Evaluation of Richardson Constant of Fruit dyes using Carmoisine and Tartrazine

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Abstract:

One of the most crucial variables to consider while analysing the current conduction process in the metal organic Schottky contact is the Richardson constant. However, there aren't many publications on the determination of the useful Richardson constant for Fruit dyes. For two different Fruit dyes, Carmoisine, and Tartrazine, we have determined the values of the effective Richardson constant in this work. By using the spin coating method, a thin organic layer of these natural colours was sandwiched between a copper plate and a piece of glass that had been coated in indium tin oxide. The current-voltage-temperature response of the cells was examined at a temperature range of 303K to 333K. The estimated effective Richardson constants for these dyes are 95.09 x 10^{-3} A/cm^{2}K^2 and 44.35 x 10^{-3} A/cm^{2}K^2 for CS and TZ dye respectively, which are different from the typical value of 120 A/cm^{2}K^2. We can analyse several electrical properties for these natural dyes with the aid of these values.

Keywords:*Natural dye, Schottky contact, Richardson constant.*

1. Introduction

The current conduction mechanism through the metal- organic contact is frequently described as the thermionic emission process in Schottky contacts [1-3]. But the main drawback for organic dye-based devices is the limited current flow through these junctions. The link between the Schottky Barrier Height (SBH) and temperature has a significant impact on the thermal stability of the majority of organic or fruit dye based electrical and photo-electronic systems. Because the SBH of a junction completely controls the current flow to electronic and photoelectric devices based connections [4]. So it is necessary to predict the SBH for various metal-organic connections. The most popular method for calculating the barrier height of the junction with the saturation current and temperature for the thermionic emission process is the Schottky thermionic emission theory [5]. The thermionic emission process in Schottky junctions is fundamentally characterised by the Richardson constant (A*) [6]. The effective Richardson constant's value is typically taken to be its theoretical value. The precise value of A* for these junctions must be known in order to precisely measure the current-voltage (I-V) response and derive the SBH. Different material-based connections exhibit varying A* values. The A* value for Ag/p-SnSe is 7.72 Acm^{-2}K^{-2} [7].

Value of the Richardson constant for Al/PVA:n-PbSe polymer nanocomposites Schottky diode is $5.72\text{x}10^{-8}\text{Acm}^{-2}\text{K}^{-2}$ [8]. But there are no such reports available on the estimation of A^* value for different natural dye based junctions.

In this work, we are trying to estimate the value of A^* for different natural dyes namely Carmoisine (CS), and Tartrazine (TZ). These dyes are completely environment-friendly. Also, the dyes have no harmful effect on the human body and are cost-effective. Typically, these dyes are used to colour foods, beverages, etc. We can estimate the SBH value and, in turn, precisely quantify the various electrical characteristics by ascertaining the A* values for these dyes. We employ the Schottky diode configuration, with the dye sandwiched between an Indium-Tin-oxide coated glass (ITO) front electrode and a copper plate (Cu) back electrode. The emission of carriers from the semiconductor over a spatially homogenous barrier into the metal dominates the carrier conduction process at forward bias in an ideal Schottky diode [9]. With a temperature range of 303 K to 333 K (30^0C to 60^0C), a Keithley-2400 source metre is used to measure the current (I) vs. voltage (V) relation.

2. Materials

The CS dye, also known as Azorubine dye, is an azo dye [10] produced only by chemical synthesis as a disodium salt. The IUPAC name of the CS dye is 'disodium 4-hydroxy-2-[(E)-(4-sulfonato-1-naphthyl)diazenyl]naphthalene-1-sulfonate' and the chemical formula is '$C_{20}H_{12}N_2Na_2O_7S_2$'. The chemical structure of CS dye is given in Figure 1. Sighting to the chemical structure we can see that this dye is composed of gaseous and metallic composites. The presence of 'OH' group and the 'N=N' bond represents that this dye is an anionic dye and can have greater conductivity.

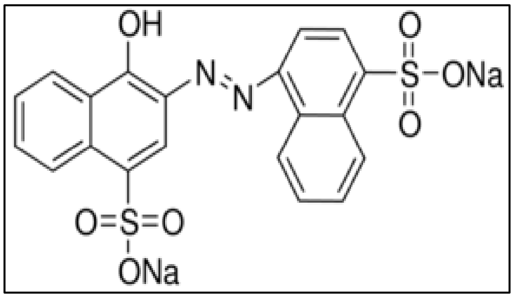


Fig.1. Chemical Structure of CS dye.

This dye is also known as Food Red 3, Azorubin S, Brillantcarmoisin O, Acid Red 14, or C.I. 14720'. In its dry form, the product appears red to maroon. It is mainly used in certain foods and beverages, such as cheeses, dried fruit, and some alcoholic beverages, and is permitted for use in medications. Azorubine has shown no evidence of mutagenic or carcinogenic properties and an acceptable daily intake (ADI) of 0–4 mg/kg was established in 1983 by the WHO [11]. No evidence supports broad claims that food coloring causes food intolerance -like behavior in children [12].

Tartrazine is a synthetic lemon yellow azo dye primarily used as a food coloring [13, 14]. It is also known as E-number E102, C.I. 19140, FD&C Yellow 5, Yellow 5 Lake, Acid Yellow 23, Food Yellow 4, and trisodium 1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-5-pyrazolone-3-carboxylate) [15]. Figure 2 depicts the chemical structure of TZ dye.

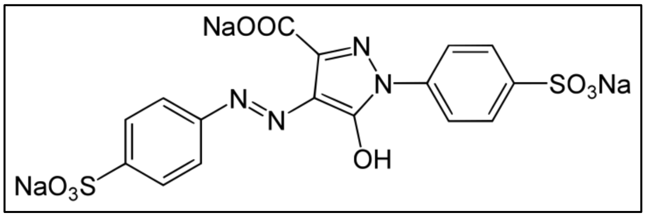


Fig.2. Chemical structure Tartrazine

Chemical formula of the TZ dye is $C_{16}H_9N_4Na_3O_9S_2$. It's an azo dye with a chromophoric azo group – N = N-, which has nitrogen atoms coupled to SP^2-hybridized carbon atoms [16]. At least one of these carbon atoms is from an aromatic carbocycle or heterocycle, whereas the second carbon atom next to the azo group could be from an enolizable aliphatic derivative [17].

3. Experiment

3.1 Cell preparation

At first, 2 pieces of each ITO-coated glass and Cu plates are swabbed under a diluted detergent (e.g. Deconex or FPD detergent, Alconox). Then soaked under the detergent at 60^0C for 10 min and rinsed with DI water. The electrodes are then sonicated for 10 minute each with DI water, 2-propanol and acetone subsequently and kept in nitrogen atmosphere for dry. Before spincoat the sample we did the UV ozone treatment for 10 minutes.

The 30% PVA solution is prepared by 1 gm of PVA, measured using Dhona-100DS measurement unit, mixed with 30 ml of de-ionized water and stirred with a magnetic stirrer for 1 hr with 313K. Here PVA plays the role of an inert binder [17]. Using the Dhona-100DS, we weight 1 mg of CS, TZ and CB dye and dissolved them separately with 0.5 ml of previously prepared 30% PVA solution using the Ultrasonic Sonicator for 30 min in room temperature.

Using a APEX spin coater we spin coat the prepared samples separately on the previously cleaned ITO glass slides with 1500 r.p.m and semi-dried in a vacuum with a desiccator. After this step, we place the Cu plate as a back electrode on the sample to make a Metal-Dye-Metal (MDM) structure. These devices are then kept in a vacuum with dark condition for 12 hours before characterization to dry. The schematic diagram of the cell is given in Figure 3.

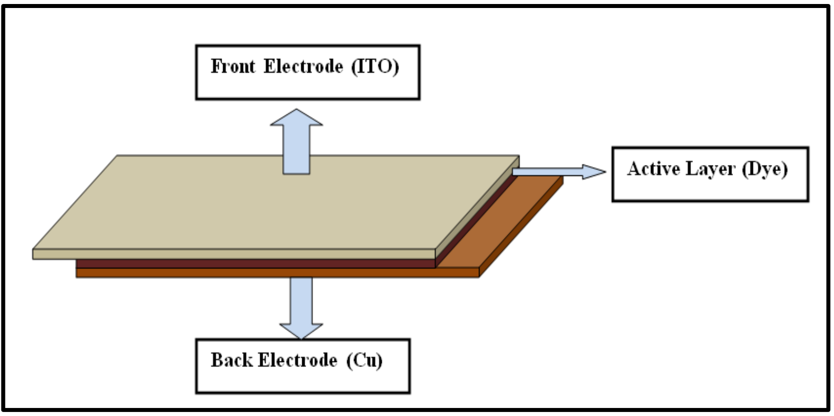


Fig.3. Schematic diagram of ITO/Dye/Cu cell.

3.2 Measurement

Using a Keithley 2400 source unit and a Regulated Heat Source unit, the dark current-voltage-temperature (I-V-T) characteristics of the cells have been observed. The temperature changes simultaneously from 303 K to 333 K. The bias voltage is changed from 0V to 5V in steps of 0.5V with a 1500 ms delay during the test. Figure 4 shows the simple circuit diagram for our experiment. The tests were conducted in a glove box with a completely dust-free environment.

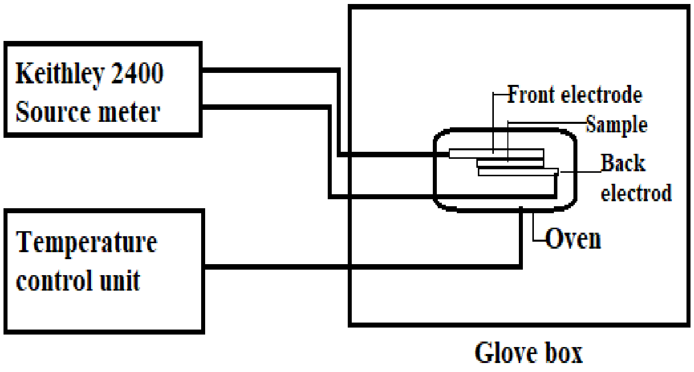
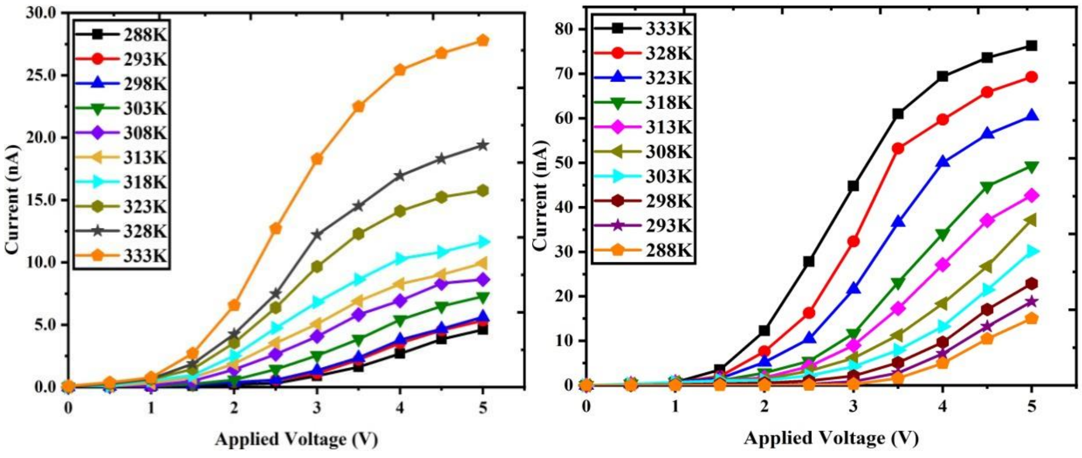


Fig.4. Schematic circuit diagram of temperature-dependent I-V-T characteristics.

4. Result

The I-V-T characteristics for all the dyes at room temperature are shown in figure 5(a), and 5(b) respectively. From the plots, we have observed that the current flow has been increased exponentially with the increasing forward bias voltage. Also we can observe good rectifying behavior at all temperatures. The total area that contributes to the current transport in inhomogeneous Schottky-barrier diodes (SBD) depends on temperature and bias, and the carrier conduction process in forward bias is dominated by the emission of carriers from the semiconductor over a spatially homogeneous barrier into the metal.



(a) *(b)*

Fig.5. I-V-T characteristics of (a) CS dye, (b) TZ dye.

We used the Richardson-Schottky thermionic emission theory to investigate the current flow [18]. A Schottky diode's forward-bias I-V relation can be written as follows:

$$I = [AA^{*}_{eff}T^{2}\exp(\frac{-q\phi_{beff}}{kT})]\exp[\frac{qV}{nkT}] \quad (1)$$

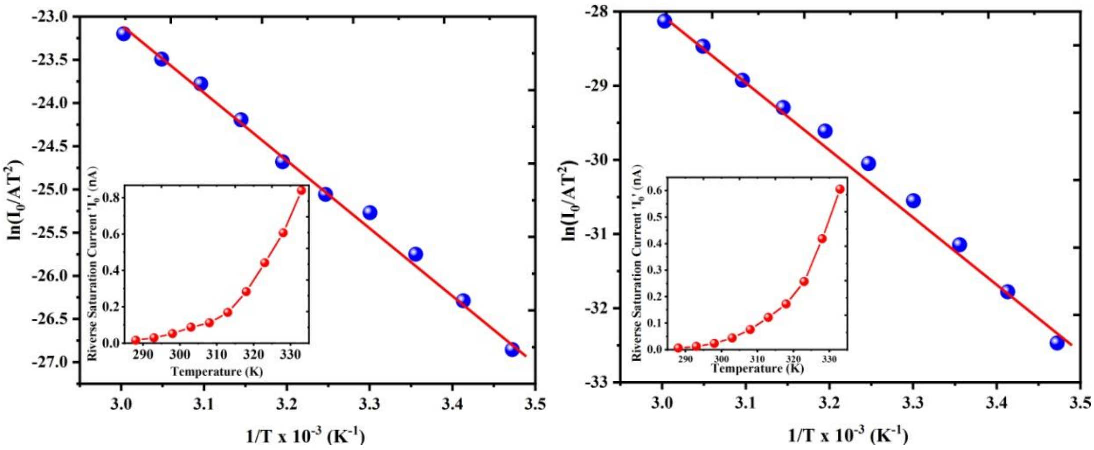
where "q" denotes the charge carrier, "k" is the Boltzmann constant, "T" is the temperature in Kelvin, "n" is the ideality factor, which indicates how well a diode complies with the ideal diode equation, "A" is the device's area, "ϕ_{beff}" is the junction's barrier height, and "A^{*}_{eff}" is the effective Richardson constant. As stated, "I_0" is the reverse saturation current.

$$I_0 = AA^{*}_{eff}T^{2}\exp(\frac{-q\phi_{beff}}{kT}) \quad (2)$$

Taking 'log' in the Equation (2), we have:

$$\ln(\frac{I_0}{AT^2}) = \ln(A^{*}_{eff}) - q\frac{\phi_{beff}}{kT} \quad (3)$$

A typical Richardson plot of $\ln(\frac{I_0}{AT^2})$ versus $\frac{1}{T}$ extracted from the I-V-T characteristics are shown in Figure 7(a) and 7(b) respectively. The dependency of reverse saturation current (I_0) with the temperature are shown in the inset of Figure 7(a) and 7(b) of respective dye.



(a) *(b)*

Fig.7. Typical Richardson plot extracted from I-V-T data of (a) CS and (b) TZ dye. In Inset Dependency of I_0 with temperature for (a) CS Dye and (b) TZ dye.

Effective Richardson constant (A^*_{eff}) of the dyes are depicted in Table 1 bellow. The most significant observation from the Table 1 is that the extracted values of the $A^*_{eff}$for the dyes are different from the conventional value of n-type and p-type semiconductors.

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Table 1. Extracted effective Richardson constant value for different dyes.

Name of the Dye	A^*_{eff} ($\mathrm{Acm^{-2}K^{-2}}$)
CS	$95.09 \text{ x } 10^{-3}$
TZ	$44.35 \text{ x } 10^{-3}$

5. Conclusion

Here, Richardson constant of two Natural dyes, namely Carmoisine and Tartrazene dye, were estimated. The dyes are spin coated separately on an Indium-Tin-Oxide coated glass. We use a Cupper-plate as a back electrode. The current-voltage-temperature (I-V-T) characteristics of the CS and TZ dye are studied with the temperature range 303K-333K under dark condition and the Richardson plots are nearly straight line. Obtained Richardson constant values for CS and TZ dyes are $95.09 \times 10^{-3}\mathrm{Acm^{-2}K^{-2}}$ and $44.35 \times 10^{-3}\mathrm{Acm^{-2}K^{-2}}$ respectively. We can extract the accurate SBH value by the linear correlation between Richardson constant and effective barrier height. This A^* values will be very much helpful for the study on the ideality factor and other electrical and opto-electrical parameters, charge transport mechanism for those dyes. Further studies using these natural organic dyes are going on in our lab.

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Conflict of Interest

The corresponding author, on behalf of all the authors, states that there is no conflict of interest regarding this manuscript file.

Data Availability

The data that supports the findings of this study are available within the article [and its supplementary material].

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