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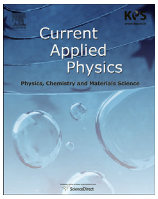

Dark currents in bulk heterojunction devices for imaging applications: The effect of a cathode interfacial layer

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ABSTRACT

While sol–gel-processed metal oxides are widely used as an electron transport layer to enhance photovoltaic performances, their effect on photodetector application was not studied. We found sol–gel-processed titanium oxide deteriorated dark current characteristics in reverse biases by almost two orders of magnitude, whereas bare Al cathodes exhibited ideal dark current characteristics. Increased dark current came from space charge limited currents in microscopic p-i-p metal-semiconductor-metal configurations. The spatial variation of workfunction values was believed to form local leakage paths by partial filling of traps on the surface of sol–gel titanium oxide.

1. Introduction

Organic photovoltaics (OPVs) have attracted much attention due to their simple structures and potential for low-cost manufacturing. The current state-of-the-art devices are known to have power conversion efficiencies (PCEs) as high as 10% in bulk-heterojunction (BHJ) devices [1], in which an active layer is formed from a blend of donor polymer and acceptor fullerene-derivative materials [2]. Recently, OPV devices are regarded as viable candidates for low-cost organic photodetectors (OPDs) because of low temperature fabrication on any substrate, such as flexible substrates or on top of silicon transistor circuitry [3–5]. Although the use of a BHJ device as an OPD appears straightforward, there are much to be considered on the device physics of the BHJ solar cells to increase signal-to-noise ratio (SNR) [6,7].

Recent advances have led to an understanding of the device behavior in OPV operations [8]: the active material is an effective p-doped semiconductor with its conduction band being substituted by electron-accepting fullerene derivatives [9], and the interfacial layers enhanced PV performance by blocking of undesired charge carriers [10] or by increasing the immunity of the internal electric field to changes in the external bias thus obtaining higher fill factor [11]. These positive effects of the interfacial layers are reported repeatedly [12,13]. However, the effects of interfacial layers on dark characteristics have not been as thoroughly studied [14], though the dark current of the devices sets the lower bound of detection limit in OPD operations [6]. In this work, we found titanium metal oxide interfacial layer increased dark current under reverse bias because the landscape of workfunction variation in sol–gel titanium metal oxide extended to space charge limited current (SCLC) regimes at specific local environment, whereas PV performance under forward bias was still increased. And we suggest a minimum condition for the reduced dark leakage current for imaging applications.

2. Materials and methods

Poly(3-hexylthiophene) (P3HT) and a soluble fullerene, [6,6]-phenyl-C60-butyric methyl ester (PCBM) were used as donor and acceptor materials, respectively. A typical device with a conventional structure was fabricated with a 180-nm-thick active layer and 40-nm functional layers of poly(3,4-ethylenedioxylthiophene):poly(styrenesulfonate) (PEDOT:PSS) as a hole transport layer (HTL) and titanium oxide (TiO_x) as an electron transport layer (ETL). The BHJ devices were fabricated as described in detail in earlier publications [10] with or without the TiO_x solution (diluted by 1:200 in methanol) spin-cast in air on top of P3HT:PCBM (5000 rpm for 40 s). The device was heated to 80 °C for 10 min in air. The BHJ cells were completed by evaporating aluminum (Al) electrodes through a shadow mask under high vacuum (10^{-6} mbar). Current density–voltage (J–V) characteristics of the unit cells were measured using a Keithley 236 Source Measure Unit under dark or Air Mass 1.5 Global (AM 1.5G) simulated solar illumination at

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100 mW cm^{-2}. The workfunctions were measured by KP6500 Digital Kelvin probe (McAllister Technical Services Co. Ltd) [15]. Kelvin probe force microscopy (KPFM, n-Tracer Nanofocus) was carried out using a Pt/Ir coated silicon cantilever tip in a dry nitrogen atmosphere to suppress contamination from moisture and oxygen [9,16].

3. Results and discussion

As previously reported, the photovoltaic performance of devices incorporating TiO_x ETL is superior to that of devices with a bare Al cathode [12], as shown in Fig. 1a. Short circuit current (J_{sc}) and fill factor (FF) are simultaneously increased. The increased current is due to an optical spacer effect that shifts the maximum absorption node to the central region of active space, and the large-bandgap metal oxide acts as a hole blocking layer at the cathode-metal interfaces [10]. The enhancement of the cathode interface by this metal oxide provides another advantage by reducing the contact resistance or forming a favorable contact as the electron flows from the active layer to the metal cathode [14]. However, these advisory effects of ETL in the photovoltaic operation do not ensure superior dark current characteristics. Fig. 1b depicts the dark currents of each device in linear and logarithmic scales. In the general diode equation, the current–voltage relationship can be treated as follows by including series- and shunt-resistance effects [17]:

$$J = J_0 \times \left[\exp\left(\frac{V - JR_S}{nV_t}\right) - 1\right] + \frac{V - JR_S}{R_{sh}} \tag{1}$$

in which J_0 is a reverse saturation current, the thermal voltage $V_t = kT/q$, R_{sh} is the shunt resistance, R_S is a series resistance, and n is an ideality factor. At forward biases greater than tens of V_t (above 0.4 V at room temperature), the currents are asymptotically linear with respect to the voltage. The increased current slope depicted in linear scale confirms that the ETL helped to improve the contact. However, under reverse biases or near the zero biases, on the contrary, the current is governed by shunt leakage, which is determined by R_{sh} in the Eq. (1). Although the simple shunt resistance picture looks quite satisfactory in linear scale, the detailed shunt resistances on a logarithmic scale are known to be nonlinear, and hard to be determined as consistent values in many different samples or different processes [18]. Dark shunt resistance is generally much larger than that of illumination because photoconductivity of active layer is main shunt leakage path under illumination condition [19]; thus, the photovoltaic operation is not severely hindered by this highly fluctuating or deviating 'dark' leakage parameter. However, solution-processed BHJ layers have recently been considered and actively adopted as next-generation photo-detectors due to their ease of processing and versatility in tuning the absorption band [4,5]. In this imaging application, dark leakage is most important because it determines the lower boundary of the detectable signal [3]. When we attempt to enhance the SNR by increasing the accumulation time of the desired signal, the dark current is also integrated; however, the amplifying circuit noise is added only one time [3]. Thus, decreasing the dark current must be a primary focus for imaging devices [20]. For example, by introducing an ETL, we can increase the photocurrent by less than 10% while operating in the PD mode as depicted in Fig. 1a, whereas the dark current increased by approximately two orders of magnitude in Fig. 1b. Thus, reducing the dark current is more important, and a bare Al electrode is better than the state-of-the-art compound cathode for PD-mode operation in BHJ devices.

To understand these dark characteristics, the absolute values of the current and voltage are plotted in Fig. 2a. The dark current of the ETL-incorporated device exhibits symmetric behavior at less than 0.2 V and has a power exponent of $\alpha \approx 1.4$, in which $|J| \approx |V|^{\alpha}$ under reverse current. In contrast, a bare Al device exhibits a shunt leakage that is asymmetric down to 0.05 V and almost two orders of magnitude smaller than that of the ETL-incorporated device; thus, with its power exponent of one, the bare Al device can be modeled using the linear shunt resistance R_{sh} in Eq. (1). As reported by Dongaonkar et al. [21], the shunt leakage in the ETL device is nonlinear and can be treated as a SCLC depending on the exponent $\alpha = \gamma + 1 > 1$, in which γ determines the trap distribution in the bandgap of the semiconducting layer [22]. Additionally, they demonstrated that the diode current can be extracted via subtraction using the symmetric feature of the SCLC shunt current [21]. This universal property remains applicable even though we used titanium oxide instead of lithium fluoride (LiF) as the ETL in our device, as shown in Fig. 2b. The subtracted, clean current–voltage relationship behaves exponentially as it approaches zero voltage. In contrast, bare Al device already exhibits clear exponential behavior and almost coincides with the subtracted clean dark current of the ETL device.

Although these high dark-shunt leakages are reportedly universal in thin-film photovoltaics, their origin has only recently been studied [18]. Inter-diffusion or pits of metal clusters that occurred during the thermal evaporation process was considered as the reason for the reduced shunt characteristics because diffused metal forms islands that acts as a shunting path by effectively decreasing the thickness [23]. It had been justified because an ETL was typically used to prevent active layers from direct contact with the metal cathodes [24]. However, this inter-diffusion is not a sufficient reason because the bare Al cathode ultimately exhibits a reduced shunt leakage, as shown in Fig. 2b. The increased shunt leakage can be attributed to the ETL itself because the dark-shunt leakage increased after we adopted TiO_x ETL in the original suppressed-shunt current device with a bare Al cathode.

A precursor solution of as-cast TiO_x is converted into a solid film via a sol–gel reaction in ambient air [10]. The sol–gel method is known to cause local inhomogeneity on the nano-scale film

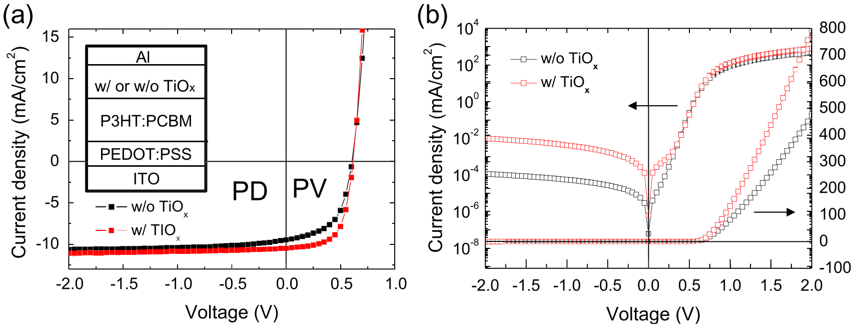

Fig. 1. Device structure and four-quadrant operation regions in a *J*–*V* curves under (a) AM 1.5G light and (b) dark conditions with linear and logarithmic scales.