

INTERFACE CHARACTERIZATION OF PPV – DERIVATIVE BASED STRUCTURES BY DIRECT CURRENT ELECTRICAL MEASUREMENTS

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Polyphenylenevinylene derivative (PPV – D) based structures with Ohmic and Schottky electrodes have been produced and investigated by direct current–voltage (I-V) measurements. Polymer solutions with different solvent concentrations are prepared and dependence of the film thickness on the amount of solvent is established. It was found that in structures of type Au/PPV-D/Al Ohmic electrodes are formed, whereas ITO/PPV-D/Al samples behave as Schottky diodes. Schottky barrier of 0.2 eV at the ITO/PPV-D interface (anode) was established. Dependence of the conductivity in Au/PPV-D/Al samples on the PPV-D film thickness was found. It shows that bulk conditions dominate the conductivity process rather than contact limited processes. The slope of the I-V characteristics increases linearly decreasing the film thickness. Measurement of 100 nm thick Au/PPV-D/Al samples differs from the linear dependence. It could be referred to a double charge carrier injection from both electrodes. The results obtained are basic point to a further electrode optimization of organic based light emitting diode and solar cell structures.

Keywords: Organic/metal interface; Ohmic and SCLC conductivity; Polymer based diodes.

1. INTRODUCTION

Organic materials have been recently investigated due to their potential applications in microelectronic and optoelectronic devices, such as organic thin film transistors (OTFTs), organic solar cells [1, 2] and organic light emitting diodes (OLEDs) [3]. The low-cost and easy processing by various techniques as sol-gel, spin-coating and ink-jet printing is the main reason for it. However some basic concepts concerning important electrical characteristics of the organic based electronic devices are not completely understood. Among them charge injection through the electrode/polymer interfaces and bulk transport inside the polymeric layer are the most important processes that determine good device performance.

Partially in OLEDs, the charge carriers injected from the electrodes and the recombination process controlled by the traps predominantly determine the device efficiency. The charge carrier injection strongly depends on the type of the injecting electrode (Ohmic, Shottky). In case of Ohmic contacts at higher voltages, the current is limited by space-charge formed in the bulk of the polymeric layer, whereas a Shottky contact determines contact limited current. There are proposed models for current–voltage behavior in OLEDs based on both space charge limited current [4]

and Schottky barrier effect [5] as well. The type of the electrode depends on the mutual position of the work function of the electrode and the corresponding transport

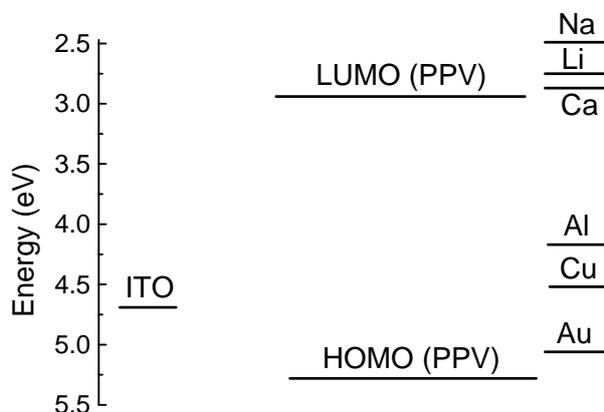


Fig. 1. Energies of MEH-PPV HOMO and LUMO orbitals together with the work functions of metals potentially used as electrodes.

(valence or conductive) band. In Fig. 1 [6-8] energy position of HOMO (valence) and LUMO (conduction) bands of MEH-PPV are plotted together with the work functions of materials proper for electrodes. Gold is a preferable anode material which forms Ohmic contact with good injecting properties. Unfortunately transparent Au electrodes with high conductivity are difficult to prepare. ITO electrode exhibits high transparency but forms an electrode barrier of 0.48 eV with the MEH-PPV semiconductor. Choosing electron-injecting material is even more difficult. Several proper metals

as Na, Li, Ca have the disadvantage of high chemical activity. They produce oxides or chemical compounds with the semiconductor in use. Among them aluminum is relatively stable but forms contact barrier for electrons of 1.23 eV. Similar behavior should be expected for polyphenylenevinylene derivative (PPV – D) under investigation. The electrode optimization is a key point in organic microelectronic and optoelectronic device production.

This article aims to investigate electrode behavior with respect to PPV-D semiconductor. Two types of experiments are implemented. The influence of – (i) the anode material and (ii) the film thickness of the active polymer semiconductor on the electrical properties of the prepared structures is investigated.

2. EXPERIMENTAL DETAILS

Samples consist of polymer active layer “sandwiched” between two electrodes (ITO or Au and Al) as shown in Fig 2. Two types of structures are prepared – one which ITO anode is used for and another one with Au anode. The bottom ITO electrode was deposited by magnetron sputtering following a procedure explained elsewhere [9]. Au electrode is thermally deposited in vacuum from molybdenum crucible. The organic material is copolymer consisting of conjugated fragments of PPV chains connected by aliphatic segments [10]. Polymer layers were spin-

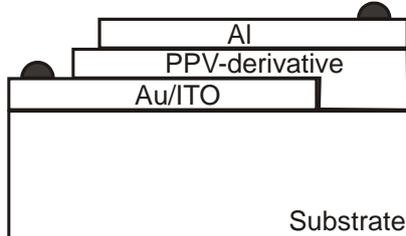


Fig. 2. Schematic draw of the “sandwich” type sample used for electrical measurements.

coated on the substrate. The Au electrode is thermally deposited in vacuum from molybdenum crucible. The organic material is copolymer consisting of conjugated fragments of PPV chains connected by aliphatic segments [10]. Polymer layers were spin-

coated at various rotation speeds and different chloroform concentrations to achieve a range of film thickness.

The initial solution concentration is 0.8 mg/ml and after every deposition 0.25 ml solvent was added. The film thicknesses were measured with Talystep thickness profilometer on films deposited at the same conditions on glass substrates. Thicknesses obtained are in the range of 100 - 1800 nm. Top electrodes for the electrical measurements were deposited in vacuum of 1×10^{-5} Torr by thermal evaporation of Al through a mask. *I-V* characteristics were measured in vacuum of 1×10^{-5} Torr by computer controlled Keithley 617 electrometer.

3. RESULTS AND DISCUSSION

Dependence of the film thickness from the amount of the solvent in the solution is presented on Fig. 3. The measured data are approximated with exponential dependence. Such results could be expected depositing from solutions, which behaves as Newtonian fluids [11]. Similar dependencies found in the literature are

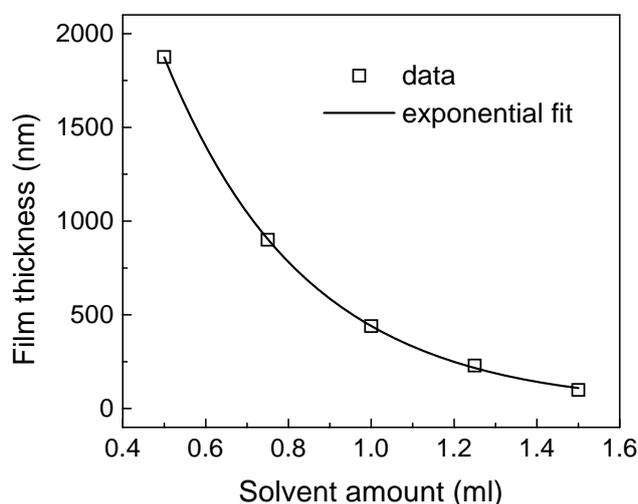


Fig. 3. Polymer film thickness obtained at different solvent amounts

associated with the solution viscosity and the rotation speed [12]. These factors may be nearly independent of the type of polymer used as long as flat films are produced. It was found that diluted solutions required higher rotation speed to be applied. Varying the rotation speed for a given solvent concentration an optimum value could be found. Rotating with lower speed leads to a piling of material on the substrate periphery. Higher rotation speeds produced films with decreasing thickness from the center to the periphery.

These results could be used for future preparation of thin PPV based films with defined parameters.

I-V characteristic measured in Au|PPV-D|Al structure is presented in Fig. 4. In the range 0,01V to 0,1V the current measured is proportional to the voltage applied (Ohmic behavior). It shows that the Au|PPV-D electrode barrier is negligible.

In the range 0,1V to 1V the characteristic show a clear defined region with slope of two ($I \sim U^2$). This could be related to charge carrier bulk injection in trap-free case.

At higher voltages (above 1 V) strong increase of the slope is observed. It could be connected with trap influence or a beginning of double charge carrier injection from both electrodes.

The influence of the barrier for electrons at PPV-D|Al electrode is not observed. The last could be explained with the p-type behavior of the PPV-D material, where holes are majority charge carriers.

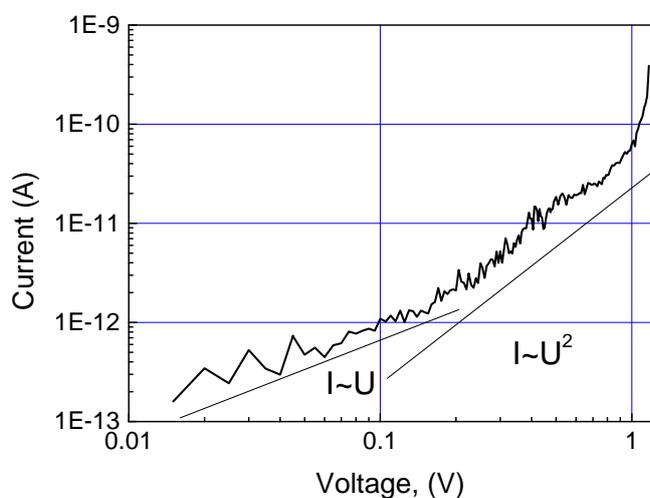


Fig. 4. *I-V* characteristic measured on Au|PPV-D|Al sample.

film thickness. This could be connected with a current flowing under SCLC conditions in a presence of traps. The higher slope obtained from samples with 100 nm thick films did not follow the linear dependence of the other data. It could be connected with an influence of double charge carrier injection from both of electrodes. Samples with Au electrodes are proper for electrical measurements

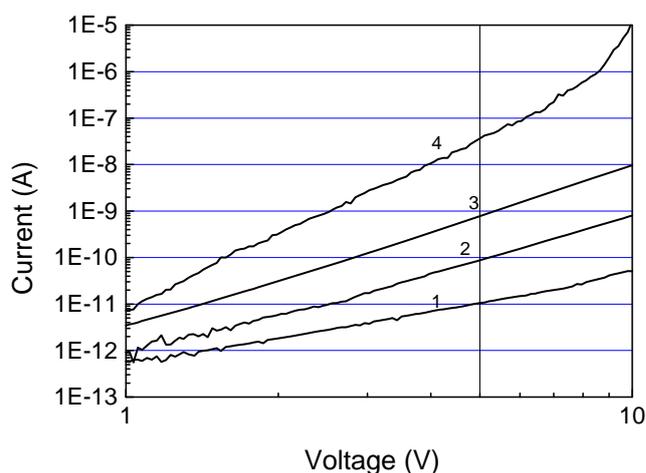


Fig. 5. *I-V* characteristics measured from samples Au|PPV-D|Al with different PPV-D film thicknesses: 1 – 1800, 2 – 900, 3 – 440, 4 – 100 nm

On Fig. 5 *I-V* characteristics of Au/PPV/Al samples with different polymer thicknesses are plotted. It was found that decreasing the film thickness leads to an increase of the film conductivity. This result confirms that in Au/PPV/Al samples bulk conditions dominate the conductivity process rather than contact limited processes. This is a clear indication that Ohmic contacts are formed.

The dependence of the slope of the *I-V* characteristic on the film thickness is plotted in Fig. 6. The slopes of curve increase linearly from 2 to 3.5 with decreasing the investigation of organic molecular devices.

For a practical use as solar cell or OLED one of the electrode must be transparent to ensure the irradiation of PPV-D with the light. In Fig. 7 *I-V* characteristic measured in ITO|PPV-D|Al structure with transparent ITO anode is shown. Plotting in log-log scale it could be seen that barrier of about 0.2 eV is formed. The barrier is related to the difference between the ITO work function and the PPV-D HOMO band. For seek of clarification the

sign of the negative current below 0.2 V is changed. The negative current values are

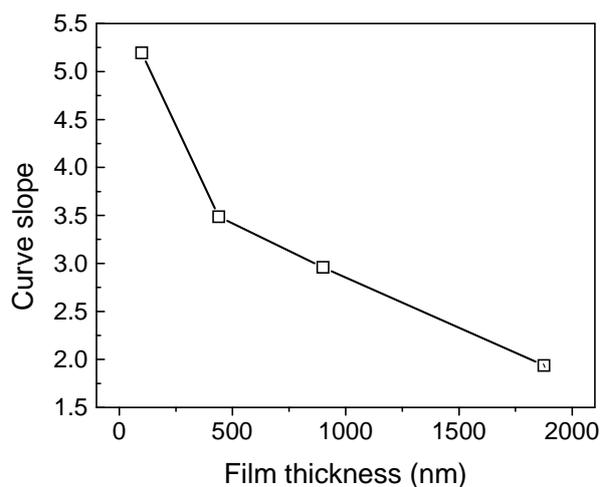


Fig. 6. Dependence of the curve slope on the film thickness in Au|PPV-D|Al samples

related to a separation of thermally generated on the electrode barrier charge carriers. On the inset of Fig. 7 the same data are plotted in linear scale. The shape of the curve could be related to a Schottky junction polarized in forward direction.

4. CONCLUSION

The conditions for PPV-D spin coating are optimized so that thin films with controllable and reproducible thicknesses are produced. “Sandwich” Au(ITO)|PPV-D|Al samples for electrical measurements were constructed. Measurements of structures with Au electrodes at low

voltages show typical Ohmic region. Increasing the voltage the current is limited by space charge. Such behavior is a clear indication of Ohmic contacts formed at the

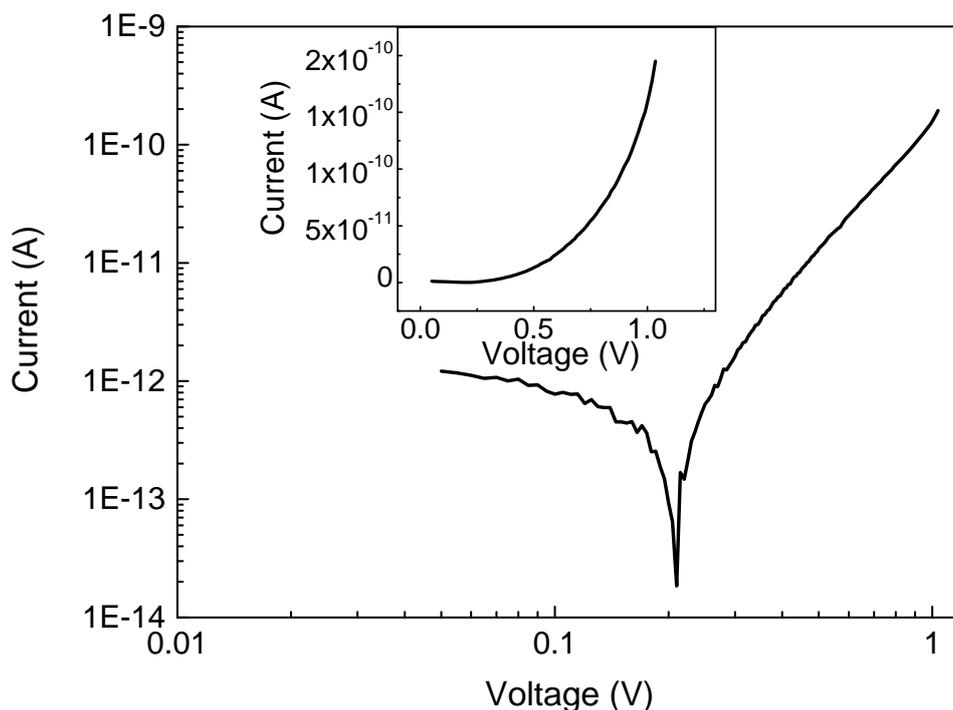


Fig. 7. *I-V* characteristic measured in ITO|PPV-D|Al sample. For seek of clarification the sign of the negative current below 0.2 V is changed. Inset – the same data plotted in linear scale demonstrating the Schottky behavior of the sample

Au|PPV-D interface. This result was confirmed by measurement of thickness

dependence of the electrical conductivity. It was found that of the slope of the I - V characteristics increases linearly decreasing the film thickness.

Unlike Au ITO electrode forms a barrier of about 0.2 eV and the I - V characteristic is similar to Schottky curve. Further optimization of the electrodes is necessary to get effective work of the structures prepared.

When strong fields are applied (case of high voltage or thin films) a deviation from the expected dependencies is observed. It could be related to strong trap influence or double injection of charge carriers from both electrodes. In all cases measured the influence of electrode barrier at Al|PPV-D interface (cathode) were not distinguish.

5. ACKNOWLEDGEMENTS

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