymer OPV cells [13]. However, the stability of these materials is an issue. Another group of electron extracting materials are low work function metal oxides, such as TiO_x and ZnO [14,15], which have both been used in standard and inverted polymer cell architectures [14,16–18]. ZnO layers have shown versatility through fabrication using a variety of methods, including solution processing, electro-deposition and pulsed laser deposition (PLD) [18–21]. Despite this, small molecule OPV cells typically incorporate the organic material bathocuproine (BCP) as the electron extracting layer [22,23]. Rand et al. demonstrated that charge transport though BCP was facilitated by defect states within the BCP band gap, induced by hot metal penetration during deposition [22]. This indicates that BCP is only suitable for use in regular architecture small molecule cells. This limitation was confirmed by Hao et al., who reported that BCP required doping with Ag in order to obtain efficient inverted small molecule devices [24]. Additionally, BCP is also known to crystallise over time [25]. Consequently, alternative more compatible materials would be desirable for the small molecule OPV cell community.

Recently, Tan et al. utilised a zirconium acetylacetonate (ZrAcac) layer as an electron extracting layer in regular architecture polymer: fullerene bulk heterojunction OPV cells [26]. Since the layer required no subsequent processing steps and used very

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small concentrations of ZrAcac, it showed great promise for use in flexible large area polymer OPV cells. Whilst the ZrAcac layer provided efficient electron extraction for regular architecture bulk heterojunction polymer cells, the compatibility of the layer with small molecule systems, in both regular and inverted architectures, requires testing to further understand the potential widespread applications of the layer. A direct comparison of ZrAcac processed in air and under N_2 would also be beneficial, since other solution processed interfacial layers have shown that preparation conditions can significantly influence cell performance [27,28].

In this report, ZrAcac is found to be compatible for use in both regular and inverted architecture small molecule OPV cells. The ZrAcac film provides similar cell performance when spin coated from a very low concentration solution processed in air ($ZrAcac_{air}$) or under N_2 ($ZrAcac_{N2}$), indicating the versatility of the film. In each case a highly transparent, low work function layer is produced. The inverted and regular architecture cells achieve similar cell stabilities when testing under constant illumination in air. The results demonstrate that ZrAcac is an attractive alternative to the commonly used BCP in small molecule OPV cells.

2. Experimental

ZrAcac films were fabricated by making solutions of 1 mg ml^{-1} of zirconium (IV) acetylacetonate (98%, Sigma Aldrich) in isopropanol under either a N_2 atmosphere or in air, followed by spin coating at 2000 rpm. All cells were fabricated on indium tin oxide (ITO) covered glass substrates (15 Ω sq^{-1}, Thin Film Devices) in either regular or inverted architectures. All other layers were deposited using a Kurt J. Lesker Spectros system with a base pressure of 1×10^{-8} mbar. C_{60} (Nano-C Inc, 99.5%) was purified by vacuum gradient sublimation prior to deposition, whilst boron subphthalocyanine chloride (SubPc, Lumtec, 99%) and molybdenum oxide (MoO_x, Aldrich, 99.99%) were used as received. The Al cathode was deposited *in situ* through a shadow mask, giving devices with an active area of 0.16 cm^2.

The current–voltage (J–V) characteristics of the OPV cells were measured under simulated AM1.5G solar illumination at 100 mW cm^{-2} from a Newport Oriel solar simulator using a Keithley 2400 sourcemeter for current detection. The light intensity was measured using a Fraunhofer calibrated silicon photodiode (PV Measurements Inc).

UV/vis electronic absorption spectra were obtained using a Perkin-Elmer Lambda 25 spectrometer. Atomic force microscopy (AFM) images were obtained from an Asylum Research MFP-3D (Santa Barbara, USA) in AC mode, using AC240TS cantilevers. Kelvin probe (KP) measurements were used to determine the surface work function, under a N_2 atmosphere with a reference of freshly cleaved highly ordered pyrolytic graphite (HOPG). Photoluminescence measurements were taken using a Horiba FluoroLog-3 spectrofluorometer with excitation at 580 nm.

3. Results and discussion

There are several key characteristics to consider when selecting a viable electron extracting layer. The film must be highly transparent across the wavelengths that the photo-active material absorb, have a surface free of defects and pin holes, and possess a favourable energetic alignment for electron extraction from the lowest unoccupied molecular orbital (LUMO) of the organic acceptor [10,11]. Therefore, these properties were explored in the characterisation of the ZrAcac layers, before incorporation into small molecule OPV cells.

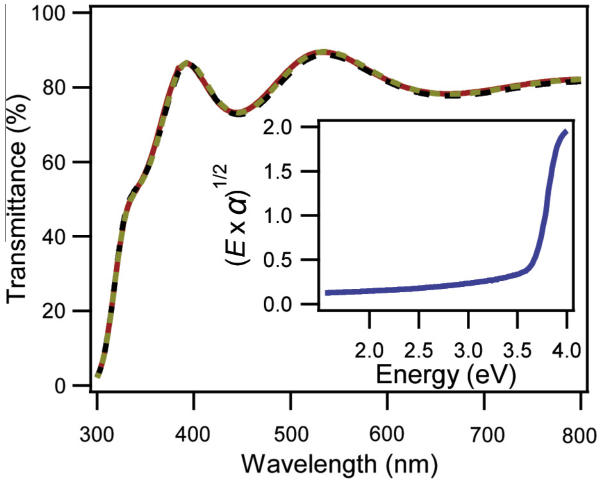

Fig. 1. Transmittance of bare ITO (gold dashed), ITO/$ZrAcac_{air}$ (black dashed) and ITO/$ZrAcac_{N2}$ (red solid). Inset: plot of $(E \times \alpha)^{1/2}$ against energy for a $ZrAcac_{air}$ layer formed on quartz using a concentrated solution (10 mg ml^{-1}), taken against a quartz background. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The transmittance spectra of bare ITO, ITO/$ZrAcac_{air}$ and ITO/$ZrAcac_{N2}$ are displayed in Fig. 1. Both methods of preparing the interfacial layers produce highly transparent films, with only very small losses in comparison to bare ITO. The inset of Fig. 1 shows a plot of $(E \times \alpha)^{1/2}$ against energy for a $ZrAcac_{air}$ layer made from a higher concentration of ZrAcac (10 mg ml^{-1}) on quartz, where E is energy in eV and α is absorbance. From this plot the band gap of $ZrAcac_{air}$ is shown to be very wide at 3.7 eV, and is the reason for the high transparency of the spin coated films between 300 and 800 nm.

The surface morphology of electron extracting layers can have a significant influence on cell performance. Since a small molecule donor/acceptor system with a total thickness of either 30 nm or 54 nm was to be fabricated onto the ZrAcac layers, smooth and homogeneous surface topographies are required so as not to create pin holes or large protruding features. The surface topographies of ITO, ITO/$ZrAcac_{air}$ and ITO/$ZrAcac_{N2}$ were obtained using an AFM in

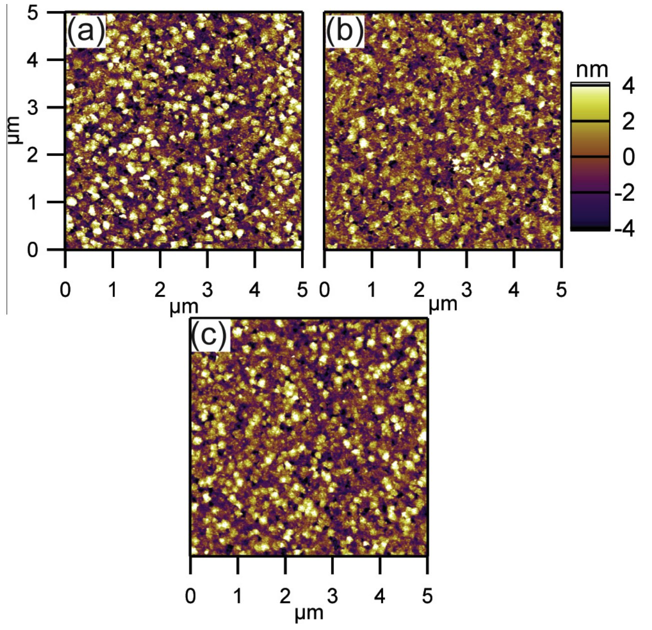

Fig. 2. 5 μm AFM topographical images of (a) bare ITO, (b) ITO/$ZrAcac_{air}$ and (c) ITO/$ZrAcac_{N2}$. All images have the same height scale (±4.05 nm).