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Effect of back electrode on trap energy and interfacial barrier height of crystal violet dye-based organic device

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Abstract. In this work, we have studied the effect of aluminium-coated mylar (Al–M) sheet-based back electrode and aluminium (Al)-coated back electrode on trap energy (E_t) and barrier height (ϕ_b) of crystal violet (CV) dye-based organic device. Two devices have been prepared using two different back electrodes. In both the devices, ITO-coated glass is used as front electrode. Both the organic devices have been prepared by using spin-coating techniques. We have measured the steady state current–voltage (I–V) characteristics of these devices to estimate the trap energy (E_t) and barrier height (ϕ_b) of the devices. Because of the insertion of a reflecting back electrode, the charge carriers are confined in the active layer, which reduces the E_t from 0.044 to 0.034 eV and ϕ_b is reduced from 0.80 to 0.77 eV. The barrier height is also estimated by using another alternative method, which is known as Norde method. By using Norde method, ϕ_b is estimated, which reduces from 0.83 to 0.79 eV in the presence of reflecting back electrode. Both the methods show good consistency with each other. The reductions of these parameters indicate the enhancement of charge injection through the metal-organic dye interface. With the use of polished back electrode in the CV dye-based organic device, it is possible to modify the barrier height and trap energy and thereby modifies the conductivity.

Keywords. Barrier height; back electrode; crystal violet dye; trap energy.

1. Introduction

Nowadays, the organic/polymer materials are being widely investigated to develop different electronic and optoelectronic devices. Organic devices are more flexible, light weight, cost effective and can be easily fabricated over a large area [1,2]. Despite these advantages, there are also certain limitations to organic devices. One of the major limitations is the high barrier height (ϕ_b) at metal-organic layer interface. Due to high barrier height, the charge injection from metal to organic material is low, which attributes to higher trap energy (E_t). Attempts are necessary to reduce the barrier height and concentration of traps to improve the charge injection at the interface of metal-organic layer and thereby to reduce the threshold voltage. The charge injection process is strongly dependent on the barrier height at metal-organic layer interface [3,4]. 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 [5,6]. Generally, in these organic devices, transparent glass plates with high work function is used as front electrode and materials with low work function is used as back electrode. There is not considerable study on the effect of back electrode on the barrier height and trap energy of these organic devices. In this work, we have studied the effect of two different counter electrodes namely aluminium-coated mylar (Al-M)-sheet based back electrode and aluminium (Al)-coated back electrode on the barrier height and trap energy of crystal violet (CV) dye-based organic devices. ITO-coated glass is used as front electrode. It has been found out that the barrier height and trap energy have been reduced significantly in the presence of Al–M counter electrode compared to Al back electrode. Reduction of both barrier height and concentration of traps allows the improvement of charge injection mechanism at metal-organic dye interface and thereby the conductivity. It also allows the device to turn on at much lower voltages.

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. Basically, the barrier height is caused by the difference between the fermi energy level of metal and the energy band of organic material [7]. The flow of injection-limited current at metal-organic layer interface generally occurs at below threshold voltage region. Injection current usually consists of both thermionic-injection current and field-induced tunnelling current. At the low voltage region, field induced tunnelling current is so small that it can be neglected. For this reason, Richardson–Schottky (RS) model of thermionic emission is used to characterize the device at below threshold voltage region [8,9].

2. Materials and sample preparation

Figure 1 shows CV dye, which is procured from Loba Chemie Private Ltd, India. CV dye with chemical formula

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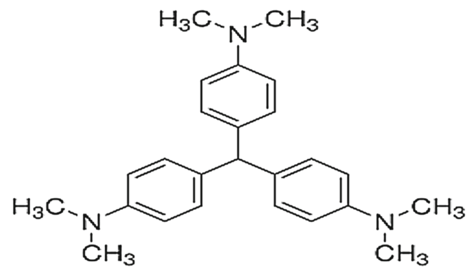

Figure 1. Structural diagram of crystal violet dye.

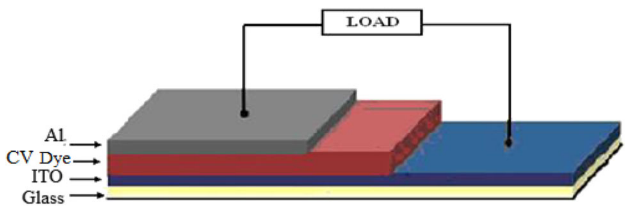

Figure 2. Schematic diagram of a sandwich-type organic device, in which CV dye is sandwiched inbetween the two electrodes.

($C_{25}N_3H_{30}Cl$) is a cationic dye that dissociates in aqueous solution to give a positively charged coloured ion [10]. CV dye is used as optical active material. ITO-coated glass with surface resistance of 15–25 ohms cm^{-2} is bought from Sigma-Aldrich. The other back electrode materials like Al and highly polished Al–M sheet are bought from the local market. As mentioned, Al–M sheet has higher reflectivity than ordinary Al. On the mylar polyester film, Al is coated with an average coating thickness of 25 μm used in our case.

To form CV dye solution, CV dye was recrystallized twice from ethanol–water mixture and mixed with polyvinyl alcohol (PVA) (S D Fine Chem. Ltd., Boisar, India) used as a transparent inert binder. In a clean test tube, 5 g of PVA was mixed with 10 cc of double distilled water and stirred to make a transparent viscous solution of PVA. Two milligrams of CV dye is mixed with this solution. PVA was used here as an inert transparent binder to form the stable film of the dye. The electrodes were cleaned in a chloroform solution and dried under vacuum. With the help of a viscous gel-like solid solution, the thin film is sandwiched between transparent ITO-coated glass plate and another Al-coated mylar sheet as reflecting back surface. Spin coating unit is used to form the film of uniform thickness. Another thin film is also formed with the help of the above procedure, where ITO-coated glass plate and Al plates are used as counter electrode. The complete cells are vacuum dried for about 12 h. The structure of the device is shown in figure 2.

3. 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 volts in steps of 0.5 volt with 1000 ms delay. The experiments have been done in the clean open atmosphere of the laboratory at a room temperature of 25°C.

4. Results and discussion

The current through a metal-organic semiconductor interface due to thermionic emission can be expressed as [11–15]:

$$I = I_0\left(\exp\left(\frac{qV}{nkT}\right) - 1\right), \tag{1}$$

where I_0 is the saturation current, which is given by

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

and

$$A^* = \frac{4\pi qm^*k^2}{h^3}. \tag{3}$$

Here q is the electron charge, V the applied voltage, A the area of the device, k the Boltzmann's constant, T the absolute temperature, A^* the effective Richardson constant of 120 A m^{-2} K^{-2} for crystal violet dye, ϕ_b is the interfacial barrier height obtained from the extrapolation of I_0 in the semi log forward bias $I-V$ characteristics and n the ideality factor.

The interfacial barrier height of metal-organic semiconductor device can be determined from the following relation [16,17]:

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

The dark $I-V$ characteristics of CV dye-based organic device in the presence of Al–M back electrode and Al back electrode

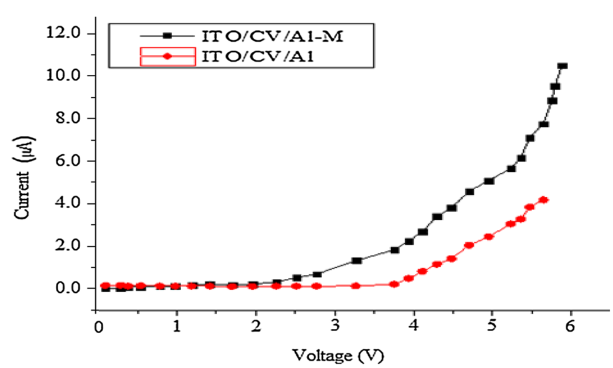

Figure 3. Dark I–V characteristic of ITO/CV/Al-based organic device and ITO/CV/Al–M-based organic device.

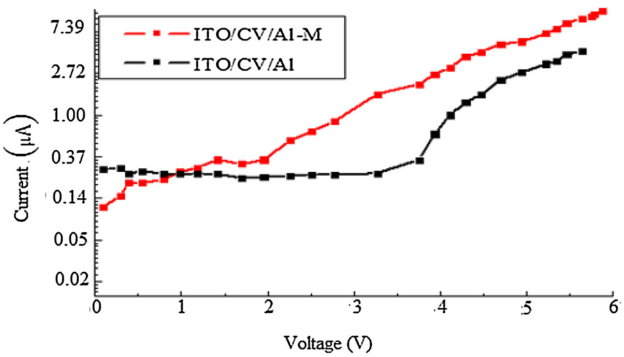

Figure 4. Semi-logarithmic plot of ITO/CV/Al-based organic device and ITO/CV/Al–M-based organic device.

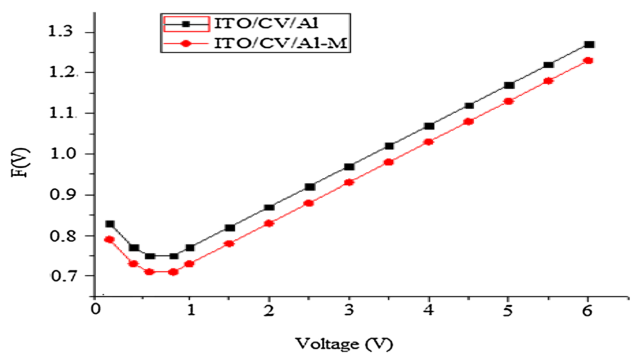

Figure 5. Norde function $F(\mathrm{V})$–V plot of ITO/CV/Al structure and ITO/CV/Al–M structure.

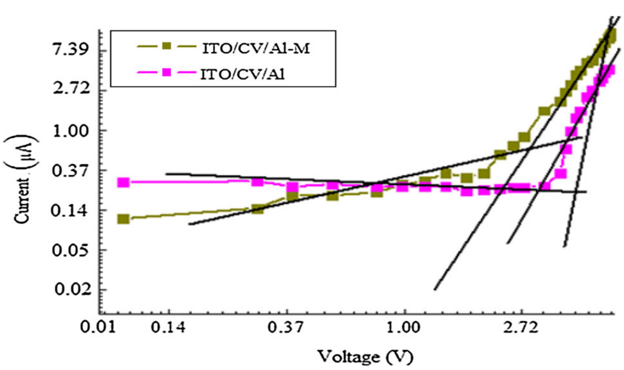

Figure 6. ln I–ln V plot of ITO/CV/Al structure and ITO/CV/Al–M structure.

are shown in figure 3. The current flow in the organic device in the presence of Al–M back electrode, improves significantly compared to Al back electrode.

To obtain the interfacial barrier height, we have plotted the semilogarithmic plot of current–voltage characteristics of the ITO/CV/Al-based organic device and ITO/CV/Al-M based organic device and which is shown in figure 4. From the semilogarithmic plot of the two devices, it has been found out that the barrier height has been reduced in ITO/CV /Al-M based organic device in comparison to ITO/CV/Al-based organic device.

The interfacial barrier height can also be calculated using Norde function. In this Norde function, the relationship between the function $F(\mathrm{V})$ and the measured current $I(\mathrm{V})$ can be expressed in equation (5) [18,19]. $I(\mathrm{V})$ is the current measured from $I-V$ characteristics of the device.

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

where X is the first integer greater than n. The value of current $I(V_0)$ corresponding to minimum value of Norde function $F(V_0)$, where V_0 is the corresponding voltage.

In figure 5, for both ITO/CV/Al structure and ITO/CV/Al–M structure, the interfacial barrier height has been calculated by using the following equation (20). V_0 is estimated from the plot which is shown in figure 5.

$$\phi_{\mathrm{b}} = F(V) + \frac{V_0}{X} - \frac{kT}{q}. \tag{6}$$

To calculate the trap energy, we have plotted the ln I–ln V curves of the both ITO/CV/Al structure and ITO/CV/Al–M structure in figure 6.

The trap charge concentration (N_{t}) can be expressed as

$$N_{\mathrm{t}}(\epsilon) = N_0 \exp\left(-\frac{\epsilon}{kT_{\mathrm{c}}}\right), \tag{7}$$

where t refers to traps, ϵ refers to the depth of traps below conduction band mobility edge and T_{c} is the effective temperature of the trap distribution (i.e. $T_{\mathrm{c}} = E_{\mathrm{c}}/k$, where E_{c} is the

Table 1. Calculation of of barrier height and trap energy of ITO/CV/Al structure and ITO/CV/Al–M structure.

Device	Value of m	Trap energy E_{c} (eV)	Barrier height from $I-V$ characteristics (eV)	Barrier height using Norde function (eV)
ITO/CV/Al	1.71	0.044	0.80	0.83
ITO/CV/Al–M	1.30	0.034	0.77	0.79

characteristic trap energy). $m = T_c/T$, where T is the room temperature. The trap energy can be written as [21]:

$$E_c = mkT. \tag{8}$$

The values of barrier height and trap energy of ITO/CV/Al structure and ITO/CV/Al–M structure are shown in table 1.

5. Conclusions

In this article, we have studied the effect of back electrode on the interfacial barrier height and trap energy of CV dye-based organic devices. Values of interfacial barrier height for CV dye-based organic devices in presence of two different electrodes are estimated by analysing the plot of I–V characteristics and also by using Norde method. Both the methods show good consistency with each other. It can be said that in presence of Al–M back electrode, the barrier height and the trap energy at the metal-organic layer interface have been reduced significantly compared to Al back electrode. Reduction of injection barrier and trap energy improves the charge injection in this CV dye-based organic device which results in better conductivity.

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