Organic Electronics 14 (2013) 193–199

Contents lists available at SciVerse ScienceDirect

Organic Electronics

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

Reverse breakdown behavior in organic pin-diodes comprising C60 and pentacene: Experiment and theory

H. Kleemann [a,*], R. Gutierrez [b], S. Avdoshenko [b], G. Cuniberti [b], K. Leo [a], B. Lüssem [a]

[a] Institut für Angewandte Photophysik, Technische Universität Dresden, 01069 Dresden, Germany
[b] Institute for Materials Science and Max Bergmann Center of Biomaterials, Technische Universität Dresden, 01062 Dresden, Germany

ARTICLE INFO

Article history:
Received 13 March 2012
Received in revised form 1 November 2012
Accepted 1 November 2012
Available online 17 November 2012

Keywords:
Organic semiconductors
Organic pin-diodes
Reverse breakdown
Tunneling
Zener-diodes

ABSTRACT

Charge carrier transport under reverse voltage conditions is of major relevance in devices like organic photo-detectors, organic solar cells (tandem cells), organic light emitting diodes (generation contacts), and organic Zener diodes. We present organic pin-diodes comprising molecular doped layers of pentacene and C60 with an adjustable and reversible reverse breakdown behavior. We discuss the electric field and temperature dependence of the breakdown mechanism and propose a coherent charge transport scenario to describe the experimental findings. Within this model a field assisted tunneling of charge carriers over a rather large distance from valence to conductance states (and vice versa) governs the breakdown behavior. This is in accordance to experimental observations where charge carriers can overcome a layer thickness of 110 nm in the breakdown regime.

1. Introduction

Charge transport mechanisms in reverse biased inorganic semiconductor diodes are well-understood and devices such as Zener diodes, avalanche diodes, and thyristors make use of them [1,2]. Proposed mechanisms are the coherent Zener tunneling and the incoherent avalanche breakdown. Both mechanisms are distinguishable by their electric field dependence and their temperature coefficient. However, little work has been done to understand the underlying mechanisms of charge carrier transport in organic semiconductor devices [3,4]. Experimental and theoretical investigations on these effects in amorphous and polycrystalline organic semiconductor materials are challenging since these materials typically exhibit at room temperature no band-like transport. Charge carrier transport occurs via a hopping mechanism between spatially and energetically distributed states, denoted as highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMOs) for holes and electrons, respectively. Thus, the energetic and structural disorder in such system requires a theoretical description that takes this complex situation for charge carrier transport into account. Moreover, to address the reverse transport phenomena by experiment, a precise control of the local electric field is indispensable to disclose the field-driven nature of reverse breakdown mechanisms.

In this contribution, we report on organic Zener diodes comprising a polycrystalline intrinsic layer of pentacene sandwiched between molecularly doped hole and electron transport layers of pentacene and C60, respectively. In particular, we show a precisely adjustable reverse breakdown up to −20 V without any influence to the forward direction. This control of reverse breakdown is possible since the field inside the pin-junction can be directly addressed by the thickness of the intrinsic interlayer. We have recently demonstrated organic Zener diodes with a precisely adjustable reverse voltage breakdown. These devices, however, contain low mobility materials resulting in low current densities and long transit times, which makes them partially inappropriate for some electronic applications,

* Corresponding author.
E-mail address: hans.kleemann@iapp.de (H. Kleemann).

1566-1199/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.orgel.2012.11.001

e.g. as rectification diodes working in the ultra-high-frequency (UHF) region. In the present work, substantial differences of the reverse breakdown mechanism in comparison to [4] are obtained. In particular, rather large distances for charge carrier transport in reverse direction are observed. This significant difference to the previous study (distances <10 nm) can partially be attributed to the difference in energy levels of the materials. However, as we will point out, caused by the polycrystalline nature of the intrinsic interlayer of pentacene, the breakdown condition is predominantly affected by layer morphology and interface formation. This effect is shown for nip- and pin-diodes where we demonstrate that the effective tunneling barrier width (given by the interlayer thickness) is strongly affected by the layer sequence. This leads to the fact that the breakdown voltage of nip-diodes is almost doubled in comparison to pin-devices for the same interlayer thickness.

Besides these experimental investigations, we develop and discuss a theoretical model to provide a first insight into possible mechanisms of charge carrier transport under reverse voltage conditions. As starting point a coupling scenario that accounts for HOMO–LUMO level interaction of nearest and next nearest neighbor sites is considered. Owing to the small degree of static disorder within a pentacene grain, we employ a coherent charge transport model which can describe the experimental findings concerning voltage and interlayer thickness dependence.

In the present study we have chosen C60 and pentacene since they are favorable candidates for future electronic devices due to their rather high mobility in the field of organic semiconductors. In this context, the control of reverse charge transport as reported here is of particular importance to balance forward and reverse current in order to design organic diodes working up to the GHz regime [5–7].

2. Experimental and theoretical model

2.1. Sample preparation

The devices are prepared on cleaned (ultrasonic treatment in acetone, ethanol, and isopropanol for 5 min and ozone plasma etching) glass substrates by thermal evaporation of metals and organic materials under high-vacuum conditions (base pressure $<10^{-5}$ Pa) without breaking the vacuum. The organic layers are sandwiched between a bottom contact (aluminum, thickness 50 nm) and a top contact (aluminum, thickness 100 nm) structured by deposition through a shadow mask (see Fig. 1a). Therefore, the active area is defined by the overlap of both contacts, which is 6.38 mm^2. The evaporation conditions and sequences of the organic hole transport layer (HTL), the intrinsic interlayer (IIL), and the electron transport layer (ETL) can be taken from the captions of the individual figures. The thicknesses and deposition rates are measured by quartz crystal monitoring (QCM). The pentacene rate is kept constant at 0.2 nm/s, while C60 is deposited with a rate of 0.05 nm/s. The material F6-TCNNQ (2,2-(perfluoronaphthalene-2,6-diylidene) dimalononitrile) is used as an effective p-type dopant for pentacene [8], while the n-type doping of the C60 can be achieved by co-evaporation of C60 and the material $W_2(hpp)_4$ (tetra-kis (1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidinato) ditungsten (II)). For p- as well as for n-type doping, free charge carriers are provided to the matrix material by charge transfer from the dopant molecule. For electronic characterization a Keithley 2400 SMU is used for current–voltage (I–V) investigations. All samples are measured in dark.

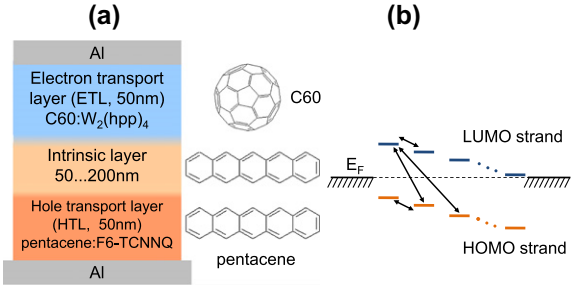

Fig. 1. (a) Illustration of the layer sequence of an organic pin-diode as used within this work and a sketch of the charge transport materials pentacene and C60. (b) Energy level diagram of a pin-diode including different coupling contributions according to Eq. (1).

2.2. Minimal model

A first-principle description of the electronic structure of the active part (intrinsic interlayer) of the device as well as of the charge migration in such a system represents a very strong challenge from the modeling point of view. Hence, the use of minimal models catching some basic physical ingredients of the system can strongly help to provide a first insight into the electrical response of the system. The model we are envisioning consists of an electronic tight-binding ladder with N sites arranged along a linear chain and describing the active device region. Each site contains two energy levels $\epsilon_j^s(V)$ whose energetic position is determined not only by the intrinsic electronic structure of the molecular unit to which they belong, but also by the built-in field and by the applied bias. In a first approximation, we will consider only the HOMO and LUMO electronic states of each molecular unit as relevant for the following discussion and allow for electronic coupling not only along HOMO and LUMO pathways (lower and upper strands, see Fig. 1b), but also cross-terms providing communication between, e.g. the HOMO on molecule j and the LUMO on molecule $j+1$. In general, the precise spatial ordering of the molecular building blocks in the experiments is not fully known, but it should have roughly the structure of a two-dimensional network. To mimic this 2D arrangement within the linear chain topology, our model will also include next nearest neighbor interactions.

The Hamilton operator for the proposed tight-binding model reads (see also [4]):