Organic Electronics 39 (2016) 77–84

Contents lists available at ScienceDirect

Organic Electronics

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

Charge trapping in doped organic Zener diodes

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ARTICLE INFO

Article history:
Received 2 August 2016
Received in revised form
19 September 2016
Accepted 24 September 2016

Keywords:
Organic Zener diodes
p-i-n junction
Charge trapping
Molecular doping
Mott-Schottky relation

ABSTRACT

Understanding charge trapping in organic semiconductors is key to the development of highly efficient organic devices. Here, charge trapping in organic *p-i-n* Zener diodes is studied and an analytical model able to describe the influence of the trapped charges on the electrical performance is proposed. The model shows a good agreement with the experiment and allows quantifying the density of trapped charges and the molecular doping efficiency from capacitance spectroscopy of systematically stressed devices. This work is expected to provide a platform to understand and quantify charge trapping in organic electronic devices, especially two-terminal *p-i-n* devices such as organic light-emitting diodes and organic solar cells.

1. Introduction

Recent progress in the field of organic semiconductors has led to highly efficient organic light emitting diodes (OLEDs) [1] and organic solar cells (OSCs) [2], which allowed for the commercialization of OLEDs in the form of displays used in handheld devices or TV sets. Some of the most efficient devices use the *p-i-n* structure consisting of a *p*-doped layer, an intrinsic layer, and an *n*-doped layer. These organic *p-i-n* structures have not only been extensively adopted for OLEDs [3,4], OSCs [5], but as well for promising new device concepts such as organic light-emitting transistors [6], ultra-high-frequency organic diodes [7], or organic Zener diodes [8]. Most of these *p-i-n* structures use molecular *n*- or *p*-dopants to generate Ohmic contacts to corresponding electrodes, enhance charge transport, and thus inject charges efficiently into the intrinsic layer [9]. Although numerous studies on molecular doping have been published [8,10,11], the fundamental physical mechanisms of doping have not been completely explored yet. In particular, it was shown that trap states in the molecular layer dominate the doping effect at low doping concentrations and limit the overall doping efficiency [12,13].

Not only the doped layers, but the intrinsic layer as well has a significant influence on the characteristic of the *p-i-n* structure. Most intrinsic organic semiconductors show a significant density of trap states at the interface or in the bulk. Filling these undesirable charge traps leads to a space charge region that not only does not contribute to the current, but even electrostatically opposes charge transport [14,15]. Thus, it is of particular significance to develop a comprehensive understanding of charge trapping in organic semiconductors in order to realize stable and reliable *p-i-n* devices.

In this context, much efforts have been devoted to the investigation of charge trapping in a wide range of organic devices, for example, OLEDs [16,17], OSCs [18–21], and Schottky diodes [22,23]. In most of these studies, traps states were characterized by frequency dependent capacitance or impedance spectroscopy and a comparison to numerical modeling. To deduce the density of trapped charge carriers, the capacitance spectra is fitted by elaborated models, which sometimes depend on a drift-diffusion simulation of the organic device. Furthermore, a Gaussian distribution of trap states and Boltzmann statistics are often assumed [21,22]. Unfortunately, due to the large number of unknown parameters such as the effective charge transport level and the precise shape of density of states of the trap states, extraction of trap parameters from these models is arduous and can lead to ambiguous results.

To avoid this ambiguity and simplify trap analysis in organic *p-i-n* diodes, we propose a new approach to systematically study charge trapping and the influence of the trapped charges on the

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http://dx.doi.org/10.1016/j.orgel.2016.09.023
1566-1199/

electric characteristics of organic *p-i-n* Zener diodes. A novel bias stress protocol is developed to reliably quantify trapping. Furthermore, an analytical model based on an adapted Mott-Schottky analysis is introduced, which is capable of explaining the experimental results obtained on organic *p-i-n* junctions consistently without numerical simulation. Abnormally large built-in potentials or open-circuit voltages, often obtained when using the classical Mott-Schottky model, can be avoided by our analysis. Based on our model, we are able to determine the effective molecular doping concentrations and the density of trapped charges.

2. Experiment

The glass substrates are cleaned using acetone, methanol, and isopropyl alcohol in sequence and rinsed by deionized water. In the *p*- and *n*-doped layers, the host material 2,2,7,7-tetrakis-(*N*,*N*-dimethylphenylamino)-9,9-spiro-bifluorene (Spiro-TTB) (50 nm) is doped with the *p*-dopant 2,2-(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F_6-TCNNQ) at 4 wt%, and 2,9-bis(naphthalen-2-yl)-4,7-diphenyl-1,10-phenanthroline (NBphen) (50 nm) is doped with the *n*-dopant tetrakis(1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinato)ditungsten(II) ($W_2(hpp)_4$) at 5 or 10 wt%, respectively. Spiro-TTB, F_6-TCNNQ, and NBphen are purchased from Lumtec Corp., Taiwan, and $W_2(hpp)_4$ is synthesized by Prof. S. D. Bunge as described in our unpublished study [24]. All materials are used as provided without further purification.

The host materials and the dopants are thermally co-evaporated. Doping concentration is determined by controlling the evaporation rates of the hosts and the dopants individually monitored with two quartz crystal microbalances. The intrinsic layer of NBphen (8 or 12 nm) is positioned between the *p*- and *n*-doped layers. The aluminum anode and cathode contacts (both 50 nm) are prepared as the corresponding electrodes to *p*- and *n*-doped layers, respectively. All layers are deposited by thermal evaporation in a single vacuum chamber (Angstrom Engineering Inc.) at a base pressure of 5×10^{-8} Torr, and structured by shadow masks. The effective device area is 2×2 mm^2.

Both the capacitance-voltage and the current-voltage characteristics are measured using a semiconductor parameter analyzer (Keithley 4200-SCS). The capacitance-voltage sweep is performed at a modulation amplitude of 20 mV (root mean square voltage) and at a frequency of 5 kHz. The bias stress at each voltage is applied for 20 min, and the current values are extracted every 10 s during stressing. The stressing voltage is varied from −6 to −11 V with a step of −1 V. All electrical measurements are performed in a glovebox with the nitrogen environment at room temperature.

3. Results and discussion

3.1. Organic Zener diodes design

An energy level diagram of the organic Zener diodes is schematically illustrated in the inset of Fig. 1(a). In the *p*-doped layer, electrons are spontaneously transferred from the highest occupied molecular orbital (HOMO) of host material Spiro-TTB (4.9 eV [25]) to the lowest unoccupied molecular orbital (LUMO) of *p*-dopant F_6-TCNNQ (5.4 eV [26]). Similarly, the LUMO of the host NBphen (3.2 eV [27]) lies below the HOMO of the *n*-dopant $W_2(hpp)_4$ (2.4 eV [26]) so that the host molecules accept electrons from the dopant molecules, forming an *n*-doped layer. The *n*-type host material NBphen also serves as an intrinsic interlayer, and thus a homojunction is formed at the interface in contact with an *n*-doped layer, whereas the heterojunction is formed at the other side as depicted in the inset of Fig. 1(a).

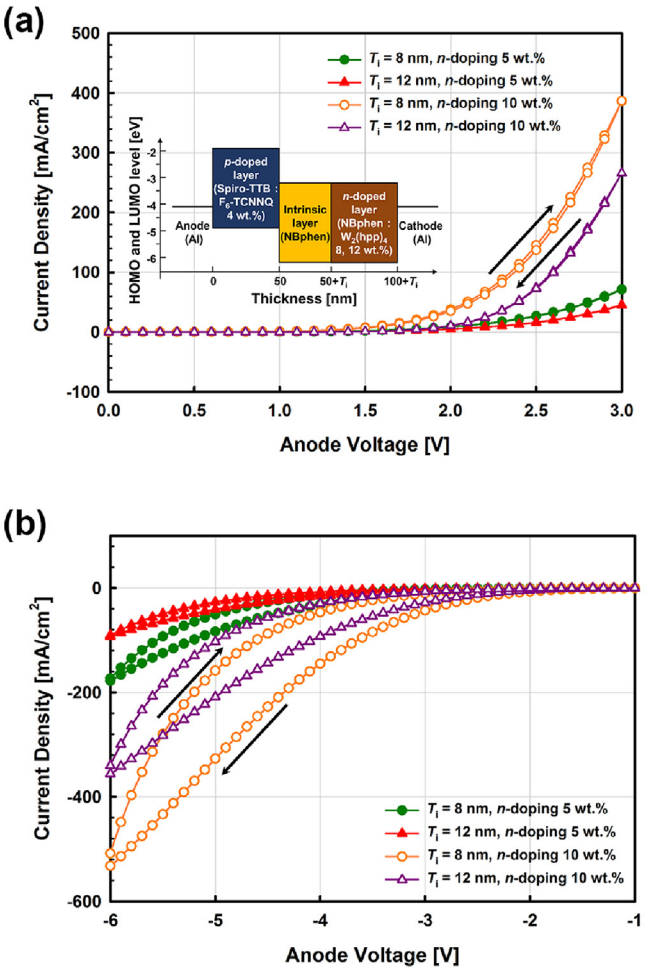

Fig. 1. Current density-voltage characteristics under (a) forward bias and (b) reverse bias for different thickness of the intrinsic layer, 8 nm (circle) and 12 nm (triangle) and different *n*-doping ratio, 5 wt% (closed symbols) and 10 wt% (open symbols). The inset of (a) illustrates an energy level diagram of organic *p-i-n* Zener diodes consisting of a *p*-doped layer, an intrinsic layer (T_i denotes the thickness), and an *n*-doped layer.

3.2. Experimental results

3.2.1. Current-voltage characteristic

In Fig. 1(a) and (b) the current-voltage characteristics under both forward bias and reverse bias of four types of organic Zener diodes fabricated with varied thickness of intrinsic layer T_i and *n*-doping ratio are shown. The *p-i-n* diodes clearly exhibit Zener diode behavior: breakdown occurs at reverse bias, and the breakdown voltage V_{BD} increases for thicker intrinsic layers and lower doping concentrations. The breakdown at reverse voltage was explained by Kleemann et al. by (Zener)-tunneling from the HOMO state to the LUMO state of neighboring molecules in the intrinsic layer (see process (a) in Fig. 4) [8,28]. Increasing the intrinsic layer thickness decreases the electric field inside the intrinsic layer, i.e. tunneling sets in later and the breakdown voltage increases. In forward direction, the current density decreases with increasing thickness of the intrinsic layer and decreasing doping concentration. The decrease in current with decreasing doping concentration can be explained by an increase in the depletion layer thickness, which increases the overall resistance of the junction. To study charge trapping, the anode voltage is scanned in both directions, i.e., starting from 0 V to positive or negative direction, and then back again to 0 V.