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Structural Characterizations and the Influence of Metal Work Function Contact for Nanocrystalline2,9-Dimethyl-4,7-Diphenyl-1,10-Phenanthroline Based Devices

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Abstract: Nanocrystalline 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP thin films were successfully deposited by dip-coating technique. Surface morphology and film thickness of the obtained films were achieved from the front and cross sectional imaging of scanning electron microscopy. The influence of several rectifying metals such as Al, In, Sn and Au on the current-voltage characteristics of BCP based devices was investigated at metal/semiconductor. Electrical parameters of the devices were extracted from the forward current-voltage characteristics and compared with each other. The relationship of barrier height and the metal work function were found to vary almost linearly due to the pinning of Fermi-level in the lowest unoccupied molecular orbital of BCP. Moreover, the prepared devices of Al, In, Sn, and Au/ BCP show different rectifying characteristics. High value of rectification characteristics of Au/ BCP can be interpreted by means of high value of work function of Au metal as compared with the other metals at M/S interface. In addition, analyses of current-voltage characteristics confirm that using of different metals (Al, In, Sn, and Au) have considerable influence on electrical characteristics of the prepared devices. The transient of the photocurrent of the prepared devices suggests the validity of these devices for optoelectronic application due the sensitivity for the white incident light.

Keywords: Nanocrystalline; Metal contact; Work function; Current-voltage characteristics; Optoelectronics.

1 Introduction

Organic semiconductors offer motivating physical and chemical characteristics that basically distinguish them from inorganic ones and that rationalize the considerable potential offer into a vibrant field of research on their prospects as semiconductors and conductors for electronic and optoelectronic device applications. These materials have unique properties like low cost, easy for manufacturing, several varieties for technology, suitability with numerous substance types, possibility for achieving flexible structures, infinite variety of organic compounds. Recently, organic semiconductor thin films have established various applications in organic light-emitting diodes, thin film transistors, organic photovoltaics, solar cells and lasers.

In addition, most of the manufactured devices shifted from the ideal case due the effect of various factors such as the presence of native oxide layer between the metal and the semiconductor, interface states and series resistance [4-5]. Then, the interface states and series resistance perform serious part in extracting the main important parameters and its behaviors such as barrier height and ideality factor and determining the Schottky barrier height and other characteristic parameters. Thus, these restrictions can influence the stability, performance, reliability as well as the stability of the device. [6]. Consequently, one can conclude that the barrier height calculated from the *I–V* characteristics are monitored by the presence of interface states energy distribution in balance with the semiconductor under biased applied potential status[6-7]. Actually, major contributions concerned the main characteristics parameters of diodes like barrier height, ideality factor, and series resistance for various metal–semiconductor contacts [8-12]. The common of such studies comes from their importance to semiconductor industry.

In the present work, different Schottky based BCP devices were prepared using several rectifying metal contacts that have different work functions. Structural characteristics of BCP film such as morphological and microstructural characteristics were studied using SEM and TEM, respectively. These devices were characterized by using dark current-

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voltage characteristics under forward and reverse bias. The important parameters of the obtained devices from the electrical measurements were compared and discussed. The important relations for the barrier height and metal work functions were extracted to realize the kind of barrier and interface characterization. In addition, the transient current characteristics were also considered to understand the effect of light on the prepared devices for optoelectronic device application.

2 Experimental

2.1 Preparation of BCP thin films

2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP (96%) was purchased from Sigma–Aldrich Chem. Co., USA without any further purification. The empirical formula, molecular weight and CAS number are respectively $C_{26}H_{20}N_2$, 360.45 and 4733-39-5. The schematic diagram of the chemical structure of **BCP** is shown in Fig. 1. Thermal evaporation technique using a coating unit (Edward, E-306 A, England), under a pressure of about 2 x10^{-5}Torr and the rate of deposition (2 nm s^{-1}) was used for obtaining nanostructure thin films of **BCP** with thickness~570 nm using a quartz crucible heated by a tungsten coil. Quartz crystal monitor (FTM4, Edwards) was used to control the deposition rate and measured the film thickness.

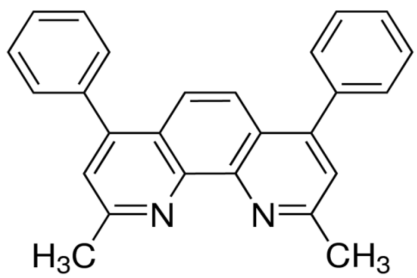

Fig.1 Schematic diagram of 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline.

2.2 Top and back contacts

Before preparing the **BCP** thin film, a bottom ohmic contact was prepared and the top contact was deposited by thermal evaporation using special musk to form the grids of mesh spacing of 0.5 mm. The total mesh size was 10 x 10 mm. Four pure metallic contacts (Al, In, Sn, and Au) were separately deposited as a top contact on **BCP**.

2.3 Characterization and Measurements

The surface morphology and the thickness of the prepared films were characterized by Scanning electron microscopy of type JEOL-JSM-636 OLA using a flat and cross sectional imaging of the film and film/substrate edge, respectively. Particle size measurements were estimated using N5 Submicron Particle Size Analyzer. In addition, the microstructural properties of the prepared film was examined by selected area electron diffraction using JEOL 1200 EX2 transmission electron microscopy.

The dark current-voltage and transient photocurrent, using a white halogen-tungsten lamp, measurements for Al, In, Sn and Au on **BCP** structures were carried out by using a highly impedance electrometer type Keithley 2635 A source meter at 300 ºC.

3 Results and discussion

3.1 Surface Characterization of BCP films

The surface morphology of the **BCP** structure was studied by SEM as shown in Fig. 2(a). As observed, the mean grain size is changed from position to another position with agglomeration of fine particles. The higher magnification image of 100,000× shows that the particles can be resolved to be also agglomerated and of mean particle size in the range of 50-70 nm, which confirms the nanocrystalline characteristics of the prepared films. In addition, some aggregation was taken place to get a considerable size grains. Furthermore, particle size analyzer (Fig.2 (b) measured the particle size and the size is found to be 70 nm, in agreement with the value determined from SEM. Moreover, the film thickness was measured from the film/substrate edge using the cross sectional image of SEM. A high adherence of the film to substrate as well as a nearly homogenious film on the substrate is observed and the average value of the film thickness is determined from the vertical boundaries of the **BCP** film /substrate and found to be ~ 570 nm.

The experimental results from selected area electron diffraction SAED (Fig. 2(d)) demonstrates polycrystalline properties for the obtained films which is in good agreement with those obtained from SEM.

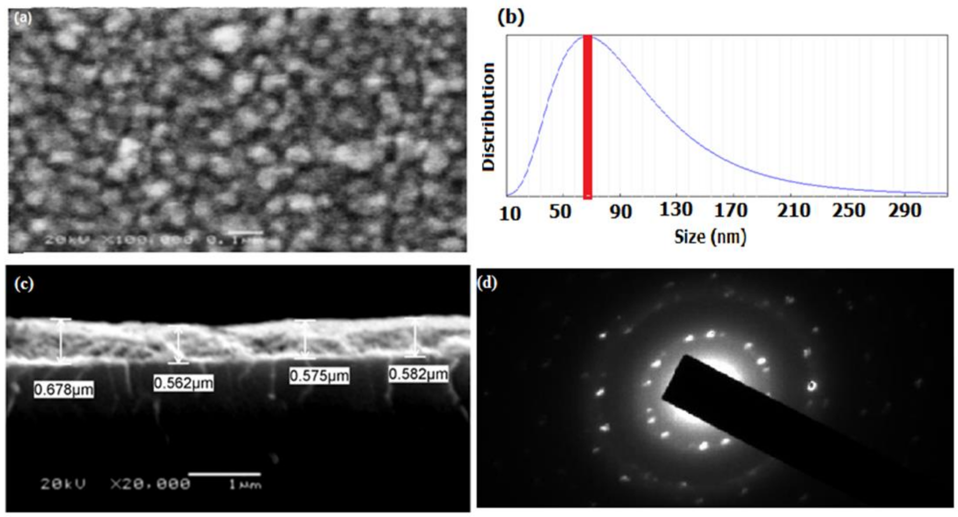

Fig.2 (a) Plane view of SEM, (b) Particle size distribution , (c) Cross section view and (d) SAED image of ,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP

3.2 Influence of metallic contacts on the BCP junctions

Semilogarthmic plot of the forward and reverse bias *I-V* measurements of the Al, In, Sn and Au on BCP structures were carried out at room temperature (~300 K) and shown in Fig.3. The main electrical parameters of these structures such as ideality factor (n), zero-bias barrier height (Φ_{B0}), series resistance (R_s) and shunt resistance (R_{sh}) were deduced. The current-voltage characteristics were described by using the following equation [13]:

$$I = I_0\left(\exp\frac{q(V-IR_s)}{nkT} - 1\right) + \frac{(V-JR_s)}{R_{Sh}} \quad \textbf{(1)}$$

where I_0 is the saturation current and can be written as

$$I_0 = AA^{*}T^{2}exp\left(\frac{-\Phi_{B0}}{kT}\right) \quad \textbf{(2)}$$

Where A is contact area, A^* is Richardson constant, T is temperature in Kelvin, Φ_{B0} is the barrier height, k is the Boltzmann constantan, R_s is the series resistance, R_{sh} is the shunt resistance and n is the ideality factor. The ideality factor can be estimated from the linear region of the *I–V* curve ($n=q/kT(dV/d(lnI)$) under condition of $V > 3KT/q$. The zero-bias barrier height can be determined by making a linear region of the semi-log *I-V* plots by extracting the I_0 from the extrapolation of the intercept with the zero voltage axis($\Phi_{B0}=2.303kT/q\ log(AA^{*}T^{2}/I_0)$). For an ideal diode, the value of n should be equal to 1 but it is usually observed to be greater than unity. The high n values for the devices indicate that the $I{-}V$ plots exhibit departures from the ideal thermionic behavior. According to the literature, most diodes show deviations from the ideal thermionic model. The non-ideal $I{-}V$ characteristics might denote there is intimate contact between metal and **BCP** which can be attributed to the presence of interface state exists between metal and semiconductor and/or recombination of electrons and holes in the depletion region [14-15]

Figure 3 shows the dark current-voltage characteristics at room temperature under forward and reverse bias for Al, In, Sn and Au/**BCP** devices. These four devices of different rectifying metal contacts are used and compared with each other. At any given bias voltage, it is observed that the Au/ **BCP** device has a current larger than that of the other devices. The difference in the *I-V* characteristics can be attributed to the diverse in contact barriers and then apportionment of the states of interface at metal/semiconductor contact. The experimental values of Φ_{B0} and n were determined from the intercept and the slope of the forward bias semi-log *I-V* characteristics. The higher value of n than unity indicate that the

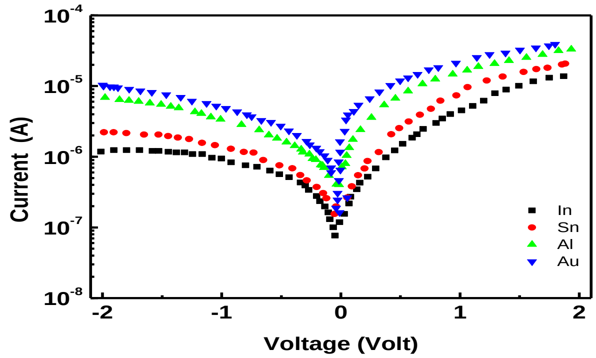

Fig.3 Current-voltage characteristics of 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP using different metal contacts.

Table1 The main important parameters deduced from current –voltage characteristics of 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP using different metal contacts.

Metal	Φ_m(eV)[16]	*n*	Φ_{B0}(eV)	R_s(kΩ)	R_{sh}(kΩ)
In	4.28	3.35	0.58	147	1480
Sn	4.08	3.85	0.51	90	910
Al	4.26	2.90	0.53	60	300
Au	5.01	2.59	0.62	40	191

diode obeys metal-interfacial layer-semiconductor configuration rather than an ideal diode. The values of *n* and other device parameters are tabulated in Table 1 for In, Sn, Al and Au / **BCP** diodes, respectively and shown in Fig.4 (a). In addition, Φ_{Bo} values were also determined. There are almost differences between the Φ_{Bo} values of In/ **BCP**, Sn/**BCP**, Al/**BCP** and Au/ **BCP** diodes. This may be explained by the fact that work functions of these metals are quite different such that: 4.26 eV for Al and 4.08 eV for In; 4.28 eV for Sn and 5.01eV for Au [16]. The work function of Au is greater than that of Al, In, and Sn. Thus, it is reasonable to expect that the barrier height increase with increasing work function and the barrier heights are nearly similar for Al and Sn the nearly equality of the work functions. The above results on Φ_{Bo}, for four different metals, and the corresponding work functions Φ_m are given in Table 1. The obtained values of barrier height is shown in Fig.4 (b) for each metal contact.

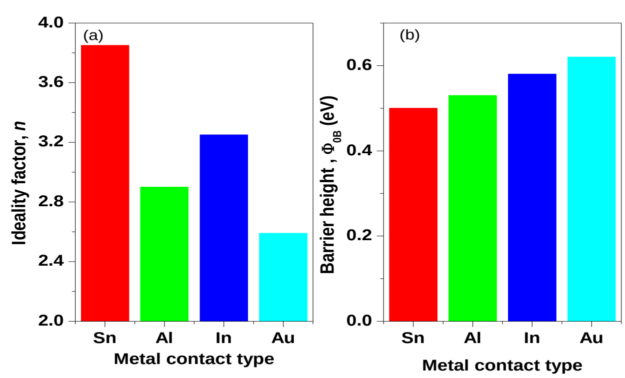

Fig.4 (a) Plot of ideality factor vs. substrate type and (b) barrier height vs. substrate type of (Sn, Al, In and Au) / BCP devices.

In addition, the *I-V* curves exhibit rectifying characteristics with the rectification ratio (RR=I_F/I_R) shown in Fig.5 for each electrode. Higher rectification ratio of Au/ **BCP** is compatible with the fact that the high work function of the Au produces high barrier height at interface of metal/semiconductor.

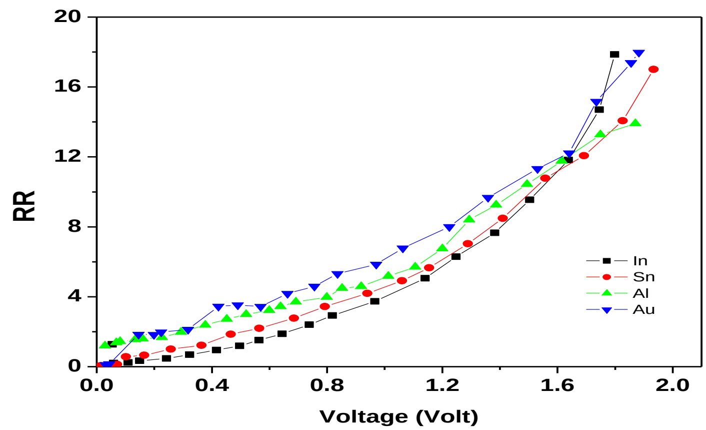

Fig.5 Rectification ratio of 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP using different metal contacts.

Furthermore, the study of the plot of the barrier height and the metal work functions of metal (Al, In, Sn and Au) / **BCP** diodes (i.e. Φ_{B0} vs. Φ_m plot) is shown in Fig.6. A nearly linear fit is obtained and the slope ($S=d\Phi_{B0}/d\Phi_m$) is defined as the index of interface behavior in Φ_{B0}-Φ_m plot. It can be used to determine the grade of the pinning of Fermi-Level at the interface [17] and the slope id determined and found to be 0.107. Small value of the slope S and weak linear relationship (Φ_{B0}=0.088+ 0.107Φ_m) between Φ_{B0} and metal work function in **BCP** based devices confirm the grade of the surface level pinning.

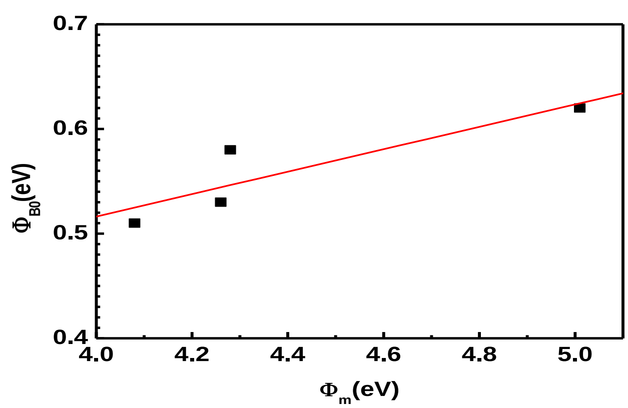

Fig.6 Plot of Φ_{B0} vs. Φ_m for of 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP using different metal contacts.

The deviation in the linearity of the semilogarithmic plot of forward *I-V* characteristics can be attributed to the effect of series resistance and the native interfacial layer effect under high applied voltage. The series and shunt resistances (R_s and R_{sh}) are important factors for improving the device performance and design obtained at room temperature (300 K) by the method mentioned in the previous work [18], by using the relation between junction resistance R_J and the applied voltage V shown in Fig. 7.

It is observed, at sufficiently high forward biasing, the junction resistance approaches a constant value characterizing the series resistance R_s. In addition, in Fig.7, the junction resistance shows a constant value at sufficiently high reverse biasing, which equals the diode shunt resistance R_{sh}. The values of R_s and R_{sh} were obtained for the devices with different metal contacts structures and listed in Table1. It is observed that the structure has high series resistance as compared to the best devices, which may be attributed to the same reasons for the un-ideality characteristics of the prepared devices.

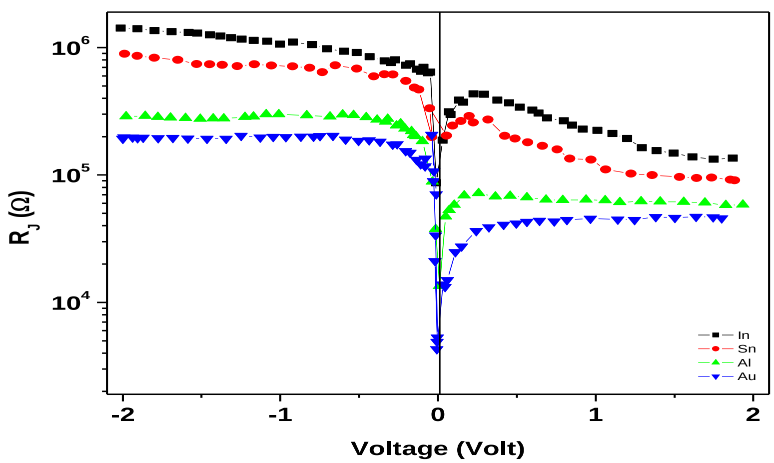

Fig. 7 Plot of junction resistance vs. applied voltage of 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP using different metal contacts.

3.3 Photoresponse characteristics of BCP based devices

Photoresponse properties of the Al/ **BCP**, In/**BCP**, Sn /**BCP** and Au/ **BCP** diodes were achieved by transient photocurrent characteristics. This study is a well-recognized method to discuss the transport characteristics of photodiodes [19]. For this investigation, the device was turned under light on and light off for time periods. Fig. 8 presents the influence of the devices structure on the transient photocurrent of the studied devices. As observed, for the turned on state of light, the current increases with high intense for all devices and reaches a maximum limit, after which it decreases when the light is turned off. This behavior can be described by the process of trapping and detrapping of charge carrier from shallow trap level [20]. The results suggest the possibility of the prepared devices for white light photodiode application [19,20].

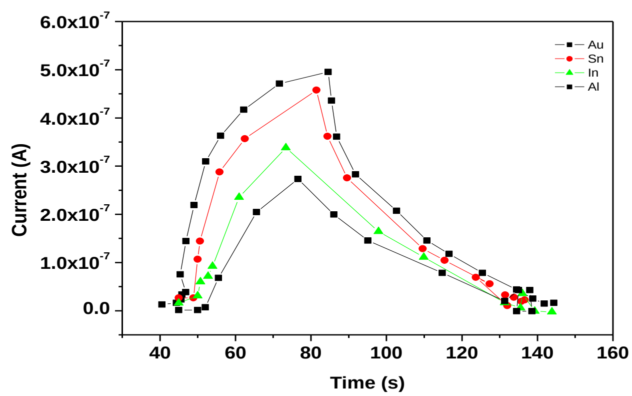

Fig.8 Plot of the transient photocurrent of BCP using different metal contacts.

4 Conclusions

Thin film of different structures based **BCP** devices were successfully prepared by dip coating technique. Effect of metal work function on the barrier height was investigated by dark *I-V* characteristics at room temperature. Values of barrier height were found be little depends on the type of the metal work function with an almost linear relationship of Φ_{Bo}=0.088+0.107Φ_m. Moreover, the metal work function dependence of the barrier height could supply more guide for the pinning of Fermi-level. The series and shunt resistances have considerable influence on the electrical properties of **BCP** based devices. The transient photocurrent measurements confirm the sensitivity of the devices to white light and the possibility for photodiode applications.

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