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ITO/PEDOT: PSS/MEH: PPV/Alq3/LiF/Au as a schottky diode

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ABSTRACT

In this research, we investigated the metal contacts using 100 nm thick films Au/PEDOT/MEH: Alq_3/ITO which is deposited onto an indium tin oxide (ITO) substrate as a test device. Electrical hysteresis phenomena were observed in the current-voltage characteristics of the device. The diode parameters such as ideality factor, series resistance, shunt resistance and barrier height are measured. These parameters are also verified by using the Norde's and Cheung functions.

Keywords: Schottky barrier diode, *I-V* Characterization, conjugated polyelectrolyte, PEDOT:PSS _ Polymeric anode, charge injection

1. INTRODUCTION

Whatever the organic semiconductors, macromolecules dyes, dendrimers, oligomers, polymers..., they are all based on conjugated π electrons. A conjugated system is based on an alternation between single and double bonds. The main properties related to this conjugation are that π electrons are more mobile than o electrons. Therefore the π electrons can move by hopping from site to site. These π electrons allow light absorption (solar cells) and emission (OLEDs) in these conjugated organic materials. Molecular π-π* orbital correspond respectively to the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).

Schottky diodes are formed at the interface between a metal and a semiconductor. The metal chosen for the contact must be stable under the high current densities applied and also generate a small Schottky barrier. The barrier height depends in part on the metal as well as the interface quality [1]. A stable metal-semiconductor interface is a re-requisite for applications at elevated temperatures. For metal contacts, the form of the interface may change at higher temperatures leading to an irreversible barrier height change [2]. Hence, an electrode material with similar barrier characteristics but with a better thermal stability would be desirable for high temperature devices.

Schottky barrier diodes are one of the simplest electronic devices in semiconductor industry. The main advantage of these diodes is their high current density and low forward voltage drop [3]. Primarily the current flow in these diodes is due to the majority carriers having an inherently fast response [4]. The current-voltage characteristics of Schottky diodes are similar to ordinary p-n junction diodes. These diodes are commonly used in switching circuits and high frequency applications because it can switch from one state to another much faster than ordinary p-n junction diodes. The behavior of organic Schottky diode depends on characteristics of the metal/organic semiconductor junction. Therefore, the understanding of electrical and electronic properties of interface between metal and organic semiconductor is important for device applications. There are more than a few possible reasons due to which the diodes show non-ideal behavior. These reasons include the effect of series resistance (Rs), formation of barrier height, insulating layer between metal and semiconductor and interface states. The series resistance is an important parameter which can lead the properties of Schottky diodes to be non-ideal [5], [6].

Special attention is given to bulk heterojunction structures in which the electron acceptor and the donor are mixed together in a solution and then is spin-coated and deposited as a thin layer [7]-[9]. The major problem of these devices is related with their time stability [10], even if many researchers are trying to solve this. To improve the photovoltaic performances of the prepared samples, as “buffer” layer between the anode and the active film is frequently used PEDOT: PSS. The architecture of the organic photovoltaic structures is important, so matching the energy level of the active layer with the work function of electrodes becomes necessary.

Due to its solubility in many solvents and optical absorption in the visible wavelength range poly(2-metoxy-5 -(20-ethyl-hexyloxy)-1,4-phenylene vinylene), or MEH-PPV is commonly used conjugated polymer in optoelectronic devices such as light emitting diodes[11],[12] solar cells[13],[14] and photo detectors.[15],[16] This polymer has been extensively investigated both experimentally and theoretically[17]-[30] and it is still a subject of various research.[31],[32]. As the MEH-PPV is one of the most studied polymers, a huge amount of collected results should be used to elucidate physical processes taking place in this material which could further lead us to a complete understanding of conjugated macromolecular systems. It is well-known that P3HT is a conjugated polymer that in exposure to oxygen and/or moisture results p-doped. Under such conditions, it has been suggested that the P3HT-Aluminum contact shows a Schottky diode behavior.

Fig-1, show the molecular structures of PEDOT: PSS and P3HT

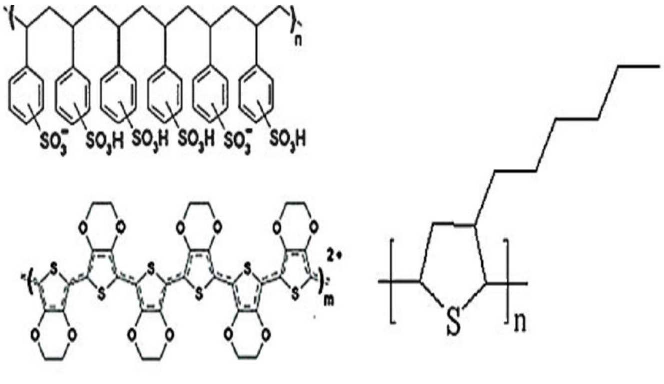

Fig-1 Molecular structures of PEDOT:PSS and P3HT

The model that includes charge carrier generation, transport, and recombination processes in the polymer photodetector which consists of indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and Al electrodes with poly(2-methoxy-5-(2 -ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) film in between (Fig. 2).

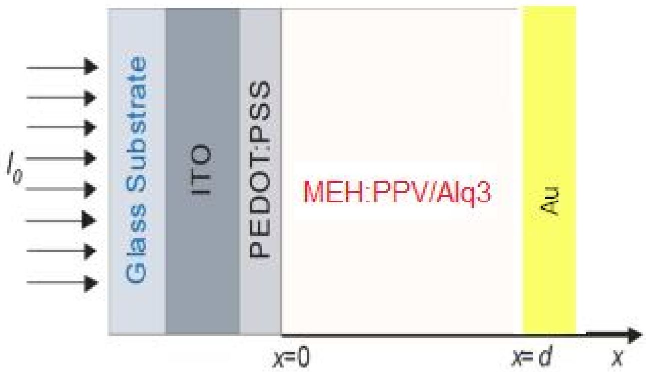

Fig. 2. Schematic layout of the ITO/PEDOT: PSS/MEH-PPV/Al photo detector on glass substrate

The polymer film morphology and consequently its optical parameters are strongly influenced by preparation conditions, molecular weight [33], solvent choice [34], solution concentration and spin-coating speed. At least one of the mentioned conditions must be varied to obtain different film thicknesses.

In present study, the blend of MEH-PPV, P3HT and Alq3 organic semiconductors was prepared as thin film on ITO to fabricate an organic diode. The electronic parameters such as barrier height, ideality factor, shunt resistance and series resistance of the organic diode were evaluated by current-voltage measurements.

2. EXPERIMENTAL

The ITO/PEDOT: PSS/MEH:PPV/Alq3/Lif/Au diode was fabricated on indium tin oxide coated (ITO) glass substrates (purchased from Sigma-Aldrich which is highly conductive and provides excellent transparency of >90% to allow the illuminated light to pass and to reach into the photoactive thin film readily). Each device has a 150 nm thick ITO anode with a 5–15 Ω/sq sheet resistance. A chloroform soluble poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is spin-coated on the ITO anodes to serve as the hole transporting layer (100 nm thick). The powdered MEH:PPV polymer (Sigma-Aldrich, USA) with molecular weight of M_w=260 000 g/mol is dissolved in chloroform using stirrers (10 mg/ml concentration) and kept at a temperature of 100 ^oC for 30 minute . The solution is filtered and spin coated. The coated substrates are allowed to dry at temperature100 ^oC for 30 minute for solvent removal. The Alq3 was deposited using spin coating with thickness about 100 nm and dry at temperature100 oC for 30 minute. Lif layer with 1 nm was deposited in glove box over this material. The fabrication process is completed by a thermal evaporation of the 100-nm-thick gold layer to serve as a cathode.

The electrical characterizations were performed at room temperature containing the current –voltage (I-V) measurements carried out both in dark and under A.M.1.5 conditions.
Ideality factor *n*, barrier height Φ_b, shunt resistance R_{sh} and series resistance R_s of junction diode are calculated from conventional *I-V* characteristics and these parameters are also verified using Cheung's functions and Norde's function.
The current-voltage characteristics of the Schottky junction can be analyzed by the following relation [35]:

$$I=I_o \exp(qV/nkT)\,[1-\exp(-qV/KT) \qquad (1)$$

Where I_o is the saturation current and can be given as:

$$I_o=AA^*T^2\exp(-q\Phi_b/KT) \qquad (2)$$

Where *V* is the applied voltage, T is the temperature, *A* is the effective diode area, *A** is the effective Richardson constant and *k* is the Boltzmann constant.
The value of ideality factor *n* can be calculated as:

$$n=q/kT\,(dV/dInI) \qquad (3)$$

Forward bias current-voltage characteristic at low voltage are linear in semi-log scale, but at higher voltages the characteristics deviate from linear behavior due to effect of series resistance.

The barrier height is obtained from (2) and is given by:

$$\Phi_b = KT/qIn\,(AA^*T^2/I_o) \qquad (4)$$

By using thermionic emission theory, the ideality factor n and BH Φ_b can be obtained from the slope and the current axis intercept of the linear region of the forward bias I-V plot, respectively. To determine the effect of series resistance on the Schottky diode characteristics, Cheung and Cheung introduced another characterization technique to determine the key parameters of diode like barrier height, series resistance and ideality factor. According to Cheung's functions, the thermionic emission model for a Schottky diode having junction resistance at V> 3kT/q in the forward *I-V* characteristics is written as [36]:

$$dV/d(\ln I) = n(kT/q) + IR_s \qquad (5)$$

The factor IR_s is the voltage drop across the series resistance of the Schottky diode.

3. RESULTS AND DISCUSSION

In order to characterize a diode, the most simple and useful method is the current-voltage (*I-V*) characterization. This method is used to extract the main parameters of diode such as series resistance, ideality factor and barrier height.
The measured forward and reverse bias current-voltage characteristics of the ITO/PEDOT: PSS/MEH: PPV/Alq3/Lif/Au surface type Schottky diode at room temperature is shown in Fig. 3.
PEDOT:PSS layer is a holes collector, facilitating the holes transport because of its work function is between the work function of the ITO and HOMO level of the active layer.

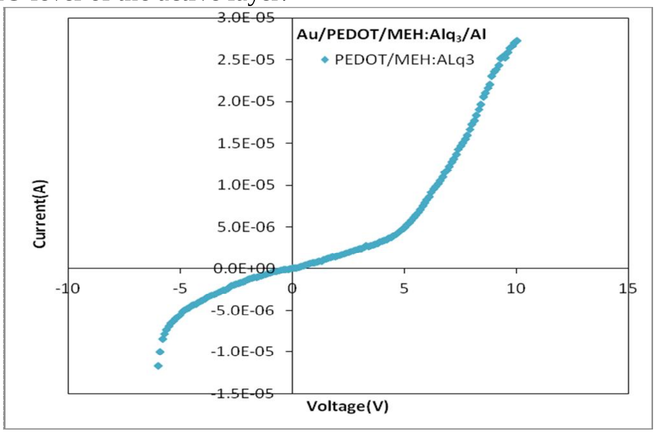

Fig. 3 Current-voltage (I-V) characteristics of ITO/PEDOT: PSS/MEH:PPV/Alq3/Lif/Au Schottky barrier diode

The weak voltage dependence of the reverse bias current and the exponential increase in the forward bias current are the characteristic properties of rectifying contacts. It can be seen from Fig. 3 that the current-voltage characteristics of the Schottky diode are nonlinear, asymmetric and show good rectification behavior with very small leakage current.

From ln *I* versus *V* characteristics, shown in Fig. 4, the current curve in the forward bias region becomes dominated by series resistance from contact wires or bulk resistance of the organic materials, giving rise to the curvature at high current in the semi log I-V plot. The n value was calculated from the linear portion of forward bias I-V curve in semi-logarithmic scale using equation (4). The value of Φ_b was determined using equation (3).

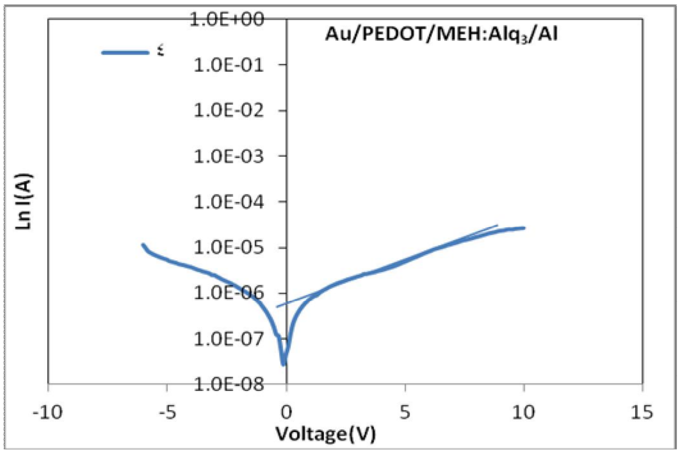

Fig. 4 Semi-logarithmic I-V characteristics of ITO/PEDOT: PSS/MEH:PPV/Alq3/Lif/Au Schottky barrier diode

As we know, the ideality factor measures the conformity of the diode to pure thermionic emission. The transport properties of the devices cannot be well modeled by thermionic emission if the ideality factor is much larger than unity [37]. Thus, the ideality factor 20.3indicates that the thermionic emission is not the dominant transport mechanism. The value of *n* for ITO/PEDOT: PSS/MEH:PPV/Alq3/Lif/Au barrier diode is greater than one because of the irregularities in thickness of organic film, oxide layer at the interface, dominant of recombination current and series resistance. This tendency is because of the non-uniform junction and the presence of in homogeneities of the barrier heights in Schottky diodes. The higher value of ideality factor may be attributed to effects of the voltage drop across the interfacial layer [38,39].
The applied bias voltage across the junction has significant effect on the barrier height [40]. The value of the barrier height of the sample ITO/PEDOT: PSS/MEH:PPV/Alq3/Lif/Au surface-type Schottky diode was determined and found to be 0.508 eV. It should be known that barrier height is the contact potential barrier that exists at the interface between the organic layer and metal.

The I-V characteristics of the diode are affected by parasitic resistances such series, R_s and shunt resistance, R_{sh}. These resistances are important factors in performance of the diode and the determination of these resistances is necessary to device performance. The series resistance R_s, which strongly contributes to the electrical characteristics of junction diodes, and was found from the junction resistance versus bias voltage V plot as shown in Fig. 5. The R_{sh} value was determined from the lower current region.

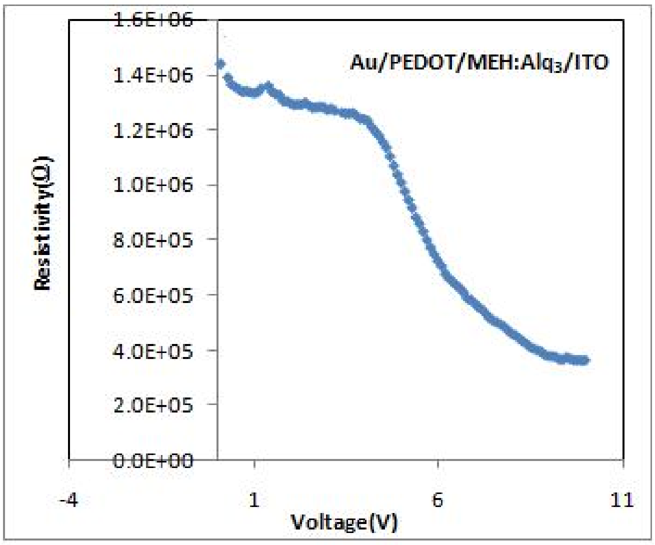

Fig. 5. Junction resistance vs. voltage graph of ITO/PEDOT:PSS/MEH:PPV/Alq3/Lif/Au Schottky diode

The value of R_s, equal to $0.37x10^6\Omega$, is extracted from the lower region in forward bias of the R vs. V characteristics. At higher voltages, the current-voltage exhibits a non-linear behavior due to the changes in the depletion layer at the interface of organic diode. This changes cause series resistance in the junction. The series resistance is significant in the non-linear of the I-V characteristics. While the shunt resistance R_{sh}, which is the highest value of resistance in the reverse bias of the R vs. V, plot, is found to be 1.360 x$10^6\Omega$. This resistance arises from the leakage of current. The resistance and ideality factors calculated from the I –V curve and Cheung's function show good agreement with each other.

The PEDOT: PSS/MEH: Alq3 organic semiconductor has low conductivity; therefore, the series resistance of the diode is very high. On the other hand, the bulk resistance, Poole-Frenkel and space charge limited current effects can cause higher values of ideality factor [41].

From fig.6 we observed that the current densities increased with increase of voltage. We concluded that electron traps – rather than hole traps—are induced. In this case electron–hole recombination will mostly take place near the electron-transporting layer. Thus, solution processing may lead to a reduction in the electron transport mobility as a result of electron charge traps.

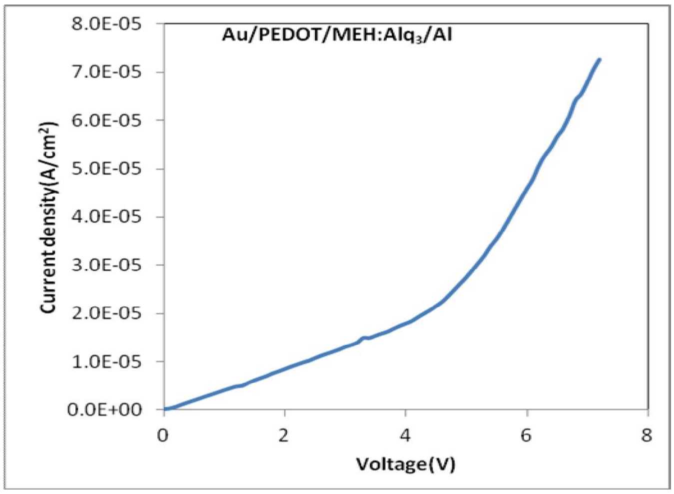

Fig. 6. Current density versus voltage for ITO/PEDOT: PSS/MEH: PPV/Alq3/Lif/Au Schottky diode.

In order to analyze these effects, we plotted current-voltage characteristics in the form of logI-logV, as shown in Fig. 7. In a diode, when the higher carrier densities from one electrical contact are locally injected into material, the space charge limited currents may take place. If not so, the contact behaves as ohmic contact without carrier injection. The ohmic behavior in current-voltage characteristic breaks down at the space charge limit and the space charge limited current (SCLC) flows for higher voltages. The dominant charge transport mechanism for the diode was determined by obtaining m values from the slopes of linear regions in Fig. 7. This mechanism suggests that at higher voltages, the current is limited by space-charge accumulation. It is clear from Fig. 7 that the forward bias double log I–V characteristics show three distinct linear regions separated by transition segments. The first region is ohmic with slope about unity .The second region of this graph is similar to the SCLC with the exponential distribution of traps in the band gap of the organic material. The third region of double logarithmic forward bias curve shows that at higher voltages the slope of the curve decreases because the device approaches the trap filled limit. When the injection level is high the behavior of this region is same as in trap free SCLC [37].

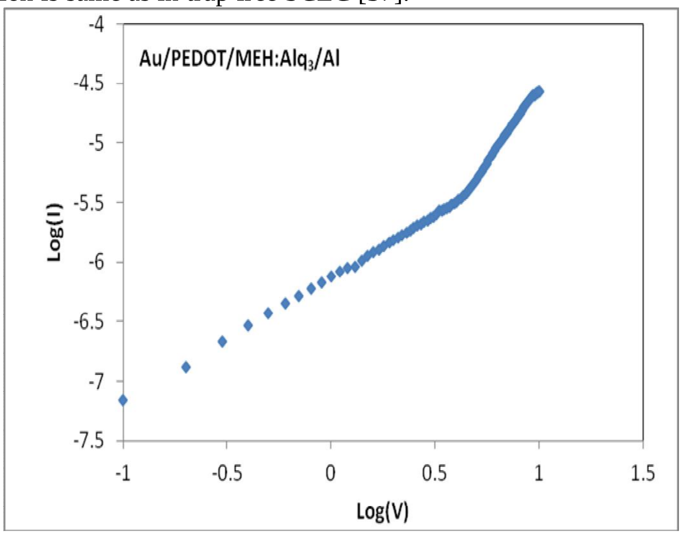

Fig.7. Semilog of I-V characteristic for ITO/PEDOT: PSS/MEH:PPV/Alq3/Lif/Au diode

Higher values of ideality factors are attributed to secondary mechanisms, which include interface dipoles due to interface doping or specific interface structure, as well as fabrication induced defects at the interface [42]-[45]. According to Tung,[44] the large values of n may also be attributed to the presence of a wide distribution of low-Schottky barrier patches caused by laterally barrier inhomogeneous. Also, recombination generation, and tunneling may be possible mechanisms that could lead to an ideality factor value greater than unity[46].

4. CONCLUSION

In this work we reports the fabrication of Au/LiF/PEDOT/MEH:Alq3/ITO Schottky barrier diode by a spin coating technique. The electrical properties of the diodes are investigated from *I-V* characteristics using thermionic emission model and Cheung's functions. The key diode parameters such as ideality factor, barrier height, shunt resistance and series resistance are also extracted from *I-V* characteristics. The diode indicates a non-ideal current-voltage behavior with ideality factor of 20.3. At higher voltages, the space limited current mechanism is dominant in the organic diode.

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