Electrospray-deposited vanadium oxide anode interlayers for high-efficiency organic solar cells

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ABSTRACT

Spray coating, in competition with conventional spin coating, has attracted extensive attention among large-scale solution casting techniques for producing high-performance organic solar cell (OSC) devices. Solution-processed vanadium oxide (VO$_x$) is used extensively as an anode interlayer (AIL) in OSCs because of its unique optical and electronic properties. In this study, we optimized VO$_x$ AILs prepared using electrospray deposition (ESD-VO$_x$) and compared them with AILs prepared using spin coating (SC-VO$_x$); various ESD-VO$_x$ properties were found to be optimized at a flow rate of 6.25 μL/min. The OSC active layer used was poly(4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl3-   fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-bthio-phenediyl]: [6,6]phenyl-C$_{71}$-butyric acid methyl ester (PTB7:PC$_{71}$BM). The ESD-VO$_x$ devices had transmittance and surface morphology comparable to SC-VO$_x$ interlayers used in high-efficiency OSC devices. X-ray photo-electron spectroscopy indicated that the obtained ESD-VO$_x$ surfaces had a favorable chemical composition. Measurement of hole mobilities using the space charge limited current method showed values of 4.36×10^{-4} and 1.39×10^{-4} cm^2 V^{-1} s^{-1} for ESD- and SC-VO$_x$, respectively. The charge transport resistance, measured by impedance spectroscopy, was very low for ESD-VO$_x$ devices, indicating that there faster charge transportation occurs within these devices because of enhanced hole mobility. These data are consistent with the carrier life-times of 1.59×10^{-8} and 4.53×10^{-4} s for ESD- and SC-VO$_x$, respectively. The enhanced charge transportation properties, which can reduce charge recombination, can be attributed to the advantageous surface and inter-facial properties of ESD-VO$_x$ AILs. Results indicate that optimized ESD had unperturbed diode characteristics with an improved power conversion efficiency, compared to spin coated VO$_x$, of 7.61%.

1. Introduction

High power conversion efficiencies (PCEs) of up to 13% [1–3] have been realized for bulk-heterojunction organic solar cells (OSCs) through the use of cost-effective fabrication methods [4,5]. Various methods have been studied over the years as part of the search for better device performance [6–8]. Fabrication through solution processing remains one of the top priorities for commercializing and mass producing OSC devices. Although solution-processible materials have been used in the design and fabrication of OSCs, most of them are confined to conventional lab-scale coating techniques [9,10]. Many research groups have attempted to resolve this issue by using various coating techniques [11–13]. Each coating technique uniquely affects the physical and chemical properties of films, thereby influencing the overall performance of OSC devices.

Among large-scale solution casting techniques, spray coating has attracted extensive attention mainly because of its inexpensive equipment and flexibility of operation, which allows for the coating of ultrathin films. Electrospray deposition (ESD) is one of the many spray coating techniques studied for fabricating both interlayers and active layers with different device architectures [14–16]. The ESD technique has undergone rapid development in recent years, and with the application of simple optimization techniques, it can be used to produce high-quality thin films with desirable properties for OSC devices [16–20]. Another important advantage of the ESD process is the uncomplicated deposition procedure, with a reduced number of nozzles

compared to multi-source spray or inkjet printing [21,22]. Therefore, industrial fabrication costs may be reduced compared to other solution processes. In addition, charged droplets are efficiently deposited on the conductive electrode and the material loss can be reduced. Today, multilayer structures and controlled polymer ordering can be realized using ESD because of faster solvent evaporation in ESD compared to conventional spray coating techniques [23,24].

Vanadium oxide (VO_x) is used extensively in OSC devices as an anode interlayer (AIL) because of its appealing electronic and optical properties [25]. VO_x AILs are usually applied by thermal evaporation in inverted OSC devices [26], and are slowly incorporated in solution-processible form [27]. Recently, Back et al. demonstrated the ESD of VO_x functional interlayers to fabricate high-efficiency polymer solar cells with pre-patterned modular architecture [28]. Although there are reports comparing spin coating with spray coating for the deposition of AILs in OSC devices, most of the device analyses have focused on the morphological and structural differences between ESD and spin-coated (SC) films [29]. In order to realize the full potential of OSC devices fabricated using these two coating techniques, the techniques should be compared in terms of the inherent properties of the deposited AILs, such as chemical composition, charge mobility, and interfacial properties.

The deposition of solution-processed layers using the SC technique has been well established. Consequently, in this study, we investigated poly(4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl3-fluoro-2-[(2-   ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl) (PTB7): [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) devices with simple ESD-VO_x interlayers, and compared them with PTB7:$PC_{71}BM$ devices with SC-VO_x interlayers. PTB7 shows high photovoltaic performance due to its expanded absorption spectrum up to the near infrared wavelength region [30]. Also, the suitability of VO_x AIL with different coating techniques has been confirmed with PTB7 polymer donor [31,32]. Apart from the different VO_x interlayer deposition techniques, all the fabrication procedures were identical for the SC and ESD devices, including the post-deposition conditions of the AILs. Smooth morphology with an advantageous chemical environment was detected in ESD-VO_x layers using X-ray photoelectron spectroscopy (XPS). Contact angle measurements were performed to analyze the surface energy of both SC- and ESD-VO_x films. Superior hole mobility and interfacial charge transportation were recorded for ESD-VO_x OSC devices using space charge limited current (SCLC) and impedance spectroscopy measurements. Overall, devices with ESD-VO_x layers demonstrated promising results, with an enhanced PCE of 7.61% and with improved photovoltaic parameters compared to devices with fully SC-VO_x layers.

2. Experimental details

2.1. Materials and solutions

Pre-patterned indium tin oxide (ITO) glass slides were purchased from Techno Print Co. Ltd. Vanadium(V) triisopropoxide oxide (96%) (VTIPO) was purchased from Alfa Aesar. PTB7 was purchased from 1-Material Inc. and $PC_{71}BM$ was purchased from Luminescence Technology Corp. Chlorobenzene was purchased from Wako Junyaku Kogyo Co. Ltd. All materials were used without further purification.

For SC of VO_x interlayers, a 0.05 M solution of VTIPO precursor was freshly prepared by dissolving 100 μL of VTIPO in 8 mL of butanol. For ESD of VO_x interlayers, a 0.01 M solution of VTIPO precursor was freshly prepared by dissolving 20 μL of VTIPO in 8 mL of butanol. Both solutions were sealed with parafilm and stirred for 10 min at room temperature. An active layer solution was prepared by dissolving PTB7 (10 mg), $PC_{71}BM$ (15 mg), and 1,8-diiodooctane (DIO, 3 vol%) in chlorobenzene (1 mL).

2.2. Thin film deposition and device fabrication

ITO glass substrates were cleaned by ultrasonication in acetone and isopropanol followed by UV-ozone surface treatment. The 0.05 M VO_x precursor solution was deposited on the cleaned ITO substrates by spin coating at 5000 rpm for 30 s to form a 25-nm-thick film. The SC films were kept in air for 10 min before annealing at 150 °C for 5 min. The experimental setup of the ESD system is described in detail elsewhere [33]. Briefly, a 0.01 M VO_x precursor solution was loaded into a glass capillary (internal diameter 50 μm), which was fabricated using a puller (PC-100, Narishige) and a microforge (MF-830, Narishige). The glass capillary was then connected to a glass syringe placed on a syringe pump.

The main optimization parameter used for the ESD process is the flow rate of solution. At each flow rate, the applied voltage was adjusted to a value which produced a stable spray. The spray deposition time (5 min) and the distance between the capillary tip and ITO substrate were kept constant. The flow rates for ESD-VO_x AIL deposition were controlled by the syringe pump, and deposition was performed at three flow rates ranging from 6.25 to 10 μL/min. Flow rates below 6.25 μL/min and above 10 μL/min produced unstable sprays, which led to non-uniform thin films and highly wet surfaces (not shown). At each flow rate, the voltage applied between the capillary tube and a counter-electrode was optimized to obtain ESD-VO_x layers with uniform film coverage and the widest possible spray angle, as observed through a CCD camera (WAT-902B, Watec) combined with a red laser (Fig. 1(a)). The optimized voltages were 3.64, 4.17, and 4.25 kV for flow rates of 6.25, 7.5, and 10 μL/min, respectively. Most of the data collected at 6.25 μL/min gave the best results, and these data are referred to when discussing ESD-VO_x in section 3, unless otherwise noted. In addition, droplet evaporation on the substrate surface was observed using an optical microscope placed below the substrate, as shown in Fig. 1(a). The distance between the glass capillary and substrate was maintained at 6 cm to control the liquid injection speed, which is proportional to spray stability and solvent evaporation time [34]. The ESD parameters were optimized to obtain 25 nm VO_x thin films, which is consistent with the thickness of the SC films.

Devices were fabricated with an ITO/VO_x/PTB7:$PC_{71}BM$/LiF/Al structure, as shown in Fig. 1(b). After depositing VO_x layers according to the above-mentioned procedures, a PTB7:$PC_{71}BM$ blended solution was spin coated at 1000 rpm for 40 s inside a glove box. Without post-deposition annealing, the substrates were transferred to a thermal evaporator with a base pressure of 5×10^{-5} Pa to deposit a 1 nm LiF interlayer; subsequently, the devices were encapsulated within a 100 nm aluminum electrode. A mask with a designated active area of 6 mm^2 was used during the evaporation process. AIL performance was evaluated by comparing the optimized ESD-VO_x devices with the SC-VO_x devices, which were used as a reference. 6 devices were constructed for same architecture. Hole-only devices were fabricated by thermal evaporation of 5 nm molybdenum trioxide (MoO_3) and 100 nm silver layers on top of ESD- and SC-VO_x AILs to obtain an ITO/VO_x/MoO_3/Ag structure.

2.3. Characterization VO_x thin films and the OSC device performance

The surface morphology of ESD-VO_x films was analyzed using a scanning electron microscope (SEM, S-4800, Hitachi) and an atomic force microscope (AFM). AFM images were obtained using a MFP-3D Origin system in tapping mode under atmospheric conditions. An ultraviolet (UV)-visible spectrometer (V650, Jasco) was used to obtain the transmittance spectra of the films. Work function measurements were carried out in air using AC2 photoelectron spectroscopy (RKI Instruments). The surface energy of the films was estimated using a contact angle meter (Kyowa Interface Science Co. Ltd.). The thickness of the thin films was measured using a profilometer (Alpha-step IQ, KLA Tencor). The chemical environment and oxidation states were analyzed