Electrical characterization of the organic semiconductor Ag/CuPc/Au Schottky diode

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Abstract: This paper reports on the fabrication and investigation of a surface-type organic semiconductor copper phthalocyanine (CuPc) based diode. A thin film of CuPc of thickness 100 nm was thermally sublimed onto a glass substrate with preliminary deposited metallic electrodes to form a surface-type Ag/CuPc/Au Schottky diode. The current–voltage characteristics were measured at room temperature under dark conditions. The barrier height was calculated as 1.05 eV. The values of mobility and conductivity was found to be 1.74×10^{-9} cm^2/(V·s) and 5.5×10^{-6} Ω^{-1}· cm^{-1}, respectively. At low voltages the device showed ohmic conduction and the space charge limited current conduction mechanisms were dominated at higher voltages.

1. Introduction

Electronic and optoelectronic properties of the organic semiconductor devices have been intensively investigated in recent years[1−6]. Organic semiconductor based device technology is relatively cheap and easy to fabricate compared to inorganic devices. Very recently, considerable interest has been shown in the fabrication and characterization of Schottky diode barriers using organic semiconductor materials[7−9]. Schottky diodes are the basis of a large number of compound semiconductor electronic devices, such as microwave diodes, field-effect transistors and solar cells[10, 11]. The advantages of these diodes over p–n junction diodes are their fast response, low threshold voltage and simple fabrication technology[12, 13]. These diodes are single layer devices, in which one of the contacts is ohmic while the other is a barrier contact. The formation of Schottky junctions of organic materials with suitable metallic electrodes has been studied in Refs. [14–17].

As a small molecule organic semiconductor, it has been reported that phthalocyanines (PCs) have interesting electrical and optical properties[18, 19]. It has been found that phthalocyanines exhibited high thermal and chemical stability[19, 20]. Therefore, these organic semiconducting materials are suitable for the fabrication of thin films by thermal evaporation without decomposition. The sensitivity of these organic semiconductor compounds usually in the visible region of the spectrum has been reported in Ref. [18]. The effect of different deposition parameters on the electrical, optical and structural properties of phthalocyanine thin films has been studied in Refs. [21–23].

The electrical properties of the metal phthalocyanine deposited between gold and lead electrodes have been investigated by Anthopoulos[24] and it has been found that the current–voltage characteristics show ohmic conduction at lower voltages followed by space-charge-limited current at higher voltages. Karimov *et al.*[25] fabricated a sandwich-type structure of Al/CuPc/Ag and investigated the electrical properties of

the device. The rectification ratio of the device was found to be 7 at $\pm$ 4 V. The electrical properties of phthalocyanines have mostly been investigated in the form of sandwich structures, and space-charge-limited conductivity was observed with current density, showing a power-law dependence on the applied voltage[25]. One of the disadvantages of the sandwich type structure is the shortening of the devices, during the deposition of the top electrodes.

As compared to the sandwich-type structure, surface-type organic thin film structures represent a simplicity, low cost and less chance of damaging the device. Because of these advantages, there is a growing interest in the fabrication and study of surface-type optoelectronic devices employing organic semiconductors[7, 26, 27]. From the available literature, it has been found that not much work has been performed on the junction properties of CuPc thin films in surface-type structures. In this work, we have fabricated and investigated the electrical properties of the surface-type Ag/CuPc/Au diode.

2. Experimental

The copper phthalocyanine powder used in this work was obtained from Sigma Aldrich and used without further purification. Its molecular structure is shown in Fig. 1. Before starting the deposition, the glass substrate was cleaned in an ultrasonic bath for 10 min using acetone, followed by rinsing in distilled water. The substrate was dried in open air in a cleaned room. The metallic electrodes of gold and silver of 100 nm film thickness were deposited by using an Edward Auto 306 thermal evaporator on cleaned glass substrates. Then thin film of CuPc was thermally sublimed onto the glass substrate in the gap of preliminary deposited metallic electrodes. The film thickness of the CuPc film was 100 nm. The width and length of the gap between the metallic electrodes were 42 μm and 2 mm, respectively. The deposition rates of all of the films were kept at about 0.2 nm/s. During deposition, the pressure in the vacuum cham-
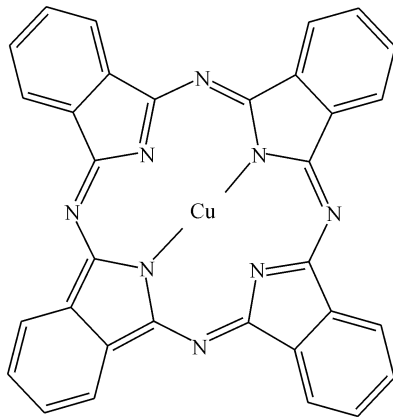

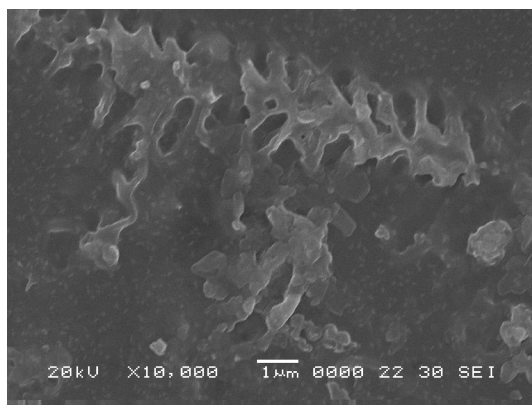Fig. 1. Molecular structure of copper phthalocyanine (CuPc).
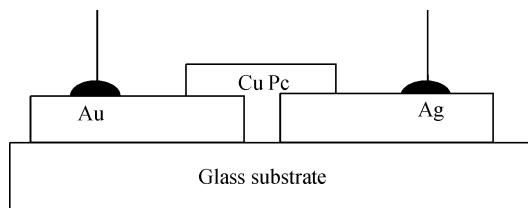

Fig. 2. SEM image of the CuPc film.

Fig. 3. Cross sectional view of the Ag/CuPc/Au diode.

ber was kept constant at about 10^{-5} mbar. The thickness of each layer and the deposition rates were monitored by a crystal-controlled thickness monitor[28]. Figure 2 shows a SEM image of the CuPc film. The surface-type Ag/CuPc/Au structure was fabricated.

The cross-sectional view of the device used in this work is shown in Fig. 3. To characterize the organic diodes, the current voltage characteristics were measured by using a Material Development Corporation (MDC) probe station connected to a Keithley 237 voltage source/picoammeter and an Agilent 4980A precision LCR meter. The set-up was computer controlled by the MDC software package CSM/Win QuietCHUCK. For the $I-V$ measurements, the bias voltage was swept from −12 to +12 V. All of the measurements were taken under dark conditiona at room temperature.
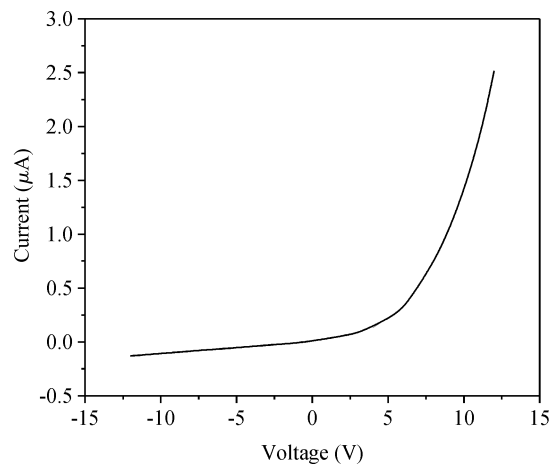
Fig. 4. $I-V$ characteristics of the Ag/CuPc/Au diode.

3. Results and discussion

The electrical properties of the metal and semiconductor contact depend upon the difference between its work function and its interfacial properties. For the formation of a rectifying contact, the work function of the metal must be smaller than that of a p-type semiconductor. Figure 4 shows the measured dark current-voltage characteristics of a Ag/CuPc/Au diode (where positive potential was applied to gold electrodes). It is seen in Fig. 4 that the forward bias current of the device increased exponentially while in the reverse bias the current was found to increase slowly with increasing applied voltage. The asymmetric and non linear $I-V$ curve shows that the device exhibits rectification behavior. The rectification ratio (RR) is a ratio of forward and reverse bias current at the same voltage and is equal to 3.2, 5, 8.8 and 16 at ±1, 6, 8 and 11 V, respectively. The rectification may be due to the formation of a rectifying contact at the metal/organic semiconductor interface.

For the analysis of dark current, the modified Shockley equation may be expressed as[29]

$$I = I_o \left[\exp \frac{q\,(V - IR_S)}{nkT} - 1 \right] + \frac{V - IR_S}{R_{Sh}}, \qquad (1)$$

where I and V are the terminal current and voltage, I_o is the saturation current, n is the ideality factor, k is Boltzmann's constant, and R_S and R_{Sh} are the series and shunt resistances, respectively. The equation of reverse saturation current is given by[30]

$$I_o = A^* A T^2 \exp \left(-\frac{q\phi_b}{kT} \right), \qquad (2)$$

where A^* is Richardson constant, A is the cross-sectional area of the diode, and ϕ_b is the Schottky barrier height. The value of the barrier height is calculated from Eq. (2). The value of the ideality factor and barrier height is equal to 85 and 1.05 eV, respectively.

The shape of the non-linear $I-V$ characteristics in forward bias depends on the series resistance (R_S) of the junction. If the series resistance is high, the non-linear forward bias $I-V$ curve will show a wide curvature, and if the effect of series resistance is less, then the non-linear region of the forward bias $I-V$ curve
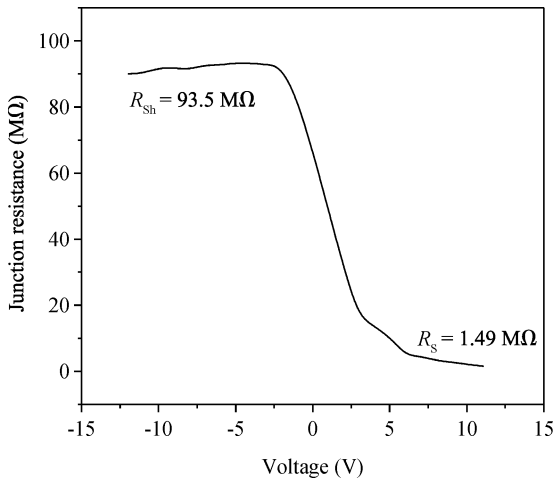
Fig. 5. Junction resistance (R_J) versus V for the Ag/CuPc/Au diode.

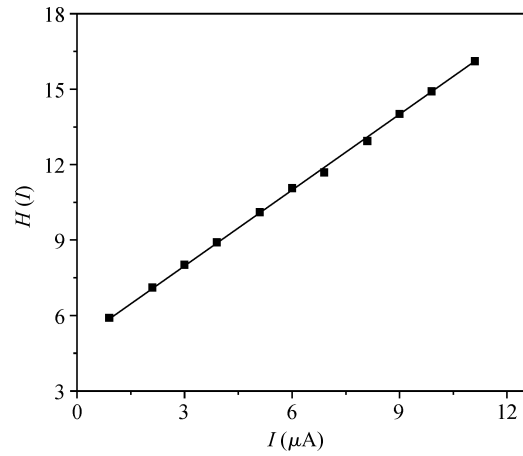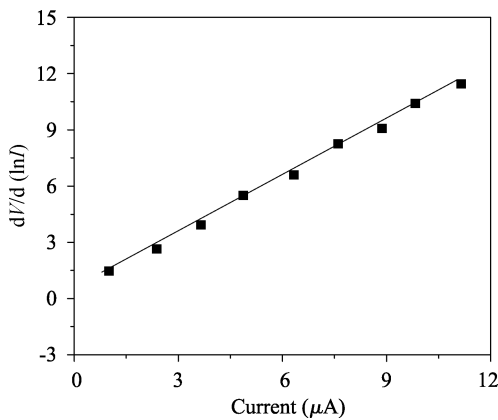Fig. 7. $H(I)$–I plot of the Ag/CuPc/Au diode.

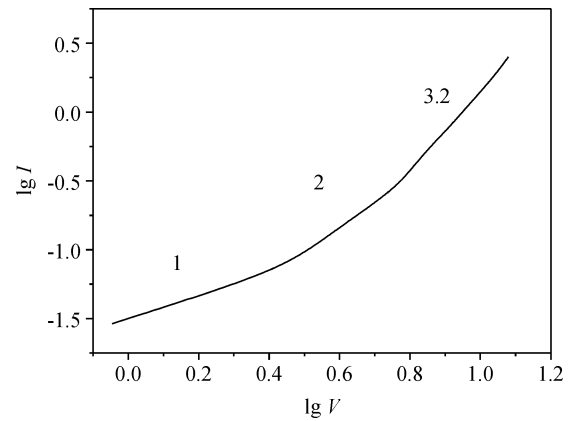Fig. 6. dV/d(ln I)–I plot of the Ag/CuPc/Au diode.

Fig. 8. Forward bias current–voltage curve in log–log presentation.

will be small[31]. The value of the series resistance is calculated from the junction resistance obtained by $R_J = \partial V / \partial I$ from the current-voltage characteristics of the diode. The junction resistance R_J versus the voltage of the surface-type Ag/CuPc/Au Schottky diode is presented in Fig. 5. The minimum value in the forward bias and the maximum value in the reverse bias of the junction resistance is known as series resistance and shunt resistance, respectively. The series resistance R_S = 1.49 MΩ and shunt resistance R_{Sh} = 93.5 MΩ are determined from the plot of diode resistance Fig. 5.

The series resistance of the Schottky diode can be evaluated by using a method developed by Cheung and Cheung[32]. Cheung's functions can be written as

$$\frac{\mathrm{d}v}{\mathrm{d}(\ln I)} = I R_S + n\frac{kT}{q}, \tag{3}$$

$$H(I) = V - n\frac{kT}{q}\ln\frac{I_o}{AA^*T^2}, \tag{4}$$

and

$$H(I) = I R_S + n\phi_b, \tag{5}$$

where R_S is the series resistance, n is the ideality factor and ϕ_b is the barrier height calculated from the I–V characteristics. Figures 6 and 7 show the plot of dV/d(ln I) versus I and

$H(I)$ versus I curves. The values of series resistance and ideality factor are calculated from the slope and y-axis intercept to the graph dV/d(ln I) versus I. We have obtained n and R_S as 56 and 1 MΩ. It is observed that the value of ideality factor obtained from the I–V curve is greater than calculated from dV/d(ln$I$)–I plots. This difference may be due to the presence of series resistance, interface states, and the voltage drop across the interfacial layer[8]. The values of series resistance are also obtained from the $H(I)$ versus I plot. The slope of the $H(I)$–I plot represent the value of series resistance and is found to be 1 MΩ. It is observed that the values of series resistance determined from the dV/d(ln$I$)–I and $H(I)$–I graphs are the same. This shows the consistency of Cheung's functions.

The double logarithmic graph of the Schottky diode in forward bias is presented in Fig. 8. The various conduction mechanisms of the sample were studied by using this graph. It was found from Fig. 8 that under forward biases Schottky diode exist three distinct linear regions. The slope of the first region is equal to one showing ohmic conduction in the low voltage range. The current density J within the ohmic region is described by the following equation[33],

$$J = e n_o \mu \frac{V}{d}, \tag{6}$$

where V is the applied voltage, e is the electronic charge, d is the gap between the electrodes, μ is the carrier mobility and n_o

is the free carrier density.

It is seen that the slope of region II is about 2.2 exhibit SCLC followed by a third region III of $I-V^{3.2}$. Such power dependence leads to the conclusion that the conduction mechanism is due to SCLC dominated by a discrete trapping level in region II and by exponential distribution in region III. The different slopes in the different regions of the $I-V$ curve are due to trap bands with different energies. The hopping model is used to justify the transport mechanism through the organic materials by localized energy states which arise due to lack of order, impurities and dislocation, etc. Theses localized states are uniformly distributed in the range of energy band gap. The current density J in the presence of shallow traps in the organic films is expressed by[34]

$$J = \frac{9\varepsilon_s \theta \mu V^2}{8d^3},\qquad(7)$$

where ε_s is the permittivity of the organic semiconductor, μ is the charge carrier mobility, d is the gap between electrodes, V is the applied voltage and θ is the trap factor. The equation for the trap factor is written as[25]

$$\theta = \frac{p_o}{p_o + p_t},\qquad(8)$$

where p_o is the density of the free carrier and p_t is the density of the trapped hole and may be calculated as

$$\theta = \frac{J_1}{J_2}.\qquad(9)$$

The value of the trap factor can be determined by using Eq. (9), where J_1 and J_2 are the ratio of current densities at the beginning and at the end of the square law region. The value of θ is calculated from the log–log graph of current-voltage characteristics and is equal to 0.44.

The conductivity at room temperature in a linear region of current voltage characteristics can be calculated as

$$\sigma = \frac{Jd}{V},\qquad(10)$$

where V is the applied voltage, J is the current density and d is the gap between the electrodes. The value of conductivity is equal to $5.5 \times 10^{-6}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$. The value of mobility can be determined by using Eq. (7) and is equal to $1.74 \times 10^{-9}\ \mathrm{cm}^2/(\mathrm{V}\cdot\mathrm{s})$. It is known that metal–semiconductor junctions can show properties of ohmic junctions or rectifying junctions[35]. It depends on the work function of the metal and semiconductor. The work function of metal is constant whereas the work functions of semiconductors depend on the dopant concentration. Originally, CuPc was an intrinsic organic semiconductor, but in the effect of oxygen unintentionally it is doped to a p-type semiconductor. The electron affinity of the CuPc is in the range of 3.1–3.3 eV, whereas the gap is in the range of 1.5–1.7 eV[36]. Usually, CuPc forms an ohmic contact with silver[35]. From experiment, it was found that in forward bias the positive polarity of the voltage source was to the gold terminal. Take into account that the work functions of Au and Ag are equal to 5.1 eV and 4.3 eV, respectively.

Taking into account the obtained results, the energy band diagram of the Ag/CuPc/Au junctions are represented in Fig. 9.
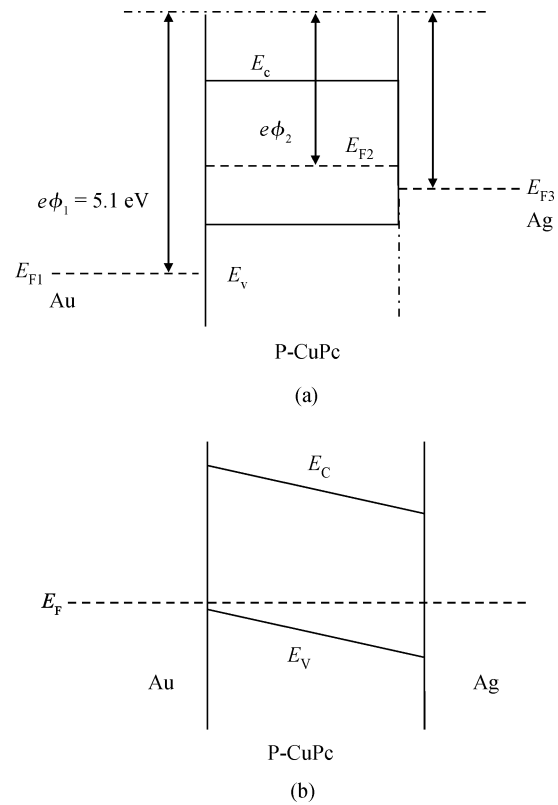

Fig. 9. Energy band diagram of the Ag/CuPc/Au junctions (a) before contact and (b) after contact. $e\phi_1$, $e\phi_2$ are work functions of Au, CuPc and Ag respectively. E_c and E_v are the bottom and top of the conduction band and valance band of CuPc.

4. Conclusions

In this paper, the electrical characteristics of the surface-type Au/CuPc/Ag diode have been investigated. It was observed that at higher forward voltages, the conduction mechanisms were dominated by space charged limited conduction (SCLC) controlled by single and aexponential trapping levels at two different ranges of applied voltages. The mobility and conductivity were calculated from the current–voltage characteristics.

Acknowledgments

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