

Electrical characterization of Al/fluorescein sodium salt organic semiconductor/Au diode by current-voltage and capacitance-voltage methods

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The organic Schottky diode of fluorescein sodium salt using aluminium and gold metals were fabricated. Electronic and interface state properties of the Al/p-FSS Schottky diode were investigated by current-voltage and capacitance-voltage methods. The electronic parameters such as barrier height ($\phi_B = 0.72$ eV), ideality factor ($n=3.05$) and series resistance (7.73 k Ω) of the Schottky diode were determined by performing different plots. The ϕ_B (C-V) value obtained capacitance-voltage measurements is 1.05 eV. The barrier height obtained from the C-V measurements is higher than that of obtained from the I-V measurements. The difference between ϕ_B (I-V) and ϕ_B (C-V) barrier height values can be due to interfacial layer, excess capacitance and barrier inhomogeneity. The shape of the density distribution of the interface states is in the range of $E_{ss}-0.02$ eV to $E_{ss}-1.21$ eV.

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1. Introduction

A large number of Schottky barriers have been prepared and characterized using organic conductive polymers with metals and inorganic semiconductors [1-3]. The fabrication and characterization of the Schottky diode barrier using organic semiconductors and their derivatives have been taken considerable attention in recent years [4-5]. Organic semiconductors can be used as activate components in electronic devices and these materials have potential advantages due to easily processable in low cost and large area device characterization. This has opened a new possibility of replacing conventional inorganic devices by the organic ones. The device performance of a Schottky diode depends on electrical and electronic characteristics of the metal/organic semiconductor junction. Therefore, the understanding of electronic properties of the interface between metal and organic semiconductor is important for device applications. A schottky diode based on organic semiconductor can be fabricated by forming an appropriate semiconductor-metal contact for electronic devices applications. In present study, Schottky barrier diode

consisting of Al metal and fluorescein sodium salt organic semiconductor was fabricated. The electronic parameters controlling the device performance, such as barrier height, ideality factor, series resistance and interface parameters were evaluated by current-voltage and capacitance-voltage measurements.

2. Experimental

The fluorescein sodium salt used in this study is a p-type organic semiconductor [6]. For the fabrication of the diode, initially p-Si was used as substrate. The substrate was rinsed in deionised water using an ultrasonic bath for 10-15 min and finally was chemically cleaned according to method based on successive baths of methanol and acetone. The substrate was placed in vacuum system for the processes. High purity (99.999%) Al metal was thermally evaporated on the substrate. The solution of the fluorescein sodium salt (FSS) was prepared in methanol. The solution of the FSS was homogenized for 2 hour by mixing with rotation before the deposition. Then, the film of the FSS was prepared on Al metal by dip coating method with subsequent drying. The

ohmic contact with FSS layer was formed by Au electrode. The standard geometry of diode is shown in Fig.1. The current-voltage (I-V) measurements were performed with 2400 Keithley sourcemeter and GPIB data transfer card for current-voltage measurements. The capacitance-voltage (C-V) measurements were performed by use of HIOKI 3532-50 LCR.

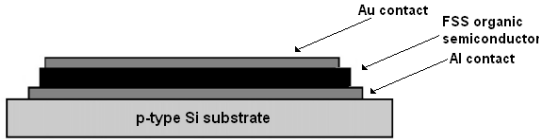
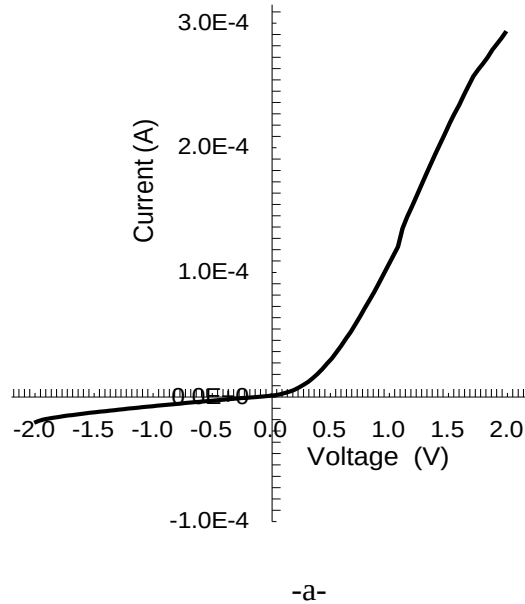


Fig. 1 Schematic structure of the Al/p type-FSS Schottky diode

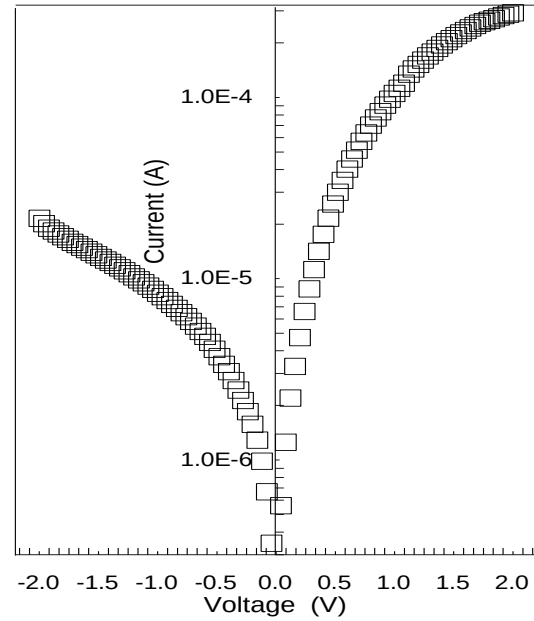
3. Results and discussion

3.1. Current-voltage characteristics of Al/p type-FSS Schottky diode

The current-voltage characteristic of Al/p type-FSS Schottky diode is shown in Fig. 2. The diode shows a rectification effect due to Schottky contact, which was formed at the Al/p-FSS. The charge transport mechanism in metal-semiconductor junctions is defined by thermionic emission theory given by [7-8]



-a-



-b-

Fig. 2 The forward and reserve current curve of the Al/p type-FSS Schottky diode a) in linear scale b) in semilogarithmic scale

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

where T is the temperature, n is the ideality factor and I_0 is the saturation current given by

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

where A is the contact area, A^* is the Richardson constant ($120 \text{ A.cm}^{-2}\text{.K}^{-2}$ for free electron), and ϕ_{bo} is the barrier height and n is the ideality factor and is equal to 1 for thermionic emission mechanism. The n ideality factor of Al/p type-FSS/Au diode was obtained from the slope of the straight linear region of forward bias $\ln I$ - V characteristic by the equation,

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

and the obtained n value is 3.32. This suggests that the diode indicates a deviation from ideal behavior and so, thermoionic emission theory is ruled out for Al/p-FSS/Au diode, i.e, I-V curve of the diode can not be analyzed by Eq.1. The non-ideal behavior of the diode can be due to series resistance, interface layer and inhomogeneous Schottky barrier height

[9]. Eq.1 can be modified due to the series resistance as [10] ,

$$I_1 = I_{o1} \exp \frac{q(V - IR_s)}{nkT} \left(1 - \exp \frac{q(V - IR_s)}{nkT} \right) \quad (4)$$

and

$$I_{o1} = AA^* T^2 \exp \left(- \frac{q(\phi_b - \Delta\phi)}{kT} \right) \quad (5)$$

The barrier height, ϕ_{b0} in Eq. 2 can be rewritten as

$$\phi_b = \phi_{b0} - \Delta\phi - \beta V \quad (6)$$

where ϕ_b is the effective Schottky barrier height, β is a constant and $\Delta\phi$ is an reduce amount in Schottky effect given by [10]

$$\Delta\phi = \left[\frac{q^3 N_A}{8\pi^2 \epsilon_s^2} \left(\phi_b - V - \xi - \frac{kT}{q} \right) \right]^{1/4} \quad (7)$$

where ξ is the energy difference between the Fermi level and the bottom of the conduction band or top of the valence band. The values of I_0 , and ϕ_b were found to be 4.36×10^{-7} A and 0.72 eV, respectively. The obtained n value confirms that the Al/p type-FSS diode is metal-insulator-semiconductor (MIS) configuration rather than an ideal Schottky diode. The various models have been developed to determine the series resistance effect. We used method developed by Cheung and et al. to the obtain the diode parameters. The Cheung's method is expressed by the following relations [11],

$$\frac{dV}{d \ln I} = n \frac{kT}{q} + IR_s \quad (8)$$

and

$$H(I) = V - n \frac{kT}{q} \ln \left(\frac{I}{AA^* T^2} \right) \quad (9)$$

where $H(I)$ is written as,

$$H(I) = n\phi_B + IR_s \quad (10)$$

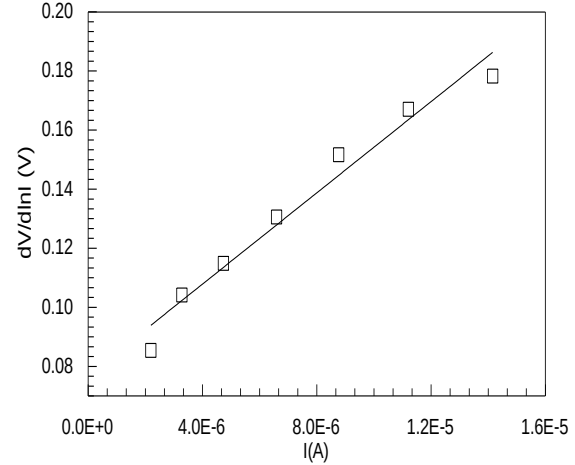


Fig. 3 Plot of $dV/d \ln(I)$ vs I for the Al/p type-FSS Schottky diode

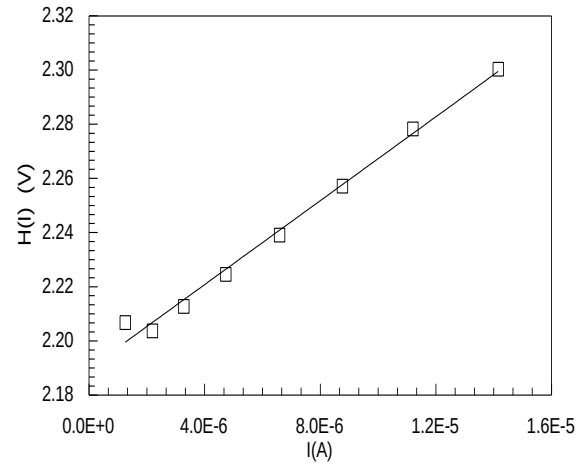


Fig. 4 Plot of $H(I)$ vs I for the Al/p type-FSS Schottky diode

Figs. 3 and 4 show the curves associated with these relations. The slope and intercept of $dV/d \ln(I)$ - I plot will give nkT/q and R_s , respectively. The n and R_s values were found to be 3.05 and 7.72 k Ω , respectively (Fig. 3). The plot of $H(I)$ - I will give a straight line whose slope and intercept are $n\phi_B$ and R_s . The ϕ_B and R_s values from the Fig. 4 were calculated as 0.72 and 7.74 k Ω , respectively. The obtained series resistance values are in agreement with each other due to consistency of Cheung method. Interfacial layer causes a voltage drop across the interface. The bias dependence on the voltage drop V_i across interfacial layer is expressed by [12,13],

$$V_i = \left(1 - \frac{1}{n} \right) V \quad (11)$$

The effect of series resistance is taken into account by substituting V in Eq. 11 with $(V - IR_s)$. After arranging the Eq. 11, it gives,

$$V_i = \left(1 - \frac{1}{n} \right) (V - IR_s) \quad (12)$$

The values of V_i were calculated using Eq. 11. In order to

obtain the voltage drop across depletion layer V_D , voltage obtained from Eq. 11 should be subtracted from the total value of applied forward voltage,

$$V_D = V - V_i \quad (13)$$

The curves of $\ln I$ v.s V were reported for obtained V_i and V_D values (Fig. 5) to indicate effect of interface layer on parameters of the diode. The n and ϕ_B values of Al/p type-FSS diode were calculated from the $\ln I$ - V_D plot and were found to be 1.35 and 0.71 eV, respectively. The obtained values are lower than equivalent values obtained previously without considering effect of the presence of interfacial layer. At higher voltages, I-V characteristic of p-FSS/Al diode is affected due to series resistance. Fig. 6 shows plot of $\log I$ - $\log V$ of the diode. This plot indicates two regions having different slopes. The first region suggests a trap controlled space charge limited. The space charge limited current is expressed by the well-known relation,

$$I = \frac{9}{8} \epsilon_o \epsilon_s \mu_p \frac{A}{d^3} V^2 \quad (14)$$

where ϵ_o is the dielectric permittivity of vacuum, ϵ_s is the dielectric constant of the semiconductor, μ_p is the electron mobility and d is the thickness of the film. The second region indicates a superquadratic behavior, which is caused by the low concentration of charge carriers. In region II, the increase rate of current with voltage decreases. This suggests that most of traps are filled and contribution of free carrier to electric filed becomes appreciable [14].

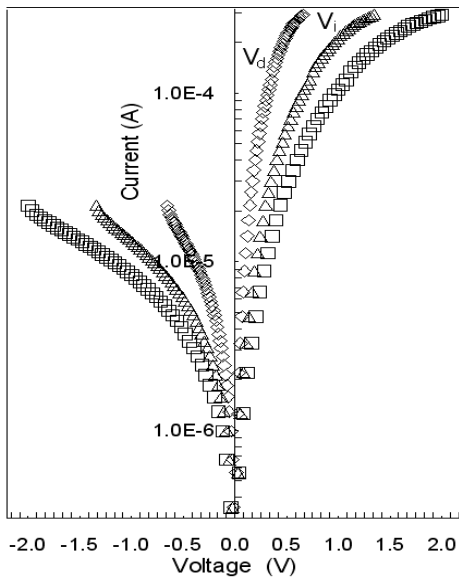


Fig. 5 Plots of the forward and reverse currents vs V_i and V_D voltages for the Al/p type-FSS diode

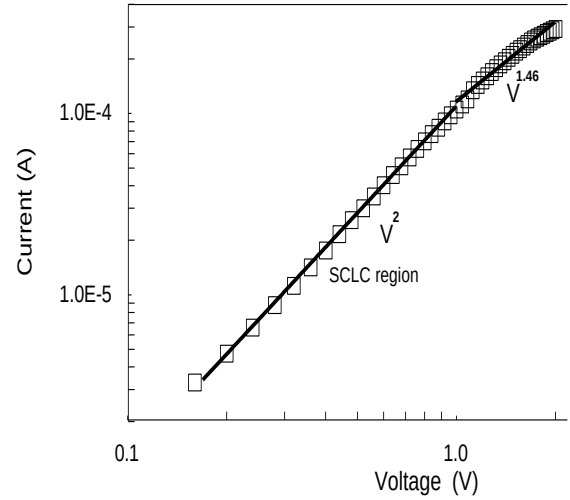


Fig. 6 Plot of $\ln I$ vs $\ln V$ of the Al/p type-FSS diode

3.2. The capacitance-voltage (C-V) characteristics of the Al/p-FSS Schottky diode

The capacitance-voltage relation for a metal-semiconductor junction is given by [7-8]

$$\frac{1}{C^2} = \frac{2(V_{bi} + V)}{A^2 \epsilon_s q N_a} \quad (15)$$

where V_{bi} is the built-in potential, which originates from the difference of work functions between metal and semiconductor, ϵ_s is the dielectric constant of semiconductor and N_a is the acceptor concentration given by [15]

$$N_a = \left(\frac{2}{q \epsilon_s A^2} \right) \frac{dV}{dC^{-2}} \quad (16)$$

The variation of C^{-2} with V for the diode is shown in Fig. 7. N_a was determined from the slope of Fig. 7 using Eq.16 and was found to be $1.69 \times 10^{10} \text{ cm}^{-3}$. The value of V_{bi} was determined from the intercept of C^{-2} vs V plot and was found to be 0.52 V. The barrier height of the diode can be calculated by the following relation

$$\phi_{b(C-V)} = V_{bi} + \frac{kT}{q} \ln \left(\frac{N_v}{N_a} \right) \quad (17)$$

where N_a is the concentration of ionized acceptors given by [16]

$$N_a = N_v \exp \left(\frac{V_p}{kT} \right) \quad (18)$$

and

$$N_v = 4.83 \times 10^{15} \left(\frac{m_h^*}{m_o} \right) T^{3/2} \text{ cm}^{-3} \quad (19)$$

where N_v is the density of states in valence band of FSS, m_h^* is the effective mass of holes, m_o is the stand mass of electron. N_v value for FSS at 298 K was found to be $2.42 \times 10^{19} \text{ cm}^{-3}$ using Eq.19. The $\phi_{b(C-V)}$ value was calculated using the V_{bi} and V_p values and was found to be 1.05 eV. The barrier height obtained from the C-V measurements is higher than obtained from the I-V measurements. The difference between ϕ_b (I-V) and ϕ_b (C-V) can be due to interfacial layer, excess capacitance and barrier inhomogeneity [16].

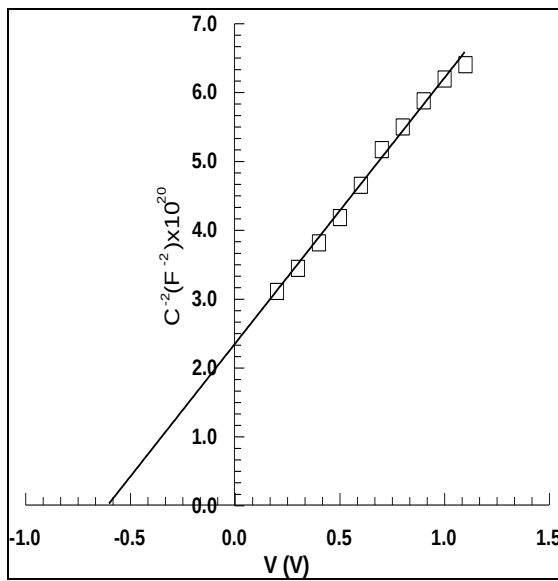


Fig. 7 Plot of C^{-2} vs V plot of Al/p type-FSS diode

3.3. Interface state density properties of Al/p-FSS Schottky diode

The ideality factor for metal-insulator-semiconductor (MIS) can be expressed as [17],

$$n = 1 + \frac{\epsilon_i}{\delta} \left(\frac{\epsilon_s}{w} + qN_{ss} \right) \quad (20)$$

where N_{ss} is the density of the interface states, ϵ_i is the dielectric constant of the interfacial layer, w is the space charge width and δ is the thickness of interfacial layer and ϵ_i/δ can be obtained from the following relation [18],

$$\frac{\epsilon_i}{\delta} = \left[\frac{\epsilon_s}{w} \left(\frac{1}{\alpha} - 1 \right) \right] \quad (21)$$

where $\alpha = (kT/q)(d \ln I / dV)$ is the slope of reverse bias I-V characteristic. ϵ_s/w was determined from the reverse current curve using Eq. 21 and was found to be 9.352. The insulator layer thickness δ was obtained from the following relation [7]

$$C_{ox} = \frac{\epsilon_i \epsilon_o}{\delta} A \quad (22)$$

where C_{ox} is the insulator layer capacitance and ϵ_i/δ was found to be 64.87. The energy of the interface states can be determined as [12],

$$E_{ss} - E_v = q(\phi_e - V) \quad (23)$$

where E_{ss} is the energy corresponding to the bottom of the conduction band at the surface of the semiconductor and ϕ_e is the effective barrier height depends on applied voltage due to an interfacial layer given by

$$\phi_e = \phi_B + \left(1 - \frac{1}{n} \right) V \quad (24)$$

where n is dependent on voltage applied. N_{ss} values were obtained via the Eq. 20. The N_{ss} dependence on $E_{ss} - E_v$ is shown in Fig. 8. It is seen that N_{ss} value decreases with increasing $E_{ss} - E_v$ value. The shape of the density distribution of the interface states is in the range of $E_{ss} - 0.02 \text{ eV}$ to $E_{ss} - 1.2 \text{ eV}$. At higher voltages, the decrease in diode current is due to interface states and series resistance effect.

The ideality factor of Al/p-type FSS diode is lower than that of metal/ FeCl_3 -doped polyaniline (B,C and D devices) Schottky diode [19], whereas it is higher than Al/FePc/Au, ITO/PANI(SA)/Al and ITO/PANI(MSA)/Al diodes [20-21]. It is evaluated that the rectifying properties of the diode change depending on the chemical structure and electrical characteristics of the semiconductor materials used in fabrication of diode. Rectifying behavior of the device is related to Fermi level of the organic semiconductor and it has been shown that Fermi level of the conducting polymer is strongly influenced by the dopant type in the polymer [22] and in turn it could affect the junction properties of the devices.

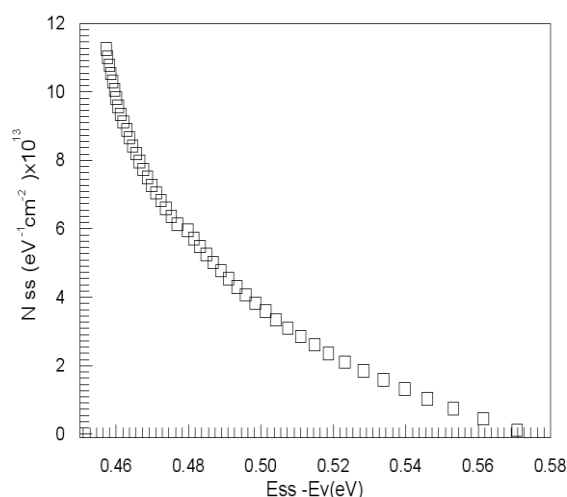


Fig. 8 The variation of N_{ss} values with $E_{ss}-E_v$ for Al/p type-FSS Schottky diode

4. Conclusions

Electronic and interface state properties of the Al/p-FSS diode were investigated by current-voltage and capacitance-voltage analyses. The electronic parameters such as barrier height, ideality factor and series resistance of the Schottky diode were found to be 0.72 eV, 3.05 and 7.73 k Ω , respectively. The $\phi_{B(C-V)}$ value obtained capacitance-voltage measurements is 1.05 eV. The I-V characteristic of the studied diode resemble the typical current-voltage characteristic for conventional Schottky diode.

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