Solar Energy Materials & Solar Cells 148 (2016) 39–43

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Thickness-dependence of S-shaped *J–V* curves of planar heterojunction organic solar cells containing NTCDA interlayer: Impedance–potential measurement and underlying mechanism

Jinpeng Tian, Chuanxi Zhao, Mingxiao Wu, Weiguang Xie, Wenjie Mai, Pengyi Liu *

Department of Physics, Siyuan Laboratory, Jinan University, 510632, China

ARTICLE INFO

Article history:
Received 6 April 2015
Received in revised form
7 September 2015
Accepted 17 September 2015
Available online 21 October 2015

Keywords:
Organic solar cells
Planar heterojunction
S-kink
NTCDA
Impedance

ABSTRACT

We present the thickness-dependence of the performance of planar heterojunction organic solar cells (OSCs) with 1,4,5,8-napthalene-tetracarboxylic-dianhydride (NTCDA) as interlayer between rubrene/C_{70}. The S-shaped current–voltage (*J–V*) characteristic is observed in the optimization process of NTCDA thickness. With the increase of NTCDA thickness, device performance first increases then decreases, with the optimum thickness of 15 nm. The observed thickness-dependence of S-kink is totally different from previous reports of BCP based OSCs. The anomalous *J–V* characteristics were investigated by using the impedance–potential technique. We find that larger impedance occurred in the device with thinner NTCDA interlayer, and the mechanism could be described by charge distribution between the interface of C_{70} and Al cathode. Finally, we propose an effective approach to eliminate the S-kink in *J–V* curves by postannealing processes.

1. Introduction

Since the last decade, organic solar cells (OSCs) have received much attention due to their outstanding properties, such as low cost, light weight, good flexibility, and easy fabrication [1]. The power conversion efficiency (PCE) has been improved steadily from 2% in 2002 and to over 12% today by using new materials or interfaces modification [2]. One of the important strategy to improve PCE of OSCs is to deposit a buffer layer between cathode and the organic acceptor materials [3]. The inserted buffer layer not only protects the acceptor material from unintentional damage of post-deposited cathode, but also provides an effective electron transport layer and exciton blocking layer [4]. Various materials have been employed to modify the interface between acceptor and cathode. For example, bathocuproine (BCP) [5], 1,3,5-tris(2-N-phenylbenzimidazolyl)benzene (TPBI) [6], and Bphen have shown a promising performance in the OCSs device [7]. However, these materials are conductive only in the presence of damage trap states induced by postmetal-deposition. In addition, the thickness is limited to less than 10 nm, which may be hard for optimizing the maximum optical field intensity in the active layer [8]. Furthermore, S-shaped *J–V* curves were observed when employing BCP as buffer layer in OSCs device [9]. The anomalous *J–V* curve is detrimental to the device performance due to the decrease of V_{OC} and fill factor (FF), even J_{SC}. In previous studies of planar heterojunctions, the reason is usually ascribed to charge accumulation at interface [9], the high resistance to the injection current [10], imbalanced mobilities [11], hole-transport limitation [12] and interfacial barriers [13]. Although the exact reason for S-kinks in *J–V* curves might be different from each other, the essential reason is the changed distribution of electric field inside the device caused by charge accumulation [14].

The S-shaped *J–V* curves of BCP buffer layer in OSCs would be appeared by gradually increasing their thickness, which are attributed to the charge accumulation effect [9]. However, in our study, we found an opposite evolution of S-shaped *J–V* curves with that of NTCDA interlayer thickness, namely, the S-kink *J–V* curve is appearing by gradually decreasing the NTCDA thickness. Understanding the origin of the S-shaped *J–V* characteristics observed in the NTCDA is essential to design efficient OSCs. Therefore, it is of great importance to figure out the role of NTCDA in S-shaped *J–V* curves. The reason behind S-shaped effect is theoretically proposed by bias-voltage-dependent photocurrent recombination [15]. However, it has not been characterized by the bias-voltage-dependent technique (eg. impedance potential technique) except for scanning Kelvin probe measurement [16]. In this work, we focus on investigating the origin of S-shaped *J–V* curves in Rubrene/C_{70} planar heterojunction OSCs. By the impedance–potential technique, the underlying reason is discussed. Finally, a

* Corresponding author. Tel.: +86 2085224802; fax: +86 2085220233.
E-mail address: tlpy@jnu.edu.cn (P. Liu).

http://dx.doi.org/10.1016/j.solmat.2015.09.032
0927-0248/

following annealing approach is proposed to effectively eliminate the S-kink in *J*–*V* curves.

2. Experimental details

In our planar heterojunction OSCs, MoO_3 (99%), rubrene (99%), C_{70} (99%) and NTCDA (99%) were used as received without further purification. Indium-tin-oxide (ITO) coated glass substrates (10 Ω/ □, 180 nm thick) were etched with hydrochloric acid (HCl) to form the desired patterns. Then it was cleaned subsequently by ultrasonic bath in acetone, ethanol and isopropanol for 15 min. Afterwards, it was dried out under nitrogen flow, and the substrates were transferred into a vacuum chamber. The organic materials were deposited successively onto ITO substrates using thermal evaporation under a pressure of 1×10^{-3} Pa at a deposition rate of 0.06–0.1 nm/s, and Al cathode was deposited under a pressure of 3×10^{-3} Pa at a rate of 0.6–4 nm/s. An oscillating quartz crystal monitor (INFICON XTM/2) was used to determine film thickness and the deposition rate. The active area of the fabricated device was 0.3 cm^2. In the work, all the other parameters of the devices were kept identical except the thicknesses of the NTCDA layers. In order to eliminate S-shaped *J*–*V* curves, all the devices were subjected to the postannealing process, which consists of rising the temperature of the hot plate from 50 °C to 200 °C in seven steps during 210 min approximately (30 min at 50 °C, 30 min at 75 °C and so on). The thermal treatment was carried out until the S-shaped *J*–*V* curve was completely removed. After each annealing, samples were cooled down to room temperature before measuring the *J*–*V* curve. The *J*–*V* characteristics of the OSCs were measured using a source meter (Keithley 2400) and calibrated using Si reference solar cell under an illumination of 100 mW/cm^2 produced by an AM 1.5G sunlight source (ABET Technologies Sun 2000 simulator). The impedance–potential characteristic was measured by an electrochemical workstation (Chenhua, CHI 660D) at a frequency of 1000 Hz. Incident photon conversion efficiency (IPCE) was determined by employing QE-R-3018 (Enli Technology Co. Ltd). All the measurements were carried out in the atmospheric environment without any encapsulation.

3. Results and discussion

Fig. 1(a) and (b) shows the schematic of typical device structure and diagram of energy levels of planar heterojunction OSCs [17], respectively. By varying the thickness of NTCDA interlayer (*X*), the efficiency of electron injection from cathode to acceptor could be tuned. Fig. 2 shows the typical *J*–*V* curves of the OSCs device with 0 and 15 nm thick NTCDA buffer layer under an illumination power of 100 mW/cm^2. In the absence of NTCDA interlayer, the device has a PCE of 0.5%, and J_{SC} of 1.44 mA/cm^2. However, in the presence of 15 nm NTCDA interlayer, the PCE and J_{SC} of device exhibits a clear increase to 0.96% and 2.9 mA/cm^2, respectively. The series resistance could be determined from *J*–*V* curves and the values are calculated to be 104 for pristine device and 74.2 Ω cm^2 for device with NTCDA interlayer, respectively. It is well known that metal–organic contact has two typical interface: ohmic or blocking contact [18]. Generally, a blocking contact is formed between the organic and Al film interface. The blocking contact would cause large series resistance, which is disadvantageous for performance of photovoltaic devices. The decrease of the series resistance demonstrates that the NTCDA interlayer could effectively improve the electron transportation and collection.

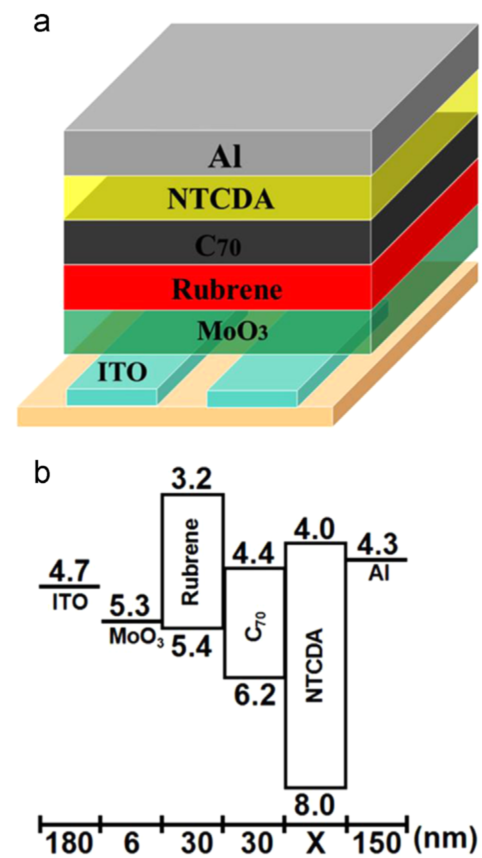

Fig. 1. The schematic diagram of a typical device structure of planar heterojunction OSCs and the schematic diagram of energy levels.

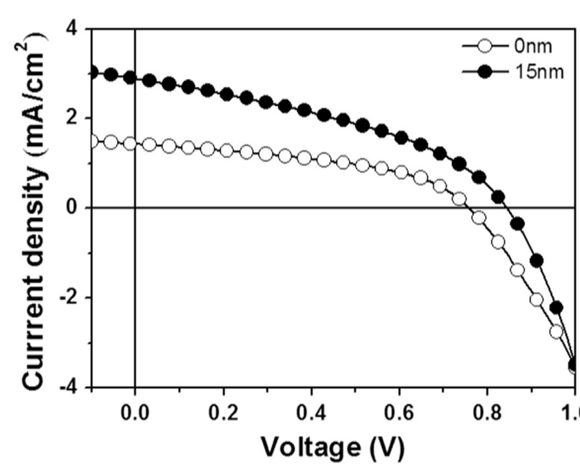

Fig. 2. The *J*–*V* curves of devices under AM 1.5G in air: with 15 nm (solid circle) and without NTCDA (open circle).

It has been reported that V_{OC} of OSCs could be empirically estimated according to the following relationship [19]

$$V_{oc} = \frac{1}{q}\left(E_{donor}^{HOMO} - E_{acceptor}^{LUMO}\right) \tag{1}$$

where q is the elementary charge e, E_{donor}^{HOMO} is the HOMO level of the donor and $E_{acceptor}^{LUMO}$ means the LUMO level of the acceptor. The V_{OC} is expected to be 1.0 V for rubrene/C_{70} heterojunction from the energy diagram of OSCs. However, in the device condition, it shows a clear decrease by 24% (0.76 V) and 16% (0.84 V) for the device without and with NTCDA interlayer, respectively. The NTCDA interlayer accounts for a favorable energy band alignment,