Bull. Mater. Sci. (2021) 44:92
https://doi.org/10.1007/s12034-020-02301-5

Interpretation of trap-assisted conduction with estimation of electrical parameters of thin indigo film-based semiconducting device

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MS received 1 May 2020; accepted 11 August 2020

Abstract. Trap-assisted charge conduction mechanism of indigo dye-based organic Schottky diode has been reported in present investigation. Signature of trapping probability has been encountered by *G*(*I*–*V*) *vs*. *V* characteristics. Non-monotonous alignment of aforementioned characteristics emphasizes the existence of trapping states in its charge conduction process. Trap energy (E_t) has also been obtained for the device. Estimated value of E_t is 0.073 eV which indicates improved outcome of 16.09 and 3.95%, when compared to other two previously reported organic dyes. Electrical parameters of the device have been estimated by analysing its *I*–*V* relationship. Cheung–Cheung method has been used to calculate the series resistance (R_s), ideality factor (n) and barrier height (ϕ) of the device. Obtained value of R_s, n and ϕ are 0.127 kΩ, 39.87 and 0.694 eV, respectively. Analysing the obtained data, Richardson–Schottky effect on charge transport mechanism has been interpreted in this context.

Keywords. Natural organic dye; charge transport; series resistance; trap energy; ideality factor.

1. Introduction

Non-conventional materials are recently achieving much more attraction because of their electrical as well as promising photovoltaic properties. Variation of their crystalline anisotropic critical molecular structures and interesting optoelectronic properties, metal-semiconductor interfacial transition, photo-induced charge transformation mechanism adds much importance to carry out more research over such material-based devices [1–3]. Such materials under consideration can basically be utilized for their highly availability, low cost, easy sample preparation procedure, etc. [4–6]. But rapid development of such kind of semiconducting substances is getting challenged for their amorphous disordered nature. Due to the disordered structure of organic semiconductor, trap-assisted charge conduction becomes dominant into the device [6,7]. Trap state is basically the energy state below the state of charge transport energy arises due to spatial disorder which has a significant impact on all herbal organic dye-based devices. Moreover, field effected lower mobility with respect to the hole mobility is attributed to the presence of huge amount of trap states in organic semiconductors. Current–voltage (*I*–*V*) relationship is distorted distinctly with the existence of high concentration of trapping [8,9]. So, knowledge over trap states and their distribution is very important because the parameter denotes the amount of imperfection into the active thin film made of organic dye. Analysing the logarithmic curve of *I*–*V* plot, trap energy (E_c) has been measured here, in this paper. During conduction, E_c produces high value of series resistance (R_s) at the bulk region of the device. R_s is another influential parameter which directly impacts on device efficiency. The main reason of deviation of *I*–*V* plot at high voltage regime is the existence of high value of R_s. Cheung–Cheung method is very popular method which is used to measure the value of R_s along with ideality factor (n) and barrier height (ϕ). The aforementioned method has also been introduced here to estimate the following parameters [10–12]. Schottky effect in electronic structures and charge conduction process and hence, related parameters have also been discussed in the rest of the paper. Natural organic semiconductor indigo dye may have wide possibility in this regard and that has been reported with quantitative information in the present investigation. Even the material under experiment shows promising results for application in electronic devices when compared to other semiconducting material. Effectiveness of the dye in electronic devices compared to other reported dyes has also been mentioned in the present work. The paper will be fruitful enough for further research over its application on

Published online: 15 April 2021

other electronic as well as photovoltaic devices, photo diode, photo collector and other photo-sensitive devices also.

2. Experimental

This section has been divided into two parts, such as (i) material description and (ii) details of the experiment.

2.1 *Material description*

Indigo dye is a herbal compound with distinctive blue colour combination. Chemical formula for indigo is $C_{16}H_{10}N_2O_2$. Indigo is a natural dye extracted from the leaves of certain plants. A variety of plants have provided indigo throughout history, but most natural indigo was obtained from those in the genus Indigofera, which are native to the tropics. The primary commercial indigo species in Asia is true indigo. This dye is taken into consideration for its significant semiconducting properties, good quantum yield and quite satisfactory spectral response [2,5]. The dye shows the latest peak of absorption spectra at 268 nm at UV light region, whereas characteristic peak can be observed at 612 nm in the visible light range [2,13]. Reported optical band gap of the dye is 1.689 eV [5]. Figure 1 shows the chemical structure of indigo dye.

2.2 *Experimental method*

Ten wt% indigo solution was prepared from the purchased indigo powder. The mentioned solution was stirred well for 2 h at room temperature to prepare homogeneous form of solution. Al and Cu electrodes were thoroughly cleaned for 15 min by using distilled water in ultrasonic cleaner. The electrodes are then plasma-cleaned for 5 min after drying. Thermal deposition process was introduced on both substrates at a pressure of 5.5×10^{-5} mbar and rate of deposition was kept 0.1 nm s^{-1} in this process. Thin film of indigo dye with few µm range of thickness was allowed to be deposited by spin-casting process with the angular rotation of 2000 rpm in the next stage and hence, sandwiched between the substrates. Finally, the prepared device is placed at 50°C for 1 h to remove the moisture of the evaporated film (figure 2).

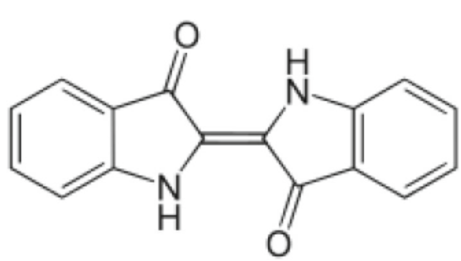

Figure 1. Chemical structure of indigo dye.

3. Results and discussion

To analyse the conduction-related properties of indigo dye-based herbal diode, the current–voltage (*I–V*) characteristics have been measured. A non-linear behaviour of diode has also been observed in the characteristics. This is due to R_s which limits the linearity of the plot. So, with minimizing the effect of R_s, greater range of linearity in semi log current–voltage (*I–V*) plot can be obtained.

The *I–V* characteristics of organic diode is explained here from the relation [9–11]:

$$I = I_0 \exp\left(\frac{q(V - IR_s)}{nKT}\right), \quad (1)$$

where IR_s is the drop of voltage across R_s and I_0 is the saturation current given by

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

where q is electronic charge, ϕ the barrier height, A the device contact area, A^* the Richardson constant having value of 32 A cm^{-2} K^{-2}, T the temperature in K, k the Boltzmann constant, n the ideality factor and I_0 the reverse saturation current. n can be calculated from the linear slope region of the positive bias ln *I–V* plot by using equation (3) as follows, whereas ϕ can be estimated from equation (4). The typical *I–V* characteristics are shown in figure 3.

$$n = \frac{q}{kT}\left(\frac{dV}{d\ln I}\right), \quad (3)$$

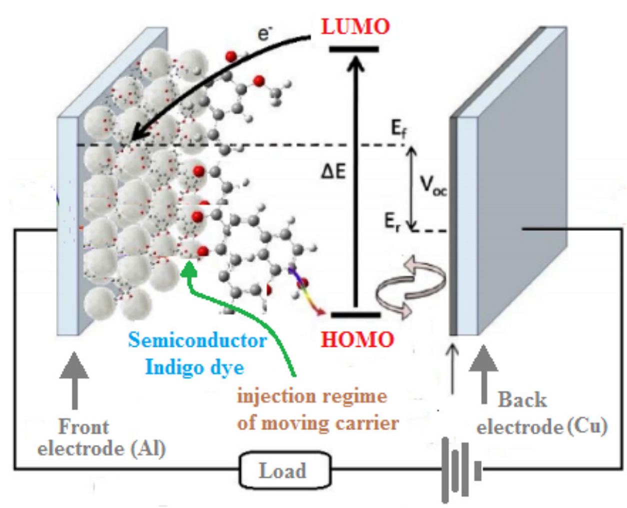

Figure 2. Dark current measurement setup where Al and Cu have been used as front and back electrodes, respectively, whereas the indigo dye has been selected as active layer sandwiched between the electrodes [6].

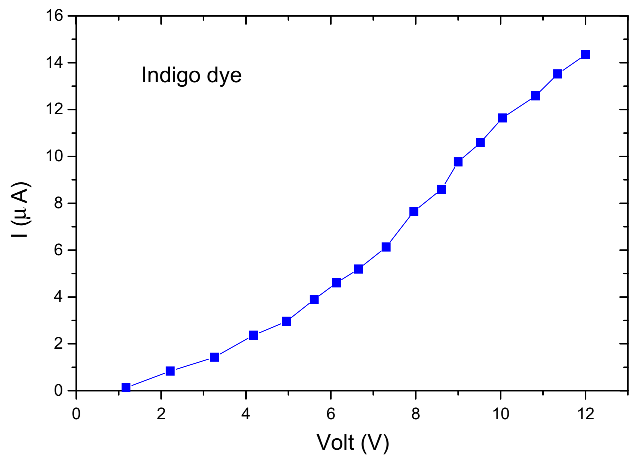

Figure 3. *I–V* Characteristics of indigo dye-based diode.

and

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

In the present discussion, a layer of herbal semiconductor is sandwiched between electrodes having different work functions which results in a built-in voltage (V_{bi}). For the sake of illustration, a specific type of carrier is considered to be injected as per the choice of electrode work functions. Two distinct regions of device operation have been observed as specified by voltage V_{bi}. Current shows exponential nature in the region below the value of V_{bi}. The following region is said to be space charge limited in the absence of trapping energy which leads to the Mott–Gurney (MG) equation [12,14]

$$I = \frac{9}{8}A\in\in_0\theta\mu\frac{V^2}{d^3}, \tag{5}$$

where V is applied voltage, μ the carrier mobility, $\in_0$ the free space permittivity, θ the trap factor and d the film thickness.

Current above V_{bi} also follows MG law, but with a modification as a value of V is changed here by an effective voltage V_x where V_x is approximately equal to ($V_{bi} - K$), where K signifies the factor that implies a transition at a voltage comparatively smaller than built-in potential. The modified equation can be described as [12,15]:

$$I = \frac{9}{8}A\in\in_0\theta\mu\frac{(V-V_x)^2}{d^3}. \tag{6}$$

Current–voltage characteristic exhibits ohmic relation when the value of V is low enough. Carriers are injected into the active region of the device with increasing applied voltage causing enhancement of trapping probability. At higher voltage, double logarithmic plot of *I–V* relation displays $I \propto V^{m}$, where m shows the increasing value from unity to 2 and then, further increment in the value of m can be observed with more increasing value of voltage as well as at the highest region of the characteristic (obtained value of m is 2.87 at this region in this experiment). These interesting results show the space-charge limited current (SCLC)-based transport mechanism is dominated by trapped-charge limited current (TCLC) with exponential distribution of trap density. When concentration of trap is large enough, distortion in *I–V* plot becomes significant and distinct regime of current–voltage relationship can be determined unambiguously. But it becomes quite difficult to identify the distinct regimes of the plot for low trapping concentration. Since differential technique is very fruitful for the enhancement of small deviations, so it can be implemented to reveal the existence of trap states. $G(V)$–V characteristics have been taken into account for that purpose [12]. Here,

$$G(V) = \frac{d\log(I)}{d\log(V)}, \tag{7}$$

$G(V)$ actually creates a sharp peak to signify a transition from exponentially rising flow of current to comparatively slower power law dependence above V_{bi}. Peak in the mentioned figure illustrates trap filling states. Hence, $G(V)$ *vs.* V plot in figure 4a emphasizes on the trap signature allowing relatively easy realization about the nature of traps. A monotonic decrement of function $G(V)$ should be observed in trap-free devices, but in the aforementioned plot, a noticeable amount of distortion exists at different voltage regimes which clearly leads to the existence of trapping states into the device. Trap charge concentration (n_t) can be represented in terms of exponential distribution as follows [6,16]

$$n_t(\in) = N_0 \exp\frac{-\in}{kT_c}, \tag{8}$$

where $\in$ represents the depth of traps below conduction band mobility edge and T_c is trap energy of exponential distribution where

$$T_c = \frac{E_c}{k}. \tag{9}$$

Here, E_c is characteristic trap energy and $E_c = mkT$. The value of trap energy can be estimated from logarithmic current voltage relation is plotted in figure 4b.

Traps play an important role in carrier conduction process in the bulk region of charge transport of such devices. Majority of generated charges suffer with immobilization of their motion due to the existence of traps [16,17]. These trapping states arise as an internal resistive property of organic substances. So, it is obvious that the movement of free carriers of these devices struggles by high series resistive influence for the presence of trapping states in the active regime [18,19]. R_s is such a parameter which impacts directly on device efficiency and other electrical properties [20,21]. R_s, n and ϕ can also be calculated by using well-known

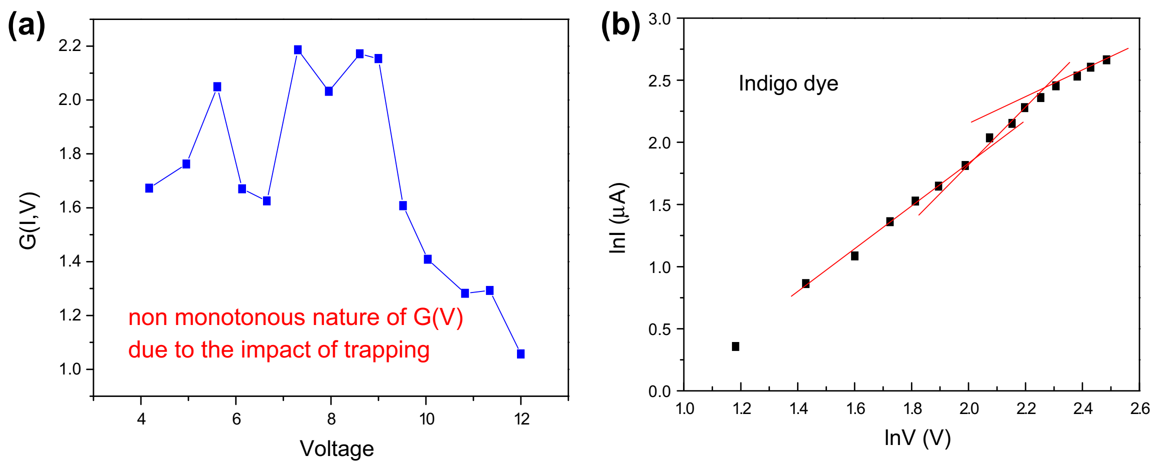

Figure 4. (**a**) $G(V)$–V plot of indigo dye-based diode. Multiple distortions in the figure explain the presence of multiple discrete traps. The first in the plot is quite suppressed and is generated due to V_{bi}. Remaining peaks arise from other deeper traps; and (**b**) log I–log V plot for indigo dye-based device used to calculate trap energy.

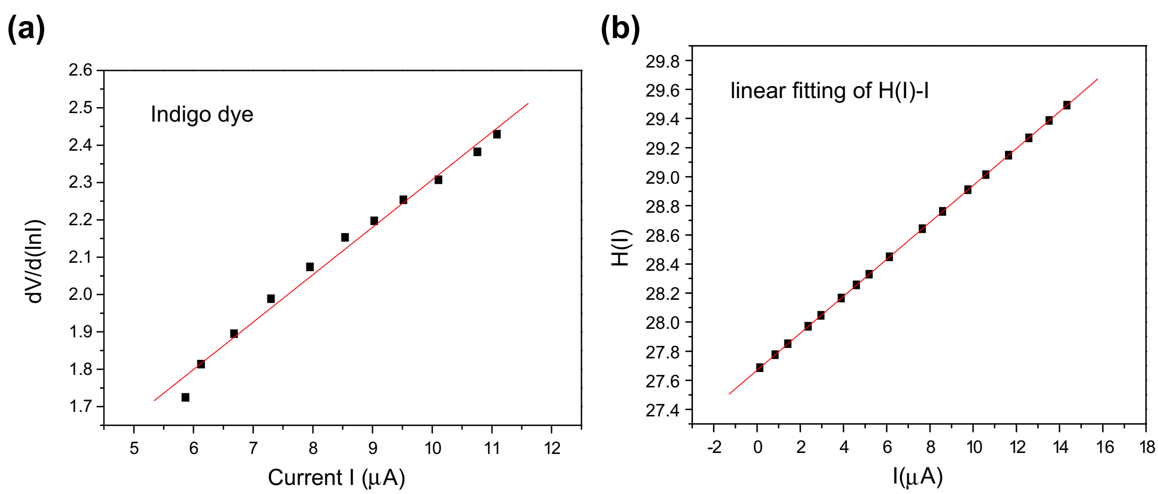

Figure 5. (**a**) (dV/d ln I)–I plot and (**b**) $H(I)$–I plot of indigo dye-based diode.

Cheung–Cheung method and its corresponding equations are given here as follows [20,22,23]:

$$\frac{dV}{d\ln I} = \frac{nkT}{q} + IR_s, \tag{10}$$

$$H(I) = V - \frac{nkT}{q}\ln\left(\frac{I}{AA^*T^2}\right) \tag{11}$$

and

$$H(I) = IR_s + n\phi. \tag{12}$$

(dV/d ln I)–I plot has been expressed at high voltage regime of the I–V relation given in figure 5. Value of R_s is estimated from the linear region of the following plot, while n can be extracted from interception with Y-axis. R_s is also obtained from the $H(I)$–I plot [20,24]. $H(I)$–I plot shows linearity with intercept at the Y-axis which is equal to ($n\phi$). The slope of this plot is basically used for the verification of the accuracy of Cheung function. The results show good agreement with each other. Obtained result containing the value of n expresses the comparison of fabricated diode to the ideal one. Generally, the value of ideality factor of organic herbal dye-based diode is much greater than unity. High value of ideality factor may be due to different interfacial states or layer of semiconductor of metal electrode surface and high value of series resistance. Incorporation of amorphous disordered natural organic material between two metal electrodes results in high value of R_s. Interaction between conductor–semiconductor interface realign the lowest unoccupied molecular orbital (LUMO)–highest occupied molecular orbital (HOMO) levels of organic natural semiconductor and work function of metal which changes electron affinity and further results in the

Table 1. Estimated electrical parameters for indigo dye-based herbal device.

Estimated parameters	Obtained values
Trap energy (in eV) (E_c)	0.073
Series resistance (in kΩ) (R_s)	127
Ideality factor (n)	39.87
Barrier height (in eV) (ϕ)	0.87

increment of barrier height [7,13,25–29]. Like other organic devices, the value of R_s is quite high also in this device due to trap prone charge conduction, disordered organic structure and interfacial disorder [20,21,28,29]. Value of E_c, R_s, n and ϕ are given in table 1.

The electrical parameters show promising results when compared to other reported organic dyes estimated in the work of Chakraborty *et al* [16,30] given in table 2. Significant reduction in E_c, R_s and ϕ has been obtained in application of the herbal organic indigo dye over previously reported organic dyes. So, the dye under present experiment may have wide possibilities to fabricate organic solar cell, photodiode, OLED, etc. [31–34].

However, its charge transport mechanism can further be predicted with interpretation of semi-logarithmic current plotted against square root of voltage before its further application. The current is segmented in two linear distinct regions [35]. Following straight line regions for low and high current regions indicate the existence of either Richardson–Schottky or Pooley–Frankel effect induced carrier flow shown in figure 6 [22,36,37].

The I–V expressions for both the mechanisms are given as follows [38]

$$I = AA^*T^2 \exp\left(\frac{-\phi_b}{kT}\right)\exp\left(\frac{\beta_{RS}V^{\frac{1}{2}}}{kTd^{\frac{1}{2}}}\right) \quad (13)$$

for Schottky effect and

$$I = I_0 \exp\left(\frac{\beta_{PF}V^{\frac{1}{2}}}{kTd^{\frac{1}{2}}}\right) \quad (14)$$

for Poole–Frankel effect.

In equations (13 and 14), ϕ_b represents Schottky barrier height, I_0 the field lowering current, β_{RS} and β_{PF} are Richardson–Schottky and Poole–Frankel field lowering coefficients, respectively. Theoretical value of β_{RS} and β_{PF} can be estimated from the following equation [39]:

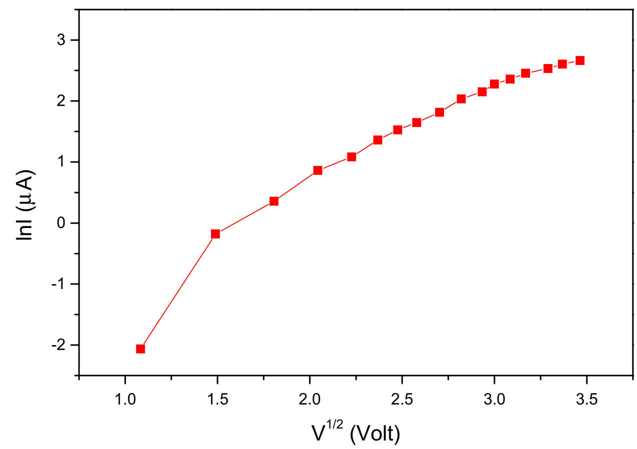

Figure 6. ln I *vs.* $V^{1/2}$ plot for indigo dye-based diode.

$$2\beta_{RS} = \beta_{PF} = \left(\frac{q^3}{\pi\epsilon_0\epsilon_r}\right)^{\frac{1}{2}}. \quad (15)$$

Theoretically obtained values from equation (15) of β_{RS} and β_{PF} are 2.64×10^{-5} and 5.28×10^{-5} eV m$^{1/2}$ V$^{-1/2}$ where ϵ_r of indigo is considered as 7.83. Values of β are further estimated from the slopes at low and high voltage regimes. In this way, experimentally calculated values of β are $\beta_{low} = 1.71 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ and $\beta_{high} = 0.96 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$. It is clearly observed that the experimentally obtained value of β_{high} is 0.36 times of β_{RS} and 0.18 times of β_{PF}. β obtained experimentally at high voltage zone is comparatively close to the theoretical value determined for Richardson–Schottky effect which leads to bulk limited carrier conduction process [22,39]. In such process, current flow is determined as minority carrier diffusion, whereas production of current is due to flow of majority carriers over extracted potential barrier which usually exists in Schottky barrier diode.

4. Conclusions

Fabrication and characterization of Al/indigo/Cu organic diode have been encountered. Values of R_s, n and ϕ have been estimated from Cheung function and hence, verified by

Table 2. Estimated reduction percentage (%) of electrical parameters obtained in indigo dye-based herbal device over other reported organic dye-based devices.

Electrical parameters	Estimated reduction percentage (%) over Rose Bengal dye	Estimated reduction percentage (%) over methyl red dye
Amount of reduction in E_c	16.09	3.95
Amount of reduction in R_s	46.86	72.51
Amount of reduction in ϕ	8.42	12.12

H(*I*)–*I* plot. Outcome of the estimation shows good agreement together. Obtained results have been compared with other reported organic semiconductor-based RB and MR dyes. R_s has been encountered with 46.86 and 72.51% improvement, whereas ϕ shows 8.12 and 12.12% improvement, respectively, than RB and MR. Existence of trapping effect of experimental dye has been explained from *G*(*V*)–*V* plot. Considerable amount of trapping defect has been found in the experiment which leads to non-ideal conduction procedure as well as hopping mechanism from one to another localized state. Estimated value of E_c is 0.073 eV which shows 16.09 and 3.95% improvement than RB and MR dye. Result shows wide possibilities to introduce it in optoelectronic devices. Bulk limited charge conduction-assisted Richardson–Schottky effect has also been examined for the device by using semi log current–voltage plot.

Acknowledgements

We are grateful to School of Energy studies, Jadavpur University, for their support to perform the required experiment and they are thankful to University Grants Commission, India.

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