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 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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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 (-CH₃) groups, which is called an amine functional group. Molecular formula of this dye is C₁₅H₁₅N₃O₂ [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.

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.

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)

\[ I = AA'T^2 \exp \left( -\frac{\Phi_b}{kT} \right) \left( \exp \left( \frac{qV}{nKT} \right) - 1 \right) \]

In both the equations, A=1.5 cm² 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)

\[ \Phi_b = \frac{1}{A} \ln \left( \frac{d_1^2}{d_2} \right) \]

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

\[ n = -\frac{\beta}{\frac{d_1^2}{d_2}} \]

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.
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).

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

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

\[
\phi_b = F(V_{min}) + \frac{2}{\beta} - \frac{1}{\beta}
\]  

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

Figure 4. In V - 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]

\[
F(V) = \beta \frac{-\ln(\frac{V}{V_c})}{\gamma} + 1
\]

\(\gamma\) 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]

\[
\phi_b = F(V_{min}) + \frac{2}{\beta} - \frac{1}{\beta}
\]

The minimum function value F (V_{min}) corresponds to the minimum voltage \(V_c\). 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.

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

\[
U(x) = \phi_b - \frac{q}{2\pi\varepsilon_0}\frac{1}{x}\cdot eFx
\]

\(x=\) 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 field 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.

### 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.

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