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Detection of a contact barrier by a temperature-modulated space-charge-limited current technique

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The possibility of the detection of a pre-contact barrier is demonstrated for an example of a sandwich ITO|MEH-PPV|Al structure. Between the ITO electrode and the poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene] (MEH-PPV) a contact barrier is formed. The barrier detection is based on the temperature-modulated space-charge-limited current method (TM-SCLC). It consists of simultaneous measurements of the current-voltage characteristic and the activation energy of the current as a function of the voltage. The increase of the activation energy with applied voltage clearly indicates the barrier occurrence. The barrier height can be reduced by the application of a poly[3,4-(ethylenedioxy)thiophene] (PEDOT) interlayer, deposited between the ITO and MEH-PPV film. This leads an increase in the current by more than four orders of magnitude.

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1. Introduction

There is a growing interest in organic semiconductors for electronic applications, as solar cells, electroluminescent diodes, rectifying devices and field-effect transistors.

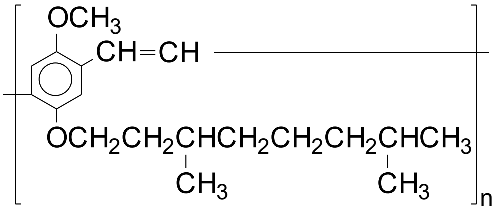


Fig. 1. Chemical structure of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene-vinylene].

Poly[2-metoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene-vinylene] (MEH-PPV) (Fig. 1) is a typical conjugated polymeric photoconductor, with a wide band-gap and an absorption maximum at about 470 nm. Charge transport occurs mainly via distributed hopping [1] transport states. MEH-PPV also exhibits remarkable electroluminescence [2] and is investigated for potential applications in the field of electroluminescent [3] panels and solar cells [4]. The electrode quality plays an important role in both applications,, especially from the point of view of charge injection, separation and exciton "quenching". There are several techniques for the testing of electrode quality in semiconductor devices. Among them, the temperature-modulated space-charge-limited current (TM-SCLC) technique plays an important role. The method is based on simultaneous measurements of the dependencies of the electrical current (*I*) and its activation energy (E_a) on the applied voltage (*U*). The existence of a electrode barrier can be detected from the increase of the activation energy with applied voltage [5].

This paper is demonstrates, for a ITO|MEH-PPV|Al sandwich structure, how the pre-contact barrier can be detected using the TM-SCLC technique.

2. Experimental details

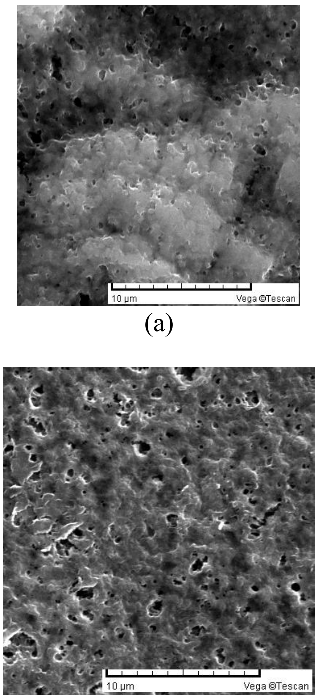
MEH-PPV powder (Aldrich Chemicals, M_w = 2×10^5 g mol^{-1}, M_n = 7×10^4 g mol^{-1}, calibrated using polystyrene standards in THF) was dissolved in a mixture of chloroform and toluene in the ratio of 1:1. The films were deposited from solution (0.0125 mg/ml) by a spin-coating (2750 rpm) procedure onto the ITO electrode. Samples were also deposited in the same way on glass substrates for film thickness control and optical measurements. After the deposition, the samples were heated to 70°C, to remove the residual solvent from the film. Finally, a top Al electrode was vacuum evaporated under a pressure of 10^{-3} Pa. The typical film thickness was 500 nm.

In some samples, a poly[3,4-(ethylenedioxy) thiophene] (PEDOT) interlayer between the ITO and MEH-PPV was used to alleviate the effect of the work function imbalance (and subsequent barrier formation). The PEDOT film was deposited in a one-step procedure [6] by spin-coating from the pre-polymer.

The pre-polymer was prepared in situ by oxidative polymerization of 3,4-(ethylendioxy)thiophene and methyl methacrylate, in the presence of iron(III) tosylate as an oxidant and a mixture of *N*-methylpyrrolidone, ethanol, isopropyl alcohol and butyl alcohol as solvents, at room temperature. Conductive PEDOT films are usually prepared by a two-step procedure [7]. The solubility problem was subsequently suppressed by using a water-soluble poly-electrolyte, sulphonated polystyrene (PSS), as the charge-balancing dopant in the polymerization to yield the PEDOT-PSS system [8]. Here, we present a new simple one-step synthetic route. Figure 2a shows the SEM pattern for a PEDOT layer. The films were prepared by dipping in prepolymerized solutions consisting of a monomer and oxidant in the ratio 1 : 1. The typical film thickness was 7 μm.

The deposited films were kept for 24 h in air, to complete the polymerization process. Then, the un-reacted remainder of the material was removed by washing in ethanol. The SEM pattern for the sample washed in ethanol is presented in Fig. 2b. The pattern shows the ethanol-insoluble phase of the films, which is disordered, quite homogeneous, but less conductive. During this procedure, the film thickness was reduced 10 times. Finally, conductive and transparent PEDOT films of thickness about 50 nm were obtained.

The *I-U* characteristics were measured with a computer controlled Keithly 617 electrometer in a vacuum of 10^{-4} Pa at 295 K The E_a-U characteristics were measured for each applied voltage changing the temperature in the interval 295 – 301 K. This small temperature change reduced the error caused by the temperature statistical shift of the Fermi level position E_F. Thus, only E_F shift caused by the applied voltage was taken into account.



(a)

(b)

Fig. 2. SEM patterns of PEDOT. An as-prepared film (a) and a film washed in ethanol (b).

3. Results and discussion

In Fig. 3, TM-SCLC characteristics, i.e., *I* vs. *U* and E_a vs. *U* are presented. The sublinear form of the current-voltage characteristic changes to a superlinear one at about 0.7 V. The dependence can be linearized in the ln *I* vs. $U^{0.5}$ coordinates, as follows from Fig. 4. At the same time, the activation energy of the current strongly decreases. The increase in E_a was observed in the voltage interval 6 – 8 V. For voltages higher than 9 V, an E_a decrease with applied voltage was observed again. The current in this region (U > 9 V) was influenced by space-charge injection: I – U characteristic was strongly superlinear, and activation energy decreased with increasing voltage. The transport properties are influenced by the sample bulk, and the influence of the contact barrier is eliminated. Note, that electroluminescence was observed for voltages higher than 9 V.

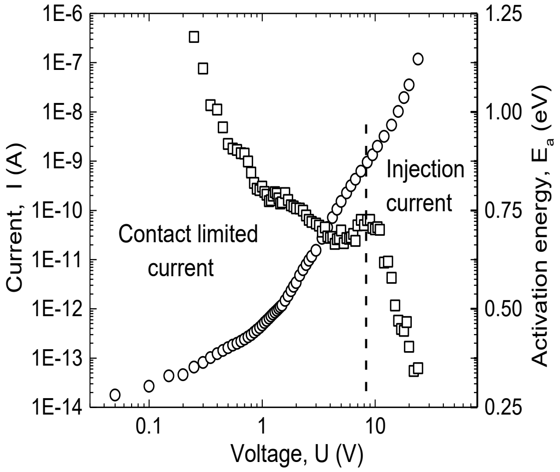


Fig. 3. Experimental TM-SCLC characteristics.

The current in the barrier region can be described by the Schottky equation [9,10]

$$J = A^{*}T^{2}\exp\left(-\frac{\phi}{kT}\right)\exp\left(\frac{\beta U^{1/2}}{kTL^{1/2}}\right) \qquad (1)$$

where $A^{*} = 1.2 \times 10^{-6}$ Am^{-2} is the Richardson constant, T is the absolute temperature, k is the Boltzmann constant, ϕ is the Schottky barrier height at the injecting electrode interface, e is the elementary charge, L is the sample thickness, $\beta_s = (e^3/4\pi\varepsilon_0\varepsilon)^{1/2}$ is the Schottky field-lowering coefficient and $\varepsilon_0\varepsilon$ is the electric permittivity.

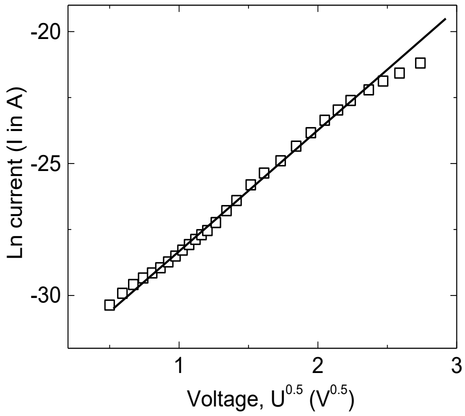


Fig. 4. Dependence of ln I on $U^{0.5}$.

The experimental value of the Schottky coefficient obtained from Fig. 4 was found to be 3.5×10^{-5} eV $(\text{mV}^{-1})^{0.5}$, which is close to the theoretical value (2.4×10^{-5} eV $(\text{mV}^{-1})^{0.5}$). A little higher experimental value of β coefficient follows probably from the fact that the entire film thickness is not depleted. From the dependence of the activation energy of the current on the voltage (see Fig. 3), it follows that the Schottky barrier height is about 1.2 eV. Thus, we believe that at low voltages the current in our structure is contact limited.

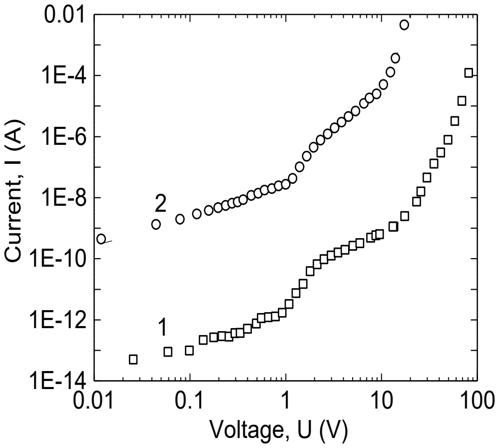


Fig. 5. Current voltage characteristics of:
1 – ITO|MEH-PPV|Al and
2 – ITO|PEDOT|MEH-PPV|Al structures.

To decrease the pre-contact barrier, the PEDOT interlayer was applied between the ITO electrode and the MEH-PPV film. The current increased by more than 4 orders of magnitude, as follows from Fig. 5. The influence of the higher work function φ of the PEDOT layer is clearly visible (cf. φ_{ITO} = 4.2 eV and φ_{PEDOT} = 5.7 eV, as obtained by the UPS technique. Note that MEH-PPV is a p-type semiconductor.

4. Conclusion

A contact barrier, which makes the electrical current contact limited, can be detected using the dependence of the activation energy of the current on the applied voltage. At the voltage at which the activation energy increases, the influence of the contact barrier is reduced and the sample bulk properties prevail. This was demonstrated on a sandwich structure of ITO|MEH-PPV|Al. The advantage of this method is that if current-voltage characteristics are studied, that the formation of the contact barrier is visible directly, without any preparation of new samples such as in the case of, e.g., application of the scaling law [11]. To overcome the barrier, a PEDOT interlayer, influencing the work function of the ITO electrode, can be applied. It was observed that in this case the current increases by several orders of magnitude.

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