Research Article
Volume 10:5, 2021

Journal of Material Sciences & Engineering

ISSN: 2169-0022

Open Access

Effect of Different Sized Multi Walled Carbon Nanotubes on the Parameters Affecting the Charge Injection Process of Methyl Red Dye Based Organic Device

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Abstract

Present paper has been done to describe the parameters related to organic device's process of charge injection and to observe how these parameters get affected by different sized multi walled carbon nanotubes such as 8 nm diameter, 30 nm diameter and 50 nm diameter respectively. Barrier height significantly affects the interfacial charge injection process. Image charge effect also plays a salient role in lowering interfacial barrier. Spin coating technique has been used to form these devices. To estimate the barrier height, the current-voltage characteristics of these devices have been analyzed. Threshold voltage and ideality factor of these devices were also estimated. All the above mentioned parameters were calculated in absence and presence of different sized multi walled carbon nanotubes to observe its effect on these parameters. The barrier height was also estimated by Norde method. Both the methods remained consistent in showing that multi walled carbon nanotubes reduced the interfacial barrier. Effective barrier height considering image charge effect was also decreased due to incorporation of multi walled carbon nanotubes. Lowering of these parameters indicated improved charge flow at the interface. This work will be informative as the lower threshold voltage will cause consumed power to decrease. As the interfacial charge injection process gets improved, device conductivity will be improved which will result in greater efficiency.

Keywords: Barrier height • Charge injection • Image charge effect • Metal-organic dye interface • Methyl red dye • MWCNT • Norde method

Introduction

Organic electronic devices are easily compatible with flexible substrates. These materials can be produced in large scale compared to the inorganic ones as they can be easily processed. Organic materials are also of low cost and adjustable to band energies [1,2]. Despite certain advantages of these devices, there are certain limitations that do exist in these devices. One of the main limitations is low charge injection at metal organic (M/O) interface. Inefficient charge movement from metal electrode to organic semiconductors can be attributed to the high contact barrier [3-6]. In this context, it is of paramount importance to decrease contact barrier for improving the device performance. Here, in this work, the barrier height has been estimated as it hinders charge injection process of the device. The ideality factor and the threshold voltage of the device have also been estimated as these are also related to charge injection process. The term "threshold voltage" has been used as the device turn on voltage. When an organic device starts to conduct at a particular voltage, that particular voltage can be specified as "threshold voltage" of that device. Generally, more than unity value of ideality factor ascribed to interfacial trap states between the metal and organic semiconductor as organic device is prone to traps [7,8]. Other researchers have also highlighted that the image charge effect may be the reason of the greater than unity value of the ideality factor [9,10]. Image charge effect also lowers the interfacial barrier which has also been studied in this work.

Among organic materials, Methyl Red (MR) dye is used in this present work. Electrons delocalized in the benzene and azo groups form a conjugated system in dye molecular structure [11,12]. Its structure and abundance of π electrons allow us to use this dye in between Aluminium and Indium Tin Oxide (ITO) coated glass substrate to prepare the device.

For different organic dye based devices, different researchers have used multi walled carbon nanotubes (MWCNT) as dye adsorbent for treatment of wastewater by removing methyl blue, methyl orange and methyl violet from aqueous solution [13-15] and researchers have also observed strong and broad band optical limiting in multi walled carbon nanotube suspensions [16]. In this work, MWCNT have been chosen due to its high aspect ratio, electrical and thermal conductivity and mechanical strength [17]. Different sized multi walled carbon nanotubes (MWCNT) such as 8 nm diameter, 30 nm diameter and 50 nm diameter MWCNT have been used to study their effects on contact barrier. Their effects have been studied on ideality factor and the threshold voltage as these parameters affect the device's charge injection process. Image charge effect in presence of different sized MWCNT has also been studied in this work.

The process of interfacial charge injection is generally analyzed by the theory of metal to semiconductor contact [18]. Our earlier works have characterized these organic devices by using Richardson-Schottky (RS) model [19,20]. Steady state current voltage characteristics of these devices have been analyzed to evaluate barrier height, ideality factor and threshold voltage. The contact barrier is also calculated by Norde method to check the consistency of the obtained result from the current voltage characteristics. The effective barrier height considering image charge effect

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Received date: 30 April, 2021; **Accepted date:** 14 May, 2021; **Published date:** 21 May, 2021

is also calculated of the prepared organic device.

Materials and Methods

MR dye was obtained from Sigma Aldrich, India. Methyl Red structure consists of aromatic or benzene rings. Azo group forms when the two aromatic rings are connected to one another by two nitrogen atoms [21]. Methyl Red also contains a carboxylic acid functional group (-COOH). Directly on the other side of the molecule from the carboxylic acid group, a nitrogen atom is connected to two methyl (-CH_3) groups, which is called an amine functional group. Molecular formula of this dye is $C_{15}H_{15}N_3O_2$ [22,23].

MWCNT was obtained from Sisco Research Laboratories (SRL), India. Different sized MWCNT i.e. 8 nm diameter, 30 nm diameter and 50 nm diameter MWCNT were used in this work.

Dichloromethane (DCM) (molecular weight: 84.93) was used as a solvent in our work as the organic compounds can be dissolved easily [24] and it was purchased from Sigma Aldrich. The structures of Methyl Red, MWCNT and DCM have been depicted in Figure 1(a), 1(b) and 1(c) respectively.

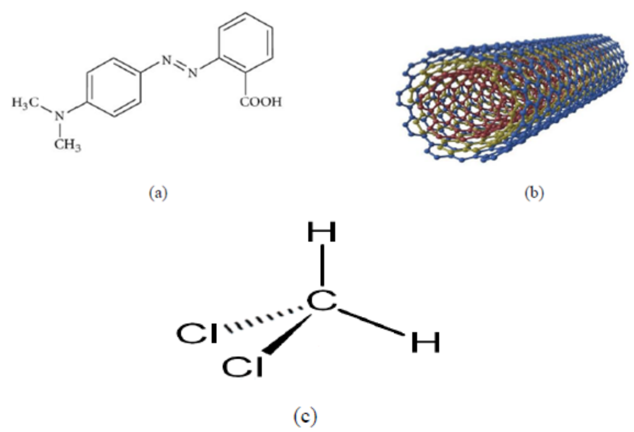


Figure 1. Structures of (a) Methyl Red dye, (b) Multi-walled carbon nanotubes (MWCNT) and (c) Dichloromethane (DCM)

A 75 mm x 25 mm x 1.1 mm ITO coated glass slide and Aluminium were used as two electrodes for preparing the device.

Poly Methyl Methacrylate (PMMA) (molecular weight: 1,20,000) was procured from Merck Specialties Pvt. Ltd, Mumbai. PMMA solution was formed by adding 15 ml Dichloromethane to 1 mg PMMA in a clean test tube. Then the mixture was stirred with a magnetic stirrer for 1 hour in the room temperature to get a clear solution. In our work, PMMA container solution was used as a binder material because of its excellent transparency and good weathering resistance capability. It possessed excellent mechanical properties and high tensile strength.1 mg MR dye was mixed with PMMA solution and stirred for 30 minutes. Prepared solution was separated in four parts in four test tubes. In the three test tubes MWCNT of size 8 nm, 30 nm and 50 nm were added respectively and stirred for 3 hours to form well mixed solution of dye and MWCNT.

During the preparation of the organic device, the 8 nm MWCNT added MR dye solution was sticked on an ITO coated glass which was spin coated with 1500 rpm speed and dried with 3500 rpm speed and similar process is followed for Al counter electrode. Both these electrodes were in semi dry state, both of them were sandwiched together for preparing 8 nm MWCNT

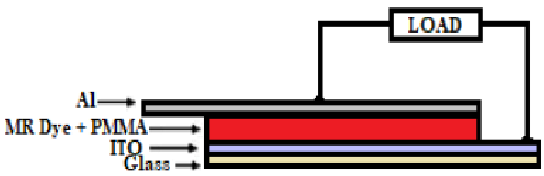


Figure 2. Structure of the Organic Device

Measurements

Same measurement technique is followed as mentioned in one of our earlier works [25]. Voltage range is 0 V-3 V with 0.2 V steps and 1000 ms delay. Measurements are performed at the temperature of 27°C. Regarding the reproducibility of the measurement, it can be said that the organic devices have charge trapping effects and due to these effects, some traps get immobilized and some residual charges may exist. Before all the experiment the cells were discharged properly around 15 minutes by connecting the two terminals directly i.e the cells were short circuited. The experimental results were reproducible within the experimental limit. Degradation of the film is common for this type of film. However the time scale for degradation of the film is much greater than the observed decay of current. So its effect is ignored for simplicity. If applied voltage is turned off then current does not recover completely and the authors think that this is a common phenomenon in this type of organic device.

Results and Discussion

As stated by Richardson-Schottky model, interfacial current at metal-organic layer is shown in the equation (1)

$$I = AA^*T^2 \exp\left(-\frac{q\Phi_b}{kT}\right)\left(\exp\left(\frac{qV}{nkT}\right) - 1\right) \quad (1)$$

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

In both the equations, A=1.5 cm^2 and all the other symbols carry their usual meaning [26-32].

The term q/kT can be replaced by the term β.

The interfacial barrier at zero bias can be expressed as shown in the equation (3)

$$\phi_b = \frac{1}{\beta}\ln\left(\frac{AA^*T^2}{I_0}\right) \quad (3)$$

Ideality factor (n) is determined from equation (4)

$$n = \beta\frac{dV}{d(\ln I)} \quad (4)$$

The dark I-V plots of device without and with MWCNT have been shown in Figure 3 (a) and 3 (b) respectively. Threshold voltage has been calculated from both these figures.

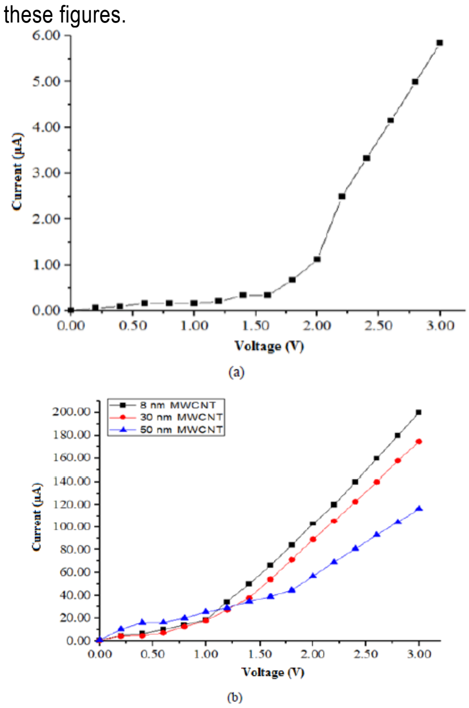
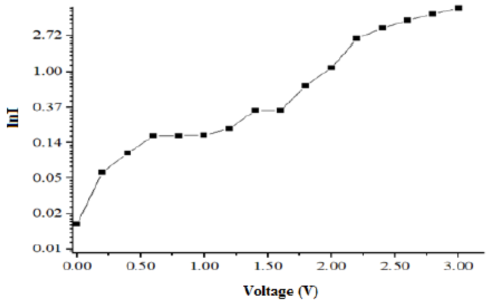
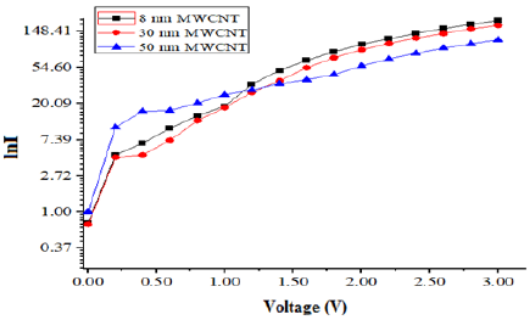


Figure 3. I-V plot (a) without MWCNT and (b) with 8 nm MWCNT, 30 nm MWCNT, 50 nm MWCNT respectively

For calculating interfacial barrier and the ideality factor at metal-organic junction the semilogarithmic plots of Figure 3(a) and 3(b) have been depicted in Figure 4 (a) and 4 (b).



(a)



(b)

Figure 4. ln I - V characteristics (a) without MWCNT and (b) with 8 nm MWCNT, 30 nm MWCNT, 50 nm MWCNT respectively

Barrier height has also been estimated by Norde method. The function F (V) is shown in the equation (5) [33-34]

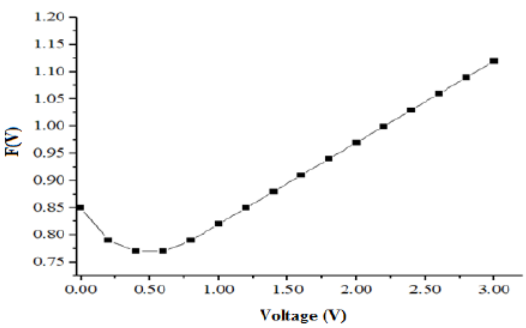
$$F(V) = \left(\frac{V}{\gamma}\right) - \frac{1}{\beta}\ln\left(\frac{I(V)}{AA^{*}T^{2}}\right) \qquad (5)$$

γ is the first integer greater than n.

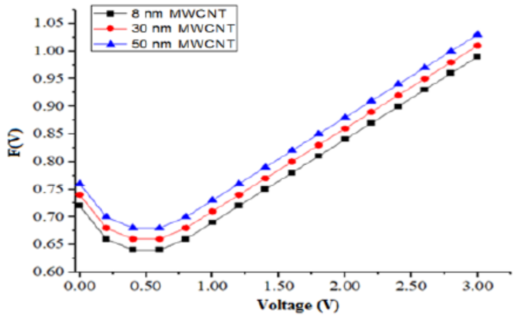
In this method, barrier height can be measured in the following form as shown in equation (6) [35-38]

$$\phi_b = F(V_{min}) + \frac{V_0}{\gamma} - \frac{1}{\beta} \qquad (6)$$

The minimum function value F (V_{min}) corresponds to the minimum voltage V_0. The minimum voltage is measured from the Figure 5 (a) and 5 (b) respectively for the device without and with 8 nm MWCNT, 30 nm MWCNT and 50 nm MWCNT.



(a)



(b)

Figure 5. Norde function (a) without MWCNT and (b) with 8 nm MWCNT, 30 nm MWCNT, 50 nm MWCNT respectively

The small differences in barrier height obtained by both these methods are due to the different processes of extraction from different regions [39].

There are also similar other methods that are compatible to Norde method. Cheung method, Rhoderick method, Werner method and Lien method are also used to estimate the barrier height.

Rhoderick method is generally used for applied voltage of (V<3 kT/q), so this method is not applicable in this work. Norde method and Cheung's method are both applicable for the applied voltages of (V>3 kT/q). The Lien method is also based on the construction of several Norde like functions [40]. But in this work, only Norde function is used to check the consistency of the obtained value of interfacial barrier from the I-V plot of device.

Barrier lowering effect happens for image charges are also discussed in this work. The carrier injection process from metal to organic layer is confined by additive effect of an external electric field and the Coulomb field [41]. This superposition binds both carrier and image of carrier on the electrode, as given by the following expression (7)

$$U(x) = \phi_b - \frac{e^2}{16\pi\varepsilon_0\varepsilon x} - eFx \qquad (7)$$

x=distance from the interface with all other symbols carry their usual meaning.

We have calculated effective barrier height considering device's image charge effect of in absence and presence of 8 nm, 30 nm, 50 nm MWCNT respectively. The applied ield is 10^6 V/cm and the value of the dielectric constant is 3.5 and the potential distribution is located at 3 nm away from the interface. Considering the image charge effect, the obtained values of effective barrier height of device under the influence of different sized MWCNT are shown in the Table I. Threshold voltage, barrier height and ideality factor without and with different sized MWCNT of ITO/MR/Al structure have also been expressed in the Table I.

In the Table I, the experimental data shows decrease in interfacial barrier considering the image charge effect of device. As shown in the above table, MWCNT reduces the interfacial barrier at M/O interface. Ideality factor and threshold voltage are also reduced due to incorporation of MWCNT.

All the experimental data also shows that 8 nm MWCNT produces better performance regarding current injection at the M/O interface compared to 30 nm and 50 nm MWCNT. MWCNT of the lowest diameter of 8 nm will have highest aspect ratio compared to MWCNT of medium and high (30 and 50 nm) diameters, respectively. Aspect ratio of MWCNT will have paramount effect on both electrical and mechanical properties when it is incorporated in the organic device [42]. The better performance is observed for MWCNT of smaller diameter. The percolation threshold of electrical conductivity also decreases with the increase of aspect ratio [43]. These properties make 8 nm MWCNT an excellent additive in electrically conductive polymer applications which results in improved charge injection process compared to 30 nm and 50 nm MWCNT. The desired level of conductivity can be achieved with much lower loadings. Improved charge injection process will also provide better performance of organic opto electronic devices.

Parameters	Devices			
	MR Dye	MR Dye + 8 nm MWCNT	MR Dye + 30 nm MWCNT	MR Dye + 50 nm MWCNT
Threshold Voltage (V)	2	1	1.5	1.75
Barrier Height (eV) using I-V characteristics	0.87	0.7	0.71	0.75
Barrier Height (eV) using Norde Method	0.85	0.72	0.74	0.77
Ideality Factor	5.57	0.76	0.98	1.57
Effective Barrier Height (eV)	0.84	0.67	0.68	0.72

Table I. Threshold voltage, barrier height, ideality factor and effective barrier height considering image charge effect of the device under the influence of different sized MWCNT

Conclusion

The motivation of the study was to assess parameters affecting the charge injection process of MR dye based organic devices and observe the effects of different sized MWCNT such as 8 nm, 30 nm and 50 nm respectively on these parameters. The contact barrier is one of the main reasons due to which injection of charges gets lowered from metal to organic layer. In the present work, interfacial barrier for MR dye based devices without and with different sized MWCNT are calculated using I-V plot and also by Norde function. Both methods show agreement regarding the obtained values. Decrease in barrier height may be also due to strong π-π bonding between the MWCNT and organic dye. The ideality factor of the device without and with MWCNT has also been calculated as it is also one of the parameters which is related to the charge injection process. It has been found out that by incorporating the different sized MWCNT, the device's ideality factor decreases significantly which can be ascribed to decrease in trap concentration at the interface. The authors have also considered the image charge effect on the lowering of the effective barrier of the device. Due to incorporation of different sized MWCNT, it has been observed that effective barrier height due to image charge effect also reduces. Incorporation of MWCNT also reduces the threshold voltage which is due to lowering of barrier height. Barrier lowering results in better conductivity. It can also be inferred that the device performance of the 50 nm MWCNT cell is found to be poor in comparison to the 8 nm MWCNT cell. Due to their smaller sizes 8 nm MWCNT enhance the charge separation and relaxation process which resulting in improved charge injection process.

Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Acknowledgements

One of the authors, Sudipta Sen is thankful to UGC for awarding a research fellowship (Grant No.3482/(NET-JULY 2016)).

References

1. Salem, GF, EAA El-Shazly, AAM Farag and IS Yahia. Optical and microelectronic analysis of rhodamine B-based organic Schottky diode: A new trend application." Appl. Phys. A (2018) 124: 744
2. Sharma, N, CMS Negi, AS Verma and SK Gupta. "C60 Concentration Influence on MEH-PPV:C60 Bulk Heterojunction-Based Schottky Devices." J Elec Materi (2018) 47: 12
3. Kumatani, A, Y Li, P Darmawan and T Minari, et al. "On Practical Charge Injection at the Metal/Organic Semiconductor Interface." Sci Rep (2013) 3: 10
4. Liu, Z, M Kobayashi, BC Paul and Z Bao, et al. "Contact engineering for organic semiconductor devices via Fermi level depinning at the metal-organic interface." Physical Review B (2010) 82: 035311
5. Thakur, AK, AK Mukherjee, DMG Preethichandra and W Takashima, et al. "Charge injection mechanism across the Au-poly(3-hexylthiophene-2,5-diyl) interface." J. Appl. Phys (2007) 101: 104508
6. Scott, JC. "Metal–organic interface and charge injection in organic electronic devices." J Vac. Sci. Technol. A (2003) 21: 521
7. Sen, S and NB Manik. "Modification of Trap Energy and Barrier Height in Crystal Violet (CV) Dye based Organic Device in Presence of Single Walled Carbon Nanotubes (SWCNT)." Int J Scient Res and Rev (2019) 07:10
8. Nawar, AM, M Abd Elsalam, AM El Mahalawy and MM El Nahass. "Analyzed electrical performance and induced interface passivation of fabricated Al/NTCDA/p-Si MIS–Schottky heterojunction." Appl. Phys. A (2020) 126: 113
9. Güllü, O. "Barrier modification by methyl violet organic dye molecules of Ag/P-Inp structures." Euro J Interdiscip Stud (2016) 2: 3
10. Amorim, CA, EP Bernardo, ER Leite and AJ Chiquito. "Effect of inhomogeneous Schottky barrier height of SnO2 nanowires device." Semicon Sci and Tech (2018) 33: 055003
11. Güllü, O. "Impedance and interface properties of Al/Methyl-Red/p-InP Solar Cell." Int J Photoenergy (2009): 374301
12. Chakraborty, S and NB Manik. "Improvement of electrical and photovoltaic properties of methyl red dye based photoelectrochemical cells in presence of single walled carbon nanotubes." Front. Optoelectron (2015) 8: 289
13. Yang, M, X Li, W Wang and S Zhang, et al. "Adsorption of methyl blue from solution by carboxylic multi-walled carbon nanotubes in batch mode." Desalination and Water Treatment (2019) 159: 365
14. Liu, Y, G Cui, C Luo, and L Zhang, et al. "Synthesis, characterization and application of amino-functionalized multi-walled carbon nanotubes for effective fast removal of methyl orange from aqueous solution." RSC Adv (2014)4: 55162
15. Ehyaee, M, F Safa and S Shariati. "Magnetic nanocomposite of multi-walled carbon nanotube as effective adsorbent for methyl violet removal from aqueous solutions: Response surface modeling and kinetic study." Korean J. Chem. Eng (2017) 34: 1051
16. Shen Xue, J, W Long, D Han Yu and L Zheng. "Optical limiting of a methyl-red dye doped suspended carbon nanotube mixture." Acta Physica Sinica (2010) 59: 2532
17. Arshadi, M, MK Abdolmaleki, F Mousavinia and A Khalafi-Nezhad, et al. "Degradation of methyl orange by heterogeneous Fenton-like oxidation on a nano-organometallic compound in the presence of multi-walled carbon nanotubes." Chem Eng Res and Des (2016) 112: 113
18. Sze, SM and KK Ng. "Physics of semiconductor devices." 3rd edn. Wiley, New York (2007): 159–181
19. Sen, S and NB Manik. "Effect of Carboxyl-Functionalized Single Walled Carbon

Nanotubes on the Interfacial Barrier Height of Malachite Green Dye Based Organic Device." Phys. Int (2019) 10: 1

20. Sen, S and NB Manik. "Effect of Different Sized Multi Walled Carbon Nanotubes on the Barrier Potential and Trap Concentration of Malachite Green Dye Based Organic Device." Adv in Mat Sci (2020) 20: 16
21. Banerjee, A, C Ghosh and P Chakraborty. "Methyl red/ indium-tin-oxide organic diode: An electrical and optoelectronic study." Microelect Eng (2019) 216: 111053
22. Abioye, OP, VT Iroegu and SA Aransiola. "Biodegradation of methyl red by staphylococcus aureus Isolated from Waste Dump Site." J Envi Sci and Tech (2015) 8: 131
23. Sarkar, P, ANM Fakhruddin, Md Kamruzzaman Pramanik and A Al- Mahin. "Decolorization of methyl red by staphylococcus arlettae pf4 isolated from garden soil." Int J Envi (2011) 1: 25
24. Shugrue, CR, HH Mentzen and BR Linton. "A colorful solubility exercise for organic chemistry." J. Chem. Educ (2015) 92: 135
25. Sen, S and NB Manik. "Study on the Effect of 8 nm Size Multi Walled Carbon Nanotubes (MWCNT) on the Barrier Height of Malachite Green (MG) Dye Based Organic Device." Int. J. Adv. Sci. Eng (2020) 6: 23
26. Svensson, J and EEB Campbell. "Schottky barriers in carbon nanotube-metal contacts." J. Appl. Phys (2011) 110: 111101
27. Parameshwari, PM, BV Shrisha, P Satyanarayana B and K Gopalakrishna N. "Electrical behavior of CdS/Al Schottky barrier diode at low temperatures." Materials Today: Proceedings (2016) 3: 1620
28. Al-Ta'ii, HMJ, YM Amin and V Periasamy. "Calculation of the electronic parameters of an Al/DNA/p-Si schottky barrier diode influenced by alpha radiation." Sensors (2015) 15: 4810
29. Sen, S and NB Manik. "Effect of back electrode on trap energy and interfacial barrier height of crystal violet dye-based organic device." Bull. Mater. Sci. (2020) 43: 60
30. Sen, S and NB Manik, "Correlation between barrier potential and charge trapping under the influence of Titanium Di oxide nanomaterials in organic devices." Results in Mat (2020) 8: 100145
31. Yildirim, M. "Determination of Contact Parameters of Au/n-Ge Schottky Barrier Diode with Rubrene Interlayer." J. Polytech (2017) 20: 165
32. Sen, S, NB Manik, "Effects of fullerene nanoparticles and fullerite nanoparticles on the charge injection mechanism of methyl red dye based organic device." AIP Advances (2020) 10: 095216
33. Norde, H. "A modified forward I-V plot for Schottky diodes with high series resistance." J. Appl. Phys (1979) 50: 5052
34. Yakuphnoglu, F, M Shah and AW Farooq. "Fabrication and Characterization of GaN/Polymer Composite p-n Junction with PEDOT Nanoparticle Interface Layer." Acta Physica Polonica A (2011) 120: 558
35. Kocyigit, A, M Yılmaz, S Aydoğan and Ü Incekara. "The effect of measurements and layer coating homogeneity of AB on the Al/AB/p-Si devices." J. Alloys Compd (2019) 790: 388
36. Türüt, A. "Determination of barrier height temperature coefficient by Norde's method in ideal Co/n-GaAs Schottky contact.". Turk J Phys (2012) 36: 235
37. Fukui, K. "Theory of orientation and stereo selection." Berlin Springer (1975): pp. 50-75
38. Sen, S and NB Manik. "Effect of Zinc Oxide (ZnO) Nanoparticles on Interfacial Barrier Height and Band Bending of Phenosafranin (PSF) Dye-Based Organic Device." J Elec Materi (2020) 49: 4647
39. Güllü, O and A Türüt. "Electronic parameters of MIS Schottky diodes with DNA biopolymer interlayer." Materials Science-Poland (2015) 33: 593
40. Kudryk, YY, VV Shynkarenko, VS Slipokurov, and RI Bigun, et al. "Determination of the Schottky barrier height in diodes based on Au–TiB2–n-SiC 6H from the current-voltageand capacitance-voltage characteristics." Semiconductor Physics, Quantum Electronics & Optoelectronics (2014) 17: 398
41. Arkhipov, VI , U Wolf and H Bässler. "Current injection from a metal to a disordered hopping system. II. Comparison between analytic theory and simulation." Physical Review B (1999) 59: 7514
42. Ayatollahi, MR, S Shadlou, MM Shokrieh and M Chitsazzadeh. "Effect of multi-walled carbon nanotube aspect ratio on mechanical and electrical properties of epoxy-based nanocomposites." Polymer Testing (2011) 30: 548
43. Zare, Y and KY Rhee. "Calculation of the Electrical Conductivity of Polymer Nanocomposites Assuming the Interphase Layer Surrounding Carbon Nanotubes." Polymers (2020) 12: 404

How to cite this article: Sudipta Sen and N. B. Manik. "Effect of Different Sized Multi Walled Carbon Nanotubes on the Parameters Affecting the Charge Injection Process of Methyl Red Dye Based Organic Device". J Material Sci Eng 10 (2021): Pgage 01-05