

Original Research Paper

Effect of Carboxyl-Functionalized Single Walled Carbon Nanotubes on the Interfacial Barrier Height of Malachite Green Dye Based Organic Device

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Abstract: In this study, we have estimated the interfacial barrier height (ϕ_b) of Indium Tin Oxide (ITO) coated glass/Malachite Green (MG) dye/Aluminium (Al) based organic device and subsequently we have also observed the effect of carboxylfunctionalized SWCNT (COOH-SWCNT) on the ϕ_b . Presence of COOH-SWCNT reduces the interfacial barrier height as SWCNT acts as filler and provides easy path for charge percolation. We have used ITO coated glass and aluminium as front electrode and back electrode respectively to form the organic device. This organic device has been prepared with and without COOH-SWCNT by using spin coating technique. We have measured the steady state current-Voltage (I - V) characteristics of the device to estimate the interfacial barrier height (ϕ_b) of the device. ϕ_b is reduced from 0.67 eV to 0.59 eV in the presence of COOH-SWCNT. We have also estimated the ϕ_b by using Norde's Method. This method also shows a reduction of interfacial barrier height from 0.72 eV to 0.64 eV due to incorporation of COOH-SWCNT. Both the methods show good consistency with each other. Reduction of the interfacial barrier height in presence of COOH-SWCNT indicates the enhancement of charge injection through the metal-organic dye interface. By suitable doping or addition of COOH-SWCNT within the MG dye it is possible to reduce the barrier height and enhance the current injection through metal-organic dye interface.

Keywords: Interfacial Barrier Height, Malachite Green Dye, Metal-Organic Dye Interface, COOH-SWCNT

Introduction

Organic/Polymeric materials are being widely studied to develop different electronic/optoelectronic devices. These devices provide flexibility, cost effectiveness and can be easily fabricated over a large area (Kim *et al.*, 2011; Tessler *et al.*, 2009). Despite these advantages, there are also certain limitations of organic devices. One of the major limitations is when a metalorganic contact is formed; the charge injection is poor due to presence of high barrier height (ϕ_b) at metal organic layer interface. There is not much study on the barrier height at the metal-organic layer interface. Attempts need to be made to reduce the interfacial barrier height in order to improve the charge injection at the interface of metalorganic layer. The injection of charges at the metal-organic layer interface has significant influence on the electrical properties of these organic devices and creates

more impact than charge transport within the organic devices. The charge injection barrier at the interface between a metal and organic material is commonly described by the interfacial barrier of metal to semiconductor contact (Kumatani *et al.*, 2013). Basically the interfacial barrier height is caused by the difference between the fermi energy level of metal and the energy band of organic material.

To reduce the barrier height at the metal-organic layer interface, we have incorporated COOH-SWCNT within the device. Presence of COOH-SWCNT decreases the barrier height at the metal-organic semiconductor interface as the high aspect ratio of COOH-SWCNT allows efficient conduction pathways for the generated charge carriers (Chakraborty and Manik, 2014). Generally, functionalized CNTs have certain advantages over their non-functionalized form. In comparison to non-functionalized forms functionalized SWCNTs have better interfacial bonding

strength and form better dispersions in solvents. It is possible that functionalized groups may be attached either to the ends or to side chain of the main tube to form a branch like structure (Luo *et al.*, 2012; Aqel *et al.*, 2012).

Reduction of interfacial barrier height will lead to better injection of charges at the interface and thus will provide better conductivity. Injection current usually consists of thermionic-injection current and field-induced tunneling current. In the case of low voltages, tunneling injection is negligible and thermionic emission dominates (Bullejos *et al.*, 2008). In this study, we have used Richardson-Schottky (RS) model of thermionic emission to characterize the organic device (De and Olawole, 2019).

Materials and Sample Preparation

Malachite Green (MG) is a cationic dye with the chemical formula $[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl$. The structure of the dye is shown in Fig. 1a. It belongs to the triarylmethane group and has a molar mass of 364.911 g/mol (chloride). The chloride and oxalate anions have no effect on the color. On a larger scale it is prepared by condensation of 2 moles of dimethylaniline with one mole of benzaldehyde at $100^\circ C$ in presence of zinc chloride or concentrated sulphuric acid (Raducan *et al.*, 2008). The cationic form of this dye has an extended π -delocalization which allows absorbance of light in the visible range. The quantum yield of MG dye is quite high (Bongsup *et al.*, 2003).

In our present work, MG dye and COOH-SWCNT are purchased from Finar Chemicals, Ahmedabad and Cisco Research Laboratories, India respectively. Figure 1(a) and 1(b) show the structures of MG dye and COOH-SWCNT

respectively. Poly Methyl Methacrylate (PMMA) and Dichloromethane (DCM) solvent are purchased from Sigma Aldrich and Merck Specialities Pvt. Ltd, Mumbai respectively. It has been selected as a solvent in our work due to its high ability to dissolve organic compounds (Shuugrue *et al.*, 2015). Figure 1(c) shows the structure of Dichloromethane (DCM).

Two different types of cells are prepared in order to observe the effect of COOH-SWCNT on MG dye based organic device, one type of cell is prepared with only MG dye and the other type of cell is prepared by adding COOH-SWCNT with this dye. To prepare the MG solution, 10 ml of DCM is taken in a clean test tube and in it 1g of PMMA is added. In this work, PMMA acts as an inert binder. The mixture is stirred with a magnetic stirrer for 30 min to get a clear solution. In this solution, 1 mg of MG dye is added and stirred for 15 min. This solution is then divided into two parts in two pre-cleaned test tubes. One test tube is kept aside and in the other 1 mg of COOH-SWCNT is added and stirred for 2 hours to get a homogeneous dispersed solution of dye and COOH-SWCNT.

To prepare the device, the MG solution is taken and coated on a pre-cleaned ITO coated glass. The film is coated on a spin coater at a speed of 1500 rpm and dried at a speed of 3500 rpm. The same solution is spin coated on the Al counter electrode. Both these electrodes are sandwiched together to form the MG dye cell. In a similar manner, another cell is prepared where COOH-SWCNT is added with MG dye. All the cells are kept in vacuum for 12 hours to dry before using them for characterization. The schematic diagram of the organic device is shown in the Fig. 2.

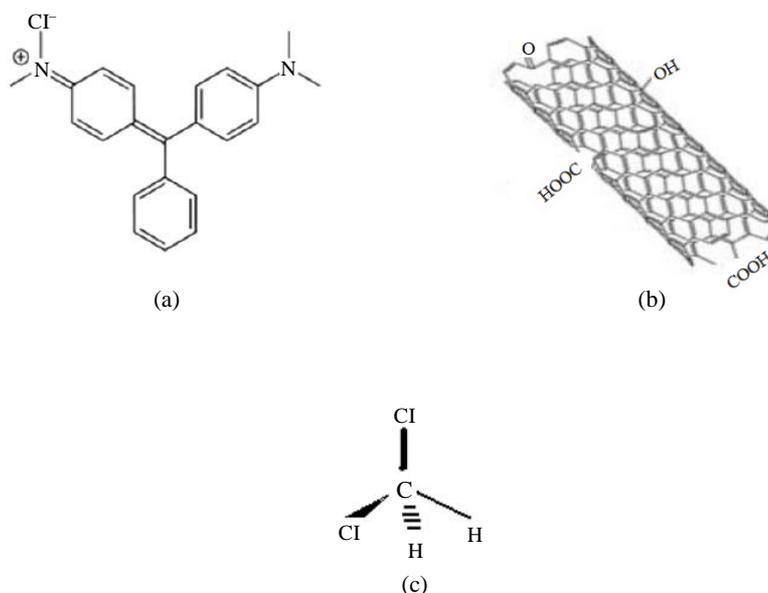


Fig. 1: Structural diagram of (a) Malachite Green (MG) (b) COOH functionalized single walled carbon nanotubes (COOH-SWCNT) and (c) structure of Dichloromethane (DCM)

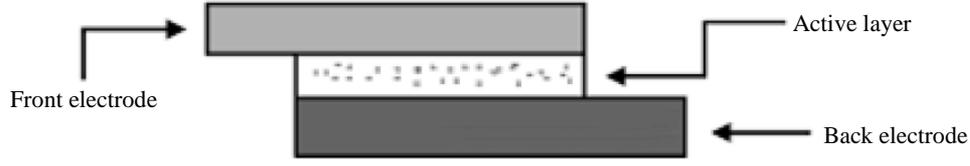


Fig. 2: Schematic diagram of the device. ITO coated glass is used as the front electrode and Al is used as the back electrode and MG dye is used as an active layer

Measurements

Dark current-Voltage (I-V) characteristics of the cells have been measured with a Keithley 2400 source measure unit. For dark I-V measurement, the front electrode is connected to the positive terminal of the battery and the negative terminal of the battery is connected to back electrode of the device. During measurement, the bias voltage is varied from 0 to 6 volt in steps of 0.5 volt with 1500 MS delay. The experiments have been done in the clean open atmosphere of the laboratory at a room temperature of 25°C.

Results and Discussion

The current through a metal-organic semiconductor interface due to thermionic emission can be expressed as (Sze and Kwok, 2007; Chakraborty *et al.*, 2018; Shah *et al.*, 2010a; Yakuphanoglu, 2010; Aydın *et al.*, 2006):

$$I = I_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] \quad (1)$$

where, I_0 is the saturation current, which is given by:

$$I_0 = AA^*T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \quad (2)$$

and:

$$A^* = \frac{4\pi qm^*k^2}{h^3} \quad (3)$$

Here, q is the electronic charge, V is the applied voltage, A is the area of the device, k is the Boltzmann's constant, T is the absolute temperature, A^* is the effective Richardson constant of $120\text{Am}^{-2}\text{K}^{-2}$ for Malachite Green dye, ϕ_b is the interfacial barrier height and n is the ideality factor.

The dark I-V characteristics of MG dye based organic device in absence and presence of COOH-SWCNT are shown in Fig. 3(a) and 3(b) respectively. The value of dark current is quite low for the MG dye under experiment. But current becomes double when

COOH-SWCNTs are incorporated with this MG dye based organic device.

Interfacial Barrier Height of metal-organic semiconductor device can be determined from the following relation (Al-Ta'ii *et al.*, 2015; Shah *et al.*, 2010b; Harrabi *et al.*, 2010):

$$\phi_b = \frac{kT}{q} \ln\left(\frac{AA^*T^2}{I_0}\right) \quad (4)$$

Figure 4(a) and 4(b) show semi logarithmic I-V curves of MG dye based organic device in absence and presence of COOH-SWCNT respectively. The reverse saturation current I_0 is determined from the y-intercept of both the semi logarithmic I-V curves. Applying Equation (4), the barrier height of MG dye based organic device is calculated which is 0.67 eV in absence of COOH-SWCNT and the value of barrier height reduces to 0.59 eV in the presence of COOH-SWCNT.

The interfacial barrier height can also be calculated using Norde's function. In this Norde's function, the relationship between the function $F(V)$ and the measured current $I(V)$ can be expressed in the equation given below (Norde, 1979). $I(V)$ is the current, measured from I-V characteristics of the device

$$F(V) = \left(\frac{V}{X}\right) - \frac{kT}{q} \ln\left(\frac{I(V)}{AA^*T^2}\right) \quad (5)$$

where, X is the first integer greater than n . The value of current $I(V_0)$ corresponding to minimum value of Norde's function $F(V_0)$, where V_0 is the corresponding voltage (Yakuphnoglu *et al.*, 2011).

Figure 5(a), for ITO/MG/Al structure, the interfacial barrier height has been calculated by using the following equation (Kocyigit *et al.*, 2019). V_0 is estimated from the plot which is shown in Fig. 5(a):

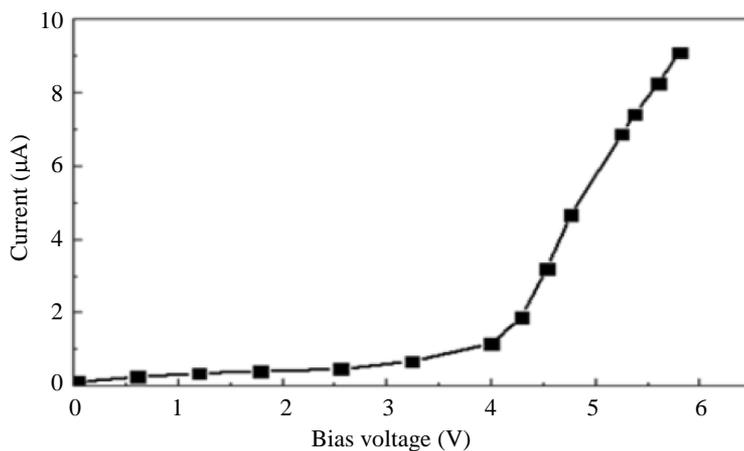
$$\phi_b = F(V_0) + \frac{V_0}{X} - \frac{kT}{q} \quad (6)$$

To compare the effect of COOH-SWCNT, we have plotted the Norde's function in Fig. 5(b), by using the Equation (5). Consequently, the interfacial barrier height has been calculated for ITO/MG+COOH-SWCNT/Al structure by using the Equation (6).

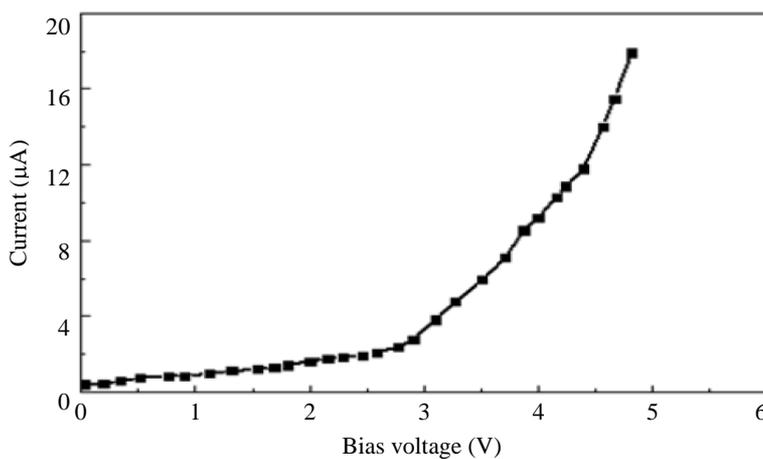
The values of barrier height of MG dye based organic devices in absence and presence of COOH-SWCNT has been shown in Table 1.

From Table 1, it can be seen that both the methods show the reduction of barrier height as 11.94% and

11.11% respectively in the presence of COOH-SWCNT. It can be said that by incorporating COOH-SWCNT, reduction of barrier height help in improving better current injection so that the organic device can be turned on at much lower voltage.

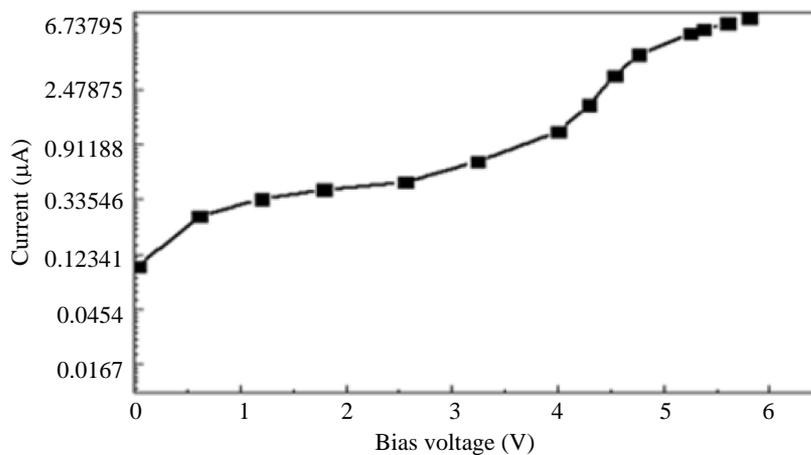


(a)



(b)

Fig. 3: Dark I-V characteristics of organic device comprising of MG dye (a) without COOH-SWCNT and (b) with COOH-SWCNT



(a)

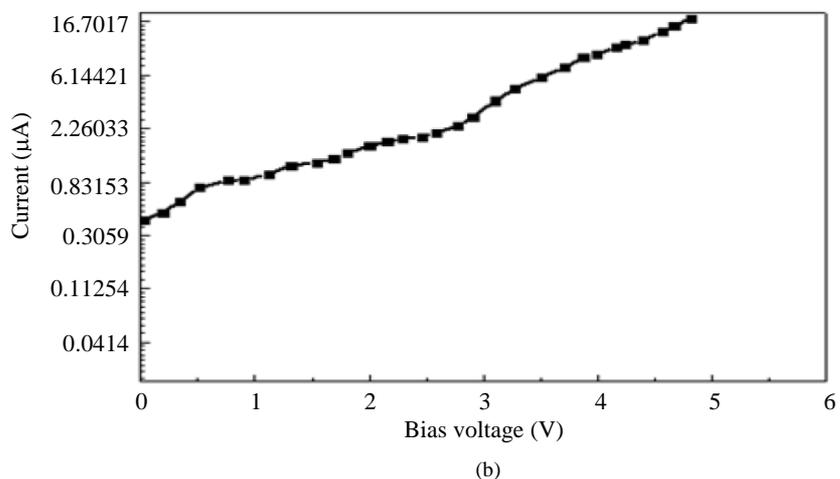


Fig. 4: In I -V characteristics of organic device comprising of MG dye (a) without COOH-SWCNT and (b) with COOH-SWCNT

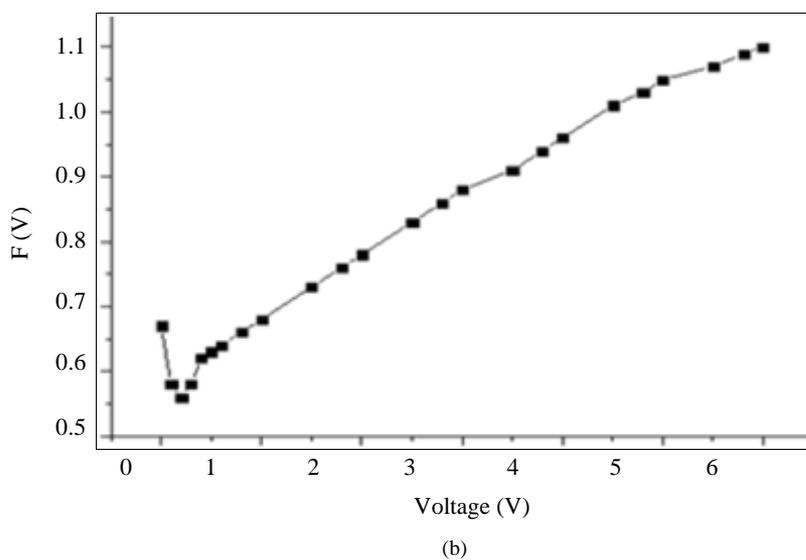
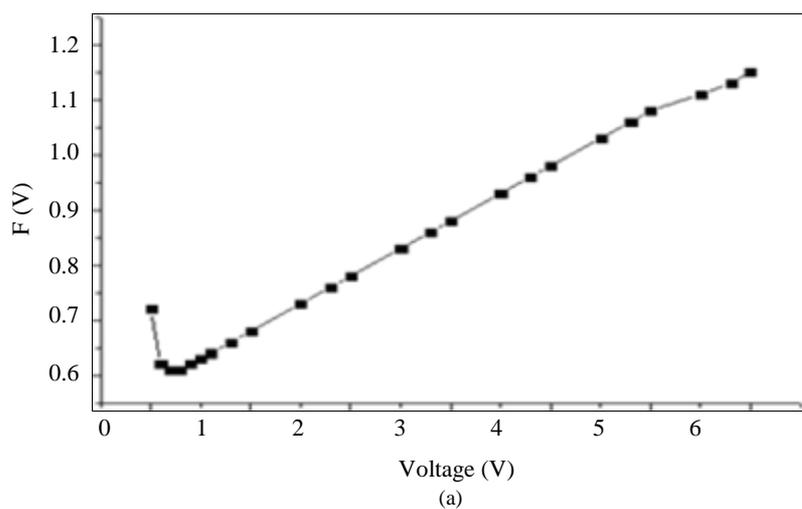


Fig. 5: Norde's function $F(V)$ - V plot of (a) ITO/MG/Al structure and (b) ITO/MG+COOH-SWCNT/Al structure

Table 1: Calculation of barrier height of MG dye based organic devices in absence and presence of COOH- SWCNT

Dye under consideration	Barrier height from I-V characteristics (eV)	Barrier height using norde's function (eV)
MG	0.67	0.72
MG+COOH-SWCNT	0.59	0.64

Conclusion

In this study, we have studied the effect of COOH-SWCNT on the interfacial barrier height of MG dye based organic device. Values of barrier height for MG dye based organic device are calculated by analyzing I-V characteristics of the device and also by Norde's function. Both the methods show good consistency with each other. It is observed that in presence of COOH functionalized single walled carbon nanotube, the barrier height at the metal-organic layer interface is reduced. Reduction of interfacial barrier height improves the charge injection which results in higher conductivity.

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Data Availability

Data used to support the findings of this study are included within this article.

Author's Contributions

Sudipta Sen: Participated in all experiments, coordinated the data-analysis and contributed to the writing of the manuscript.

Nabin Baran Manik: Designed the research plan and organized the study.

Conflicts of Interest

The authors declare that there is no conflict of interest.

References

- Kim, J.J., M.K. Han and Y.Y. Noh, 2011. Flexible OLEDs and organic electronics. *Semicond. Sci. Technol.*
- Tessler, N., Y. Preezant, N. Rappaport and Y. Roichman, 2009. Charge transport in disordered organic materials and its relevance to thin-film devices: A tutorial review. *Adv. Mater.*, 21: 2741-2761. DOI: 10.1002/adma.200803541
- Kumatani, A., Y. Li, P. Darmawan, T. Minari and K. Tsukagoshi, 2013. On practical charge injection at the metal/organic semiconductor interface. *Nature*, 3: 1026-1026. DOI: 10.1038/srep01026

- Chakraborty, S. and N.B. Manik, 2014. Effect of COOH-functionalized SWCNT addition on the electrical and photovoltaic characteristics of Malachite Green dye based photovoltaic cells. *J. Semicond.*
- Luo, Y. Z. Gong, M. He, X. Wang, Z. Tang and H. Chen, 2012. Fabrication of high-quality carbon nanotube fibers for optoelectronic applications. *Solar Energy Mater. Solar Cells*, 97:78-82. DOI: 10.1016/j.solmat.2011.09.036
- Aqel, A., M.M. Kholoud, A. El-Nour, R.A.A. Ammar and A. Al-Warthan, 2012. Carbon nanotubes, science and technology part (I) structure, synthesis and characterisation. *Arabian J. Chem.*, 5: 1-23. DOI: 10.1016/j.arabjc.2010.08.022
- Bullejos, P.L., J.A.J. Tejada, M.J. Deen, O. Marinov and W.R. Datars, 2008. Unified model for the injection and transport of charge in organic diodes. *J. Applied Phys.*, 103: 064504-064504. DOI: 10.1063/1.2884711
- De, D.K. and O.C Olawole, 2019. A three-dimensional model for thermionic emission from graphene and carbon nanotube. *J. Phys. Commun.*
- Raducan, A., A. Olteanu, M. Puiu and D. Oancea, 2008. Influence of surfactants on the fading of malachite green. *Formerly Central European J. Chem.*, 6: 2391-5420. DOI: 10.2478/s11532-007-0066-0
- Bongsup, P.C., T. Yang, L.R. Blankenship, J.D. Moody and M. Churchwell *et al.*, 2003. Synthesis and characterization of N-demethylated metabolites of malachite green and leucomalachite green. *Chem. Res. Toxicol.*, 16: 285-294. DOI: 10.1021/tx0256679
- Shuugrue, C.R. H.H. Mentzen and B.R. Linton, 2015. A colorful solubility exercise for organic chemistry. *J. Chem. Edu.*, 92: 135-138. DOI: 10.1021/ed4005408
- Sze, S.M. and K.N.G. Kwok, 2007. *Physics of Semiconductor Devices*. 3rd Edn., Wiley and Sons, ISBN-13: 978-0-471-14323-9, pp: 832.
- Chakraborty, K., S. Chakraborty and N.B. Manik, 2018. Effect of single walled carbon nanotubes on series resistance of rose bengal and methyl red dye-based organic photovoltaic device. *J. Semicond.*, 39:094001-094001. DOI: 10.1088/1674-4926/39/9/094001
- Shah, M., K.S. Karimov, Z. Ahmad and M.H. Sayyad, 2010a. Electrical characteristics of Al/CNT/NiPc/PEPC/Ag surface-type cell. *Chinese Phys. Lett.*, 27: 106102-106102. DOI: 10.1088/0256-307X/27/10/106102

- Yakuphanoglu, F., 2010. Controlling of silicon–insulator–metal junction by organic semiconductor polymer thin film. *Synth. Metals*, 160: 1551-1555. DOI: 10.1016/j.synthmet.2010.05.024
- Aydın, M.E. T. Kılıçoğlu, K. Akkılıç and H. Hoşgören, 2006. The calculation of electronic parameters of an Au/ β -carotene/n-Si Schottky barrier diode. *Physica*, 381: 113-117. DOI: 10.1016/j.physb.2005.12.254
- Al-Ta'ii, H.M.J., Y.M. Amin and V. Periasamy, 2015. Calculation of the electronic parameters of an Al/DNA/p-Si schottky barrier diode influenced by alpha radiation. *Sensors*, 15: 4810-4822. DOI: 10.3390/s150304810
- Shah, M., M.H. Sayyad, K.S. Karimov and F. Wahab, 2010b. Electrical characterization of the ITO/NiPc/PEDOT: PSS junction diode. *J. Phys. Applied Phys.*
- Harrabi, Z., S. Jomni, L. Beji and A. Bouazizi, 2010. Distribution of barrier heights in Au/porous GaAs schottky diodes from current-voltage-temperature measurements. *Physica B: Condensed Matter*, 405: 3745-3750. DOI: 10.1016/j.physb.2010.05.079
- Norde, H., 1979. A modified forward *I-V* plot for Schottky diodes with high series resistance. *J. Applied Physics*, 50: 5052-5053. DOI: 10.1063/1.325607
- Yakuphanoglu, F., M. Shah and A.W. Farooq, 2011. Electrical and interfacial properties of p-Si/P3HT organic-on-inorganic junction barrier. *Acta Phys. Polonica*, 120: 58-562.
- Kocyigit, A., M. Yılmaz, S. Aydoğan and Ü. Incekara, 2019. The effect of measurements and layer coating homogeneity of AB on the Al/AB/p-Si devices. *J. Alloys Compounds*, 790: 388-396. DOI: 10.1016/j.jallcom.2019.03.179