Organic Electronics 25 (2015) 112–120

Contents lists available at ScienceDirect

Organic Electronics

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

New insights on traps states in organic semiconductor applying illumination-free transient current method

Hippolyte Hirwa *, Veit Wagner

School of Engineering and Science, Jacobs University Bremen, D-28759 Bremen, Germany

ARTICLE INFO

Article history:
Received 26 January 2015
Received in revised form 15 June 2015
Accepted 15 June 2015
Available online 16 June 2015

Keywords:
Transient current
Density of states
Traps
Capture time
Attempt-to-escape frequency
Metal–insulator–semiconductor capacitor

ABSTRACT

A transient current measurement technique which does not need light stimulus is developed. This illumination-free transient current (IFTC) technique offers insights on trapping states characteristics such as the capture time of the trapping states, their density of states (DOS) and the attempt-to-escape frequency of trapped carriers. For the analysis of IFTC measurements carried out on metal–insulator–semiconductor (MIS) capacitors, numerical simulation of the transient current were performed as a way around usual assumptions of short transit times which can considerably distort the values from transient current measurements. A combination of experimental data and simulations revealed the need to take into account retrapping events in order to extract the correct band tail density of states and corresponding characteristic parameters. An exponential density of states with a total density of $4 \cdot 10^{23}$ m^{-3} and a width of 50 meV was found to be representative of the band tail of spin-coated poly(3-hexylthiophene) (P3HT). A broader exponential distribution with a width of 83 meV is extracted for the interface states towards SiO_2. Using a multiple trap and release model, the capturing time and the attempt-to-escape frequency of the band tail states were found to be 10^{-10} s and 10^{8} s^{-1}, respectively. With this technique, we are able to also pinpoint the energy position of the Fermi level relative to the transport energy level.

1. Introduction

The first applications of organic field effect transistors (OFETs) in e-paper displays, simple integrated circuits, and chemical and biological sensors have been recently demonstrated [1–4]. Even with OFETs making their path to real applications, understanding charge transport in these disordered materials is still not fully achieved.

A crucial obstacle to the full understanding of charge transport in organic semiconductor based devices is the characterization of the band tail states responsible of the charge transport in organic semiconductor devices. In fact, the main obstacle to high mobilities in organic semiconductors is the slowing down of charge carriers due to hopping and/or trapping of charge carriers in the band tail states [5]. These trapping states are not only characterized by their density but also by their capture and emission times. Therefore a better future for organic electronics requires tools to quantify all parameters relevant for charge transport properties in all environments. In order to obtain information on the trapping process in organic semiconductor based thin films several methods have recently attracted attention or are commonly in use. Deep level transient spectroscopy (DLTS) [6], thermally stimulated current (TSC) [7], photo-excited charge collection spectroscopy [8], impedance spectroscopy (IS) [9,10], transient photocurrent spectroscopy (TPC) [11] and time-of-flight (TOF) method [12] have been used with partially satisfactory results. The first three methods are rather complex and often inadequate for organic semiconductors due to the involvement of bias and temperature stress for DLTS and TSC and light stress for photo-excited charge collection spectroscopy. Though, the latter two methods offer several advantages from the simplicity of the measurements to the wide range of accessible information on the semiconductor properties, they still have their limitations. For IS, the need of complex equivalent circuits for the analysis restrains the accessible information for the band tail characterization [13]. TPC and TOF use a structure with a semiconductor sandwiched between two metal contacts and additionally requires light illumination, a parameter known to be a source of instability due to its potential doping effect on some organic semiconductors [14]. For TOF measurements the layer thickness must be much larger than the exciting light penetration depth, which is often much thicker than in device structures. In this paper, TPC and TOF methods were modified so that light illumination is avoided. The device of choice is a MIS capacitor. The use of a MIS capacitor opens new doors with a modified illumination-free transient current (IFTC) measurement technique.

* Corresponding author.

http://dx.doi.org/10.1016/j.orgel.2015.06.025
1566-1199/

In this new transient current measurement approach, the charge carriers packet to be transported is created at the semiconductor–insulator interface and transported through the semiconductor layer upon applying a bias step function. The transport of charge carriers through the semiconductor layer can be analyzed and subsequently reveals information on the physical properties of the interfaces and the bulk of the semiconductor.

In this paper, we provide a full description of transient current measurements carried out on organic semiconductor based MIS capacitors. The analysis shines light on crucial physical properties of the band tail states such as the density of states, the capture time associated to these trapping states and the attempt to jump frequency of a trapped carrier. Section 2describes the experimental details. In Section 3we provide a numerical model for transient current measurements simulation. In Section 4we present the experimental results according to the theoretical background developed in Section 3.

2. Experiment

A highly n-doped silicon (Si) wafer (resistivity = 2 mΩcm) with a 100 nm thick thermally grown silicon oxide (SiO_2) was used as substrate for the MIS capacitor (Fig. 1). The highly n-doped Si serves as gate and SiO_2 as insulating gate dielectric. The substrate was first wet chemically cleaned in an ultrasonic bath with solvents (acetone, isopropylacetate) and treated in an ozone cleaner for 10 min. A 170 nm thick poly(3-hexylthiophene) (P3HT) (Sepiolid-P100, Rieke Metals, regioregularity ~95%, average molecular weight $M_w = 5 \times 10^4$ g/mol) layer was then spin coated onto the cleaned substrate from a 1.5 wt.% chloroform solution. The top contact of the MIS capacitor was made by sputtering a 100 nm thick top ohmic gold (Au) contact onto the semiconductor.

The transient current measurements setup is shown in Fig. 1. As the setup reveals, a step bias function is applied on the gate terminal of the MIS capacitor, subsequently creating a charge carrier packet. The created packet of carriers moves across the semiconductor layer inducing a time dependent current. This current is measured through the load resistance (R_{Load}) with a 100 MHz bandwidth digital oscilloscope. As the measured transient current decreases with time, in order to extend the measurements time range and still be able to measure low currents, the load resistance was varied between 10 Ω and 100 kΩ. A time span of 10 ns to 100 ms could be obtained. The capacitive effect of the device produces a short RC time constant that was included in the measurements analysis. Depending on the load resistance, the RC time constant ranges from 10 ns to 100 μs. The step function was generated by a Keithley 3390 function generator. The effectively applied voltage to the MIS structure was verified using the second channel of the oscilloscope (not shown in Fig. 1). 64 discrete events were averaged to increase the 12-bit resolution of the oscilloscope. The time interval between two successive pulses was set to 10 s and for each series of pulses the background current was recorded and then subtracted from the obtained transient current.

Temperature dependent measurements were carried out in a cryostat with the sample mounted in vacuum on a cold-finger and cooled down with a closed loop liquid Helium supply.

3. Theoretical description

3.1. Time of flight (TOF) and transient photocurrent (TPC) measurements

Our approach is a modification of the usually used time of flight (TOF) and transient photocurrent (TPC) techniques. TPC and TOF measurements are widely used to measure the mobility μ and the density of band gap states (DOS) in amorphous inorganic and organic semiconductors [11,15]. In TOF measurements, a thin sheet of charge carriers is photogenerated close to the contact, while one

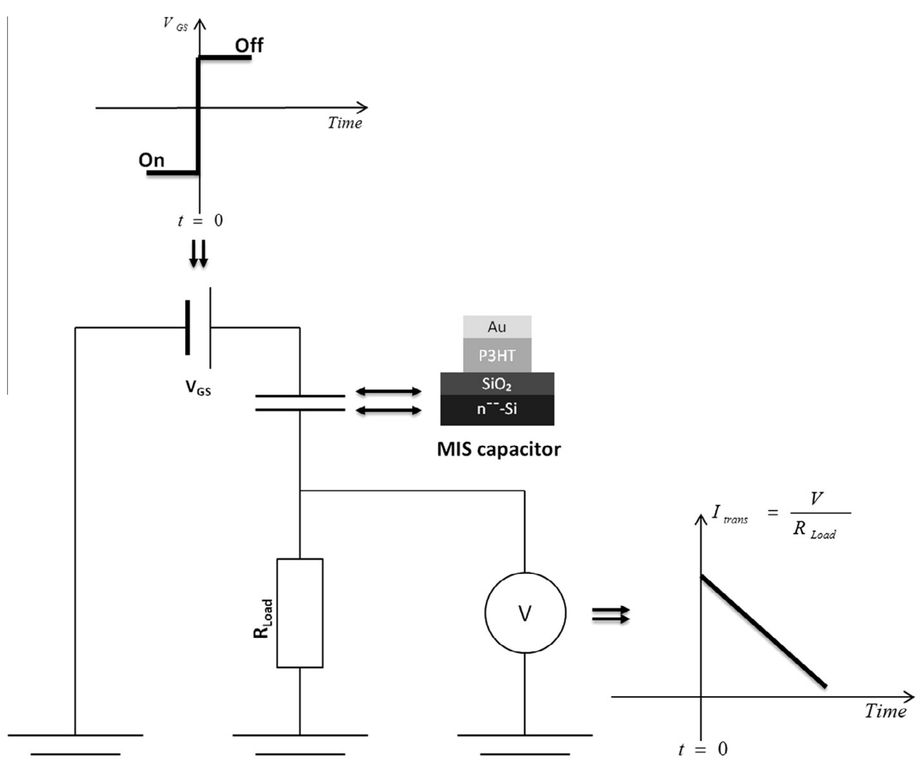

Fig. 1. The setup used for transient current measurements is shown together with a step function applied on the MIS capacitor and the current measured across the load resistance.