Studies of Transport Properties of Single Layer Devices Based on the Polyazomethine Thin Films

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This work reports results of studies on transport properties of single-layer devices based on polyazomethine thin films with different metal electrodes. Recorded $I-V$ characteristics of Au–PPI–Au and Au–PPI–Al structures were analyzed in detail. It appears that $I-V$ characteristics of Au–PPI–Au structures are consistent with the Mott–Gurney law with the mobility value of $2 \times 10^{-6}$ cm$^2$/Vs. Relatively low current in Au–PPI–Al devices is attributed to high value of the Schottky barrier and/or due to low density of longer conjugated segments in polyazomethine thin films.

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1. Introduction

Organic semiconductors (OS) have been known since many years for their great potential applications in optoelectronic devices. Among the conjugated polymers, poly(p-phenylenevinylene) (PPV) and its derivatives (like MEH-PPV) belong to the family of more extensively studied OSs and are known as revealing good properties for optoelectronic applications [1–3]. Poly(p-phenyleneazomethine) (PPI), much less known and studied polymer than PPV, being its isoelectronic counterpart and having nearly the same electronic structure, though containing nitrogen atoms in the backbone, has appeared to be very promising for optoelectronic applications, too [3–5]. The aim of this work is to study transport properties on single layer devices based on the polyazomethine thin films. For this purpose, a series of single layer structures have been prepared with different metal electrodes and their current–voltage characteristics analysed.

Charge transport in amorphous organic semiconductors is characterised by the localisation of electronic states to individual molecules and disorder in the position and energy levels of these molecules. As a result, charge transport occurs via thermally activated hops with a mobility typically increased with both electric field and temperature [6–8]. Additionally, transport strongly depends on the contact type at a metal–organic semiconductor interface. For Ohmic contacts the charges transport is the space-charge limited (SCL). Otherwise, the charge transport over an interfacial barrier at a metal–semiconductor interface is analyzed using one of two theories. For very large barriers or at low temperatures, electron tunneling has been thought to dominate, while injection being thermally activated, thermionic emission over the barrier is predominant [9].

Among technological problems the most important issues in evaluating properties and usefulness of a given material for photovoltaic applications, there are substrate preparation, deposition of organic thin films and metallic contacts. For this purpose, it is convenient to gather and analyse results on such relatively simple structures as single layer devices. To verify quality of the as-prepared devices, current–voltage characteristics have been taken and analysed in terms of the unified device model for single layer organic light emitting diodes or photovoltaic cells with charge injection, transport and space charge effects [9]. The model describes both injection and space charge limited current flows and the transition between them.

2. Device preparation and measurements details

Single layer devices have been prepared by chemical vapour deposition (CVD) method in a home-made technological setup [5]. Polyazomethine 100 nm thick films were grown via polycondensation process of aromatic diame ine and dialdehyde and sandwiched between metal electrodes with different work functions. The choice of the electrodes has appeared to influence greatly the device properties, so that various pairs of electrode materials were used from indium tin oxide (ITO), Al and Au to check practically conditions of the Schottky barrier formation and their applicability for photovoltaic devices. Metallic electrodes were thermally evaporated under vacuum of $10^{-6}$ Tr, otherwise glass substrates covered with
ITO layer were used. The processes of structure preparation consist of substrate and bottom electrode preparation, deposition of organic film by CVD or spin coating method, then post deposition thermal treatment and finally deposition of a metal top electrode. \( I - V \) characteristics were taken with the use of Keithley electrometer.

3. \( I - V \) characteristics, results and discussion

From all single layer devices prepared, the better \( I - V \) characteristics have been obtained on Au–PPI–Au and Au–PPI–Al structures. While ITO was a bottom electrode material, data were frequently more scattered, thus more difficult to interpretation. Structures with gold as the top electrode were more frequently short circuited.

Exemplary current–voltage (\( I - V \)) characteristics on Au–PPI–Au and Au–PPI–Al single layer devices presented in Figs. 1 and 2, respectively, clearly demonstrate different type of carrier conductions. Relatively large carrier density and symmetric \( I - V \) characteristics for the Au–PPI–Au structure differs significantly in the current density magnitude from Au–PPI–Al asymmetric \( I - V \) characteristics. The former structure is suggested to reveal the space charge limited character with current voltage characteristic consistent with the Mott–Gurney law [10–13]

\[
J = \frac{9}{8} \varepsilon \varepsilon_0 \mu V^2 \quad \text{(1)}
\]

where \( \mu \) and \( \varepsilon \) are mobility and dielectric constant of the material, \( \varepsilon_0 \) is the permittivity of vacuum, \( d \) is the distance between the contacts, and \( V \) is the applied voltage [13].

\[ \varepsilon \mu = 6 \times 10^{-6} \text{ cm}^2/(\text{V} \text{s}) \]

Fig. 1. Current–voltage dependence for 100 nm thick Au–PPI–Au device (symbols). Solid line represents the fitting to a square dependence \( J = \text{const} \times V^2 \) with \( \text{const} = 60 \mu \text{A}/(\text{V}^2 \text{ cm}^2) \).

In Fig. 1 we show \( I - V \) characteristics for the Au–PPI–Au structure, symbols, together with a one parameter fit to the Mott–Gurney law, solid line. The square-law dependence on applied voltage is satisfactory fulfilled in the range \(-0.5 \text{ to } 0.5 \text{ V} \). Departure from \( V^2 \) law is observed for higher voltage. The fitting quantity is the product of dielectric constant and hole mobility \( \varepsilon \mu \) of metal electrodes as well as the parameter \( n_0 \), which describes the density of conjugated chain segments times the number of ways that a chain segment can be occupied by an electron or hole i.e. its degeneracy. Ad-
ditionally, within the model a field dependent mobility is incorporated and described within two phenomenological parameters, $\mu_0$ and $E_0$.

Application of the model to PPV, and thus to PPI, is greatly simplified as due to energy levels alignment the device should be practically the only hole conducting, in particular the energy barrier to electron injection is about 1.4 eV, while the barrier for hole injection being treated as a fitting parameter. Applying the model, we have initially assumed the same material parameters as for PPV $n_0 = 10^{19} \cdots 10^{21}$ cm$^{-3}$, $\mu_0 = 1.7 \times 10^{-6}$ cm$^2$/(Vs), $E_0 = 10^5$ V/cm) and then made necessary adjustment to fit the experimental data. In this manner we have determined for our device: the barrier height $\phi = 0.716$ eV, $n_0 = 10^{18}$ cm$^{-3}$, $\mu_0 = 1.05 \times 10^{-6}$ cm$^2$/(Vs) and $E_0 = 1.2 \times 10^4$ V/cm. Calculated with this set of parameters I–V characteristics, solid lines, at $T = 25$ and 90°C, are compared with experimental data (symbols) in Fig. 2. As can be seen, an overall agreement is acceptable, although not perfect. In order to estimate contributions from thermionic and tunnelling currents to the measured device current, we have plotted also in Fig. 2 only thermionic current, dashed lines. Comparison reveals that at room temperature the almost whole current has tunnelling origin, whereas at 90°C the thermionic emission current dominates.

4. Conclusions

Several important conclusions follow from the above analysis. Firstly, determined value of the parameter $n_0$ for Au–PPI–Al is about one order of magnitude below the lowest value reported for PPV. This indicates low density of conjugated segments in this particular structure. This finding in conjunction with a large value of the barrier height suggests that only short PPI chains appeared close to Au electrode and/or that postdeposition annealing was not effective for this device. This conclusion is also consistent with common knowledge that the energy gap decreases with an increased oligomer dimension. Our investigation on Au–PPI–Au structure reveals that its I–V characteristic is consistent with the Mott–Gurney law and the mobility determined in PPI thin films is $2 \times 10^{-6}$ cm$^2$/(Vs), which is of the same order of magnitude as in PPV.

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References