PAPER

Study on the effect of singlewalled carbon nanotubes on junction properties of Safranin - T dye-based organic device

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Abstract

In this work, junction properties of metal-organic dye contact have been studied and alteration of these properties in presence of single walled carbon nanotubes has been observed. Junction properties of metal-organic interface significantly influence the device performance. Present work studies barrier potential and trap energy under the influence of single walled carbon nanotubes. Barrier inhomogeneity and the effect of image charge on lowering of barrier potential have also been studied. Formation of the organic device has been done by sandwiching Safranin - T dye in between two electrodes which are Indium Tin Oxide coated glass substrate and Aluminium respectively. Charge flow at the metal–organic layer interface has been analyzed by Richardson–Schottky thermionic emission theory. Both barrier potential and trap energy have been estimated from the steady-state current-voltage characteristics of the device. The incorporation of single walled carbon nanotubes lowers both of these parameters results in improvement of current flow at the metal-organic contact.

1. Introduction

Cost-effectiveness, mechanical flexibility and versatile chemical synthesis methods make organic materials very promising for electronic and optoelectronic devices [1–3]. The presence of π-bonded electrons arising from sp2-hybridization states of carbon atoms allows organic materials to absorb light across the entire solar spectrum [4]. Although there are certain advantages of organic materials, some constraints put them at a disadvantage. One of the major constraints is the existence of high barrier potential and barrier inhomogeneity at the metal-organic interface when these organic materials are sandwiched in between two metal electrodes. The presence of high barrier potential and barrier inhomogeneity does not allow a significant amount of mobile charge carriers to flow at the interface which results in a poor charge injection process from metal to organic semiconductor. Charge carrier trapping also plays an important role in the charge injection process of these organic devices. Organic devices are prone to traps that cause high recombination of charge carriers. Attention is required to reduce charge carrier trapping and high barrier potential in addition to barrier inhomogeneity so that the charge injection process can be improved which will result in conductivity enhancement and improved performance of the device. Image carriers are also related to the barrier potential in organic devices and some detailed study is required regarding the effect of image charge carriers on barrier potential.

In this work, we have studied the barrier inhomogeneity, barrier potential, barrier lowering due to image charge carriers and charge carrier trapping and have also observed the effect of single walled carbon nanotubes (SWCNT) on these parameters. Safranin - T dye has been used as organic material and it has been sandwiched in between two electrodes namely ITO coated glass substrate and aluminium to form the Safranin - T dye-based organic device. It has been observed that barrier inhomogeneity, barrier potential and trap energy are interrelated to each other and incorporation of SWCNT reduces these parameters resulting in an improved charge carrier injection process from metal to organic semiconductor. Image charge carriers also attribute to the...
barrier potential lowering which also gets more reduced with the incorporation of SWCNT. High aspect ratios of SWCNT allow it to work as conductive filler which plays a significant role in reducing these parameters.

Current-voltage (I-V) characterization of the prepared organic device has been done to estimate both charge carrier trapping and barrier potential. It has been found out that at ITO/Safranin - T dye interface, ohmic contact has been formed and at Safranin - T/Al interface Schottky contact has been formed. I-V characteristics of the device have been analyzed by using Richardson—Schottky model of thermionic emission [5, 6]. To study the barrier inhomogeneity and its correlation with barrier potential, a plot of apparent barrier potential with respect to 1/2kT has also been done. To understand the charge transport mechanism of organic dye-based devices, sometimes the structure of Organic field-effect transistors (OFETs) are used in the analogy which is basically three-terminal electronic devices, including source, drain, and gate electrodes, with a thin layer of organic semiconductor as the active layer in between dielectric and source/drain [7]. The principle of operation of OFETs can also be analyzed in terms of Silicon MOSFET in which the carrier escape time by thermionic emission is also dependent on the barrier potential [8].

2. Materials and sample preparation

Safranin—T is a cationic azine dye and its empirical formula is \( \text{C}_{20}\text{H}_{19}\text{ClN}_{4} \). Its molecular weight is 350.84 g/mol. This dye has been procured from Sigma—Aldrich. Figure 1(a) displays the structure of Safranin—T. Figure 1(b) shows SWCNT which was obtained from Sisco Research Laboratory (SRL), India. SWCNT is of 5 \( \mu \text{m} \) length and 1 nm diameter. We have also used Poly vinyl alcohol (PVA) as it is used as a transparent inert binder. PVA was obtained from S. D. Fine Chem. Ltd, Boisar, India. Figure 1(c) shows the structure of PVA. Figure 1(d) shows the optical absorption of Safranin-T dye. The absorption occurs from 480 to 550 nm and the absorption peak is located at 520 nm [10]. The estimated value of the bandgap of this dye is found to be 1.98 eV [11, 12].

In one of our earlier works [13], we have mentioned the PVA solution-making technique. At first, the Safranin—T dye solution is prepared without any nanoparticle. Now 1 mg of Safranin—T is added to the PVA solution and stirred for 30 min. One part of this solution is kept aside in a pre-cleaned test tube. Then in the other portion of Safranin—T dye solution, 1 mg SWCNT is added and well stirred. After preparing the solutions, the Safranin—T dye solution without any nanoparticle is spin-coated at 2500 rpm speed and dried at 4000 rpm speed on a pre-cleaned Indium Tin Oxide (ITO) coated glass substrate. Similarly, the solution is deposited on the Aluminum (Al) and then ITO-coated glass and Al are sandwiched together to form the Safranin—T cell without any nanoparticle. Similarly, Safranin—T solution with SWCNT is also spin-coated separately to prepare the Safranin—T cell consisting of SWCNT. To characterize both these cells, they are kept in a vacuum for 12 hours to dry. Figure 2 expresses the schematic of the Safranin—T dye-based organic device. The thickness of ITO coated glass electrode, MR dye with SWCNT and Aluminium electrodes are 1.5 \( \mu \text{m} \), 2 \( \mu \text{m} \) and 1.2 \( \mu \text{m} \) respectively.

3. Measurements

Measurement of steady-state current-voltage (I-V) characteristics of the prepared two cells has been done by using Keithley 2400 source measure unit. In one of our earlier works, the measurement techniques of I-V characteristics have been discussed in detail [14]. The applied voltage is varied from 0 to 6 V in steps of 0.2 V with a delay of 1000 ms. Room temperature was kept at 25 °C during the experiment.

4. Results and discussion

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

\[
I = A A^* T^2 \exp \left( - \frac{q \phi_b}{kT} \right) \exp \left( \frac{qV}{n kT} \right) \left[ 1 - \exp \left( - \frac{qV}{kT} \right) \right] (1)
\]

\( I_0 \) is the saturation current, which is expressed in equation (2)

\[
I_0 = A A^* T^2 \exp \left( - \frac{q \phi_b}{kT} \right) (2)
\]

The interfacial barrier height at metal-organic semiconductor device can be determined from equation (2), which is shown in equation (3)
\[ f = kT q \ln \left( \frac{A^2T^2}{I_0} \right) \]
$q$ is the charge of an electron, $V$ is the applied voltage, $A$ is the device area, $k$ is the Boltzmann’s constant, $T$ is the absolute temperature in Kelvin scale, $A^*$ is the effective Richardson constant, $n$ is the ideality factor, $\phi_b$ is the barrier potential and $I_0$ is the saturation current $[15–22]$. 

The term $\frac{q}{kT}$ can be replaced by the term $\beta$.

The interfacial barrier at zero bias can be expressed as shown in equation (4)

$$\phi_b = \frac{1}{\beta} \ln \left( \frac{AA^*T^2}{I_0} \right)$$  \hspace{1cm} \text{(4)}$$

The dark I-V plots of devices without and with SWCNTs have been shown in figure 3. Threshold voltage has been calculated from figure 3.

For calculating barrier potential at the metal-organic junction, the semilogarithmic plots of figure 3 have been depicted in figure 4.

Considering barrier inhomogeneities at the metal-organic interface, current flow can be expressed in equation (5) $[23]$. 

![Figure 3. Current-voltage plot of the organic device without and with SWCNT.](image3)

![Figure 4. In I-V plot of the organic device without and with SWCNT.](image4)
Where,

\[ f_{s0} = -P_{12} \exp \left( \frac{2b}{2s_0^2} \right) \]

Where, \( P(\phi_b) \) is Gaussian distribution of barrier potential at the metal-organic interface, the pre-exponential term is normalization constant and \( s_0 \) is a standard deviation from mean barrier potential \( \phi_0 \) suggested by Werner and Guttler [24, 25].

The current of the device considering Gaussian distribution of barrier potential has been expressed in equation (7) which is a combination of equations (1) and (5)

\[ I(V) = \frac{A^*T^2}{\sqrt{2\pi}s_0} \exp \left( -\beta \left( \phi_0 - \frac{\beta s_0^2}{2} \right) \right) \exp \left( \frac{\beta V}{n} \right) \left| 1 - \exp(-\beta V) \right| \]

Where,

\[ I_0 = A^*T^2 \exp(-\beta \phi_a) \]

Considering Gaussian distribution of barrier potential at the metal-organic interface, \( I_0 \) is saturation current, \( \phi_a \) is apparent barrier potential [26, 27].

The apparent barrier potential can be related to the standard deviation from mean barrier potential as shown in equation (9) [28]

\[ \phi_a = \phi_0 - \frac{\beta s_0^2}{2} \]

Where, \( \beta = \frac{q}{kT} \)

Equation (7) is identical to equation (1) except that equation (7) consists of \( \phi_a \) instead of \( \phi_b \). The data fitting of equation (7) is similar to that of equation (1).

Figure 5 shows the plot of apparent barrier potential with respect to 1/2kT. From equation (9), it can be observed that apparent barrier potential is reliant on \( \phi_0, s_0 \) and also on the temperature. In figure 5, the value of temperature has been varied from 290 K to 340 K. Figure 5 attributes to the fact that the I-V behavior of the Schottky contact is dependent on the temperature. The linearity of the plot in figure 5 remains in good agreement with the thermionic emission over a Gaussian barrier height distribution.

The advantage of the linear plot in figure 5 is that the intercept at the axis of ordinate in this plot of apparent barrier potential versus 1/2kT determines the mean value of barrier potential \( \phi_0 \) and the slope determines the standard deviation from mean barrier potential \( s_0 \). The fitting process to the experimental values was used to indicate the presence of interface inhomogeneity in the fabricated device structure. Intercept and slope of figure 5 give the value of \( \phi_0 \) and \( s_0 \). It has been estimated that the values of \( \phi_0 \) and \( s_0 \) are 0.75 eV and 0.17 eV respectively without SWCNT and both the values are reduced to 0.70 eV and 0.13 eV respectively in presence of SWCNT. Basically \( s_0 \) signifies barrier inhomogeneity. Calculated values of \( s_0 \) show a significant presence of
Barrier inhomogeneity at Safranin—T/Al Schottky contact. The charge injection process of the device will be improved as long as the value of barrier inhomogeneity is kept as low as possible. The presence of SWCNT reduces the value of barrier inhomogeneity at the Schottky contact which can result in an improved charge injection mechanism at the interface.

Barrier lowering effect happens for image charges are also discussed in this work. Effective barrier potential considering the image charge effect can be expressed as shown in equation (10)

\[ U(x) = \phi_b - \frac{e^2}{16\pi\varepsilon\varepsilon_0 x} - eF x \]  

\[ x = \text{distance from the interface, } F = \text{applied field (V/cm), } e = \text{charge of an electron, } \varepsilon = \text{dielectric constant, } \varepsilon_0 = \text{absolute dielectric permittivity of classical vacuum and } \phi_b = \text{barrier potential without image charge effect} [29]. \]

Effective barrier potential considering image charge is calculated in the absence and in presence of SWCNT. The value of the dielectric constant is 3.2 and the distance from the interface is 2 nm. The applied field is $10^4$ V/cm. The estimated values of effective barrier potential considering image charge effect without and with SWCNT are 0.79 eV and 0.74 eV respectively.

Trap energy has been measured by using the ln I- ln V plot which is shown in figure 6 without and with SWCNT respectively.

The trap energy can be written as expressed in the following equation (11)

\[ E_t = \text{mK}T \]

Where \( E_t = \text{trap energy, } m = \frac{T_c}{T}, T_c = \text{characteristic temperature, } k \text{ is the Boltzmann’s constant [30]. } m \text{ is calculated from the ln I- ln V plot of figure 6.} \]

The values of threshold voltage, trap energy, barrier potential without and with considering image charge effect and barrier inhomogeneity of organic devices in the absence and in presence of SWCNT are shown in table 1.

5. Conclusions

Present work studies the different junction properties at the metal–organic interface such as concentration of traps, barrier potential without and with considering image charge effect and barrier inhomogeneity which significantly affects the charge injection process from metal to organic semiconductor. The effect of the incorporation of SWCNT on these parameters has also been analyzed. From the current-voltage (I-V) characteristics of the device, it has been found out that in presence of SWCNT, the concentration of traps, barrier potential without and with considering image charge effect have been decreased. Trap energy and barrier potential have been lowered from 0.059 eV to 0.041 eV and from 0.81 eV to 0.77 eV respectively in presence of SWCNT. Image charge effect on barrier potential has also been observed and with SWCNT it has also been reduced from 0.79 eV to 0.74 eV. Barrier inhomogeneity at the metal–organic interface has also been lowered.
| Device | Threshold voltage (V) | Value of m | Trap energy (eV) | Barrier potential (eV) | Effective barrier potential considering image charge (eV) | Barrier inhomogeneity (eV) |
|--------|----------------------|------------|-----------------|----------------------|--------------------------------------------------------|--------------------------|
| ITO/Safranin-T/Al | 4.00 | 0.159 | 0.059 | 0.81 | 0.79 |
| ITO/Safranin-T + SWCNT/Al | 3.25 | 0.001 | 0.041 | 0.77 | 0.74 |

Table 1: Calculation of threshold voltage, trap energy, barrier potential without and with considering image charge effect and barrier inhomogeneity of organic devices in the absence and presence of SWCNT.
due to the presence of SWCNT from 0.17 eV to 0.13 eV. All these parameters greatly affect the charge injection process at metal-organic contact and interdependency among these parameters is the significant observation of this work. Lowering of these parameters in presence of SWCNT due to its high aspect ratio is also a noteworthy finding as it will improve the charge flow at the contact of metal-organic dye resulting in better conductivity and device performance. Better conductivity can be achieved with much lower operating voltages as the threshold voltage of the prepared organic device has also been lessened in presence of SWCNT.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflict of interest

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

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