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Electrical properties of organic semiconductor copper phthalocyanine thin films deposited from solution at high gravity

KH. S. KARIMOV[a,b], I. QAZI[a], S. A. MOIZ[c], I. MURTAZA[a,*]
[a] *GIK Institute of Engineering Science and Technology, Topi, Swabi, N.W.F.P, Pakistan, 23640*
[b] *Physical Technical Institute of Academy of Sciences, Rudaki Ave.33, Dushanbe, 734025, Tajikistan*
[c] *National Centre for Nanotechnology, Pakistan Institute of Engg. & Appl. Sc. (PIEAS), Nilore, Islamabad, Pakistan*

P-type organic semi conducting copper phthalocynanine (CuPc) thin films were grown from its solution in benzene on nickel (Ni) substrates, at room temperature, by using a centrifugal machine operated at 1107*g*. On CuPc films aluminum films (transparency was equal to 15 %) were deposited, by vacuum evaporation, to form Schottky junction and Al/p-CuPc/Ni samples were fabricated. *I-V* characteristics were then evaluated at 24 ^{o}C and 64 ^{o}C. It was found that dark current-voltage characteristics of the Al / p-CuPc / Ni samples are non-linear and show rectification behavior. Rectification ratio *RR* defined as the ratio of the forward and reverse currents at the same voltages (here V = ± 30 V) was equal to 2.2 and 2.9 at 24 ^{o}C and 64^{o}C, respectively. The dark I-V characteristics were simulated by space-charge limited current (SCLC) approach assuming the presence of deep trapping levels at energy above the valence band edge of the p-CuPc.

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1. Introduction

During the past decade, organic semiconductors have been investigated widely as conjugated polymers, oligomers and low molecular weight materials. Their lower material and fabrication cost are attracting extensive interest for their potential applications in organic devices [1-5]. The structural flexibility, good electric and optical properties offered by thin films of organic semiconductors have led to promising electronic and optoelectronic applications within the last few decades [6]. Recently, organic semiconductor materials have attracted electronic industry because of the prospects of high throughput manufacturing using very low cost thin film deposition techniques.

It is known that the structure and the properties of organic semiconductors are highly dependent upon the fabrication technology. To optimize the structural properties which define the electrical behavior of a device centrifugal processing techniques are commonly employed with variable processing parameters. It is thus assumed that a suitable processing technology may result in a better electrical performance of a finished device from a given organic material [4].

Generally, organic semiconductors have large molecular weight and strong intramolecular bonding in the form of specific combination of single and double bond. However, they offer weak Van der Waal's intermolecular bonding. This special arrangement causes the delocalization of charges along the molecules or chain. Under the influence of external applied voltage, the free charges move from one molecule or chain to another molecule or chain by hopping phenomenon. Whereas rate of hopping is severely affected both by the degree of energetic disorderness and positional disorderness offered by an organic semiconductor. The effects of disorderness on the charge transport mechanism can be estimated by evaluating the mobility of charge carriers in a given semiconductor.

Time of flight (TOF) measurements have been conventionally used in order to study the mobility in disordered materials including organic semiconductors. In the case of presence of space charge the *I-V* characteristics are used to evaluate electrical parameters. The *I-V* based electrical parameters extraction mechanism explains fairly well the observed response of a device and is considered a more accurate approach for most of the organic semiconductor devices [5].

Organic semiconductor phthalocyanines and in particular CuPc is one of the well-studied organic photosensitive semiconductor [7]. It has a high absorption coefficient in a wide spectrum and high photo- sensitivity at low intensities of radiation. Its deposition by vacuum sublimation is easy. Purification of CuPc is simple and economical as the sublimation occurs at relatively lower temperatures (400 – 600 ^{o}C).

Studies of dark conductivity by El-Nahass et. al [8] on copper phthalocyanine thin film with gold electrodes has shown that in the direction of film's plane the conductivity increases with increasing thickness. These authors established that the conductivity-temperature relationship exhibits a change from extrinsic to intrinsic conduction at temperature of ~ 380 K. They also measured the Seebeck coefficient which showed that CuPc thin films behave as p-type semiconductor and the thermoelectric coefficient reaches a maximum at 400 K. At lower voltages the ohmic and at higher voltages the space-charge limited current conductivities were observed [8]. Indium tin oxide (ITO)-CuPc-metal(Au,Cu,Al) samples were investigated by Maharatro etal [9] .They found that the current is injection limited when the Schottky energy barrier is high and space charge limited when the Schottky energy barrier is low .

Park et. al [10] reported studies on copper phthalocyanine (CuPc) / $PbZr_{0.2}Ti_{0.8}O_3$ (inorganic ferroelectric) heterojunction gate with $La_{0.87}Ba_{0.13}$ MnO_3 (a ferromagnetic oxide semiconductor) channel and demonstrated the non-volatile and non-destructive photomemory operation. The device could write information with combination of light irradiation and the negative gate bias, and delete only with a positive gate bias.

In an earlier work Karimov etal fabricated and investigated properties and characteristics of organic-on-inorganic Ag/*p*-CuPc/*n*-GaAs/Ag photoelectric sensors at room [11] and elevated temperatures [12] in photovoltaic mode and photoconduction mode of operation under tungsten filament lamp illumination. The photocurrent and photo-voltage spectra showed that the cell is sensitive in a large spectral wavelength range of 200-1000 nm i.e., from UV to visible to NIR spectrum. The conductivity and other electrical properties of CuPc based devices depend on a number of parameters such as thin film deposition and processing technology, thickness, nature and properties of both contact materials and presence of depletion region. In the current article, thin films of CuPc have been fabricated from solution by using centrifugal deposition technique on Ni substrates, Al thin film was deposited on CuPc to form metal-semiconductor barrier junction and electric properties of the Al/p-CuPc/Ni samples were investigated.

2. Experimental

The CuPc was obtained from Sigma-Aldrich. Fig. 1 shows the molecular structure of the CuPc molecule used as a *p*-type organic semiconductor [13, 14]: due to unintentional doping by oxygen CuPc shows properties of p-type semiconductor. It is known that, at least, seven crystalline polymorph states of CuPc exist: α, β, γ, R, δ, ε etc. [15]. The form α-CuPc is a metastable one at T = 165 °C and can be converted thermally, or if deposited at room temperature from solution, to the β-form. The α and β-forms are the most frequently encountered states of CuPc.

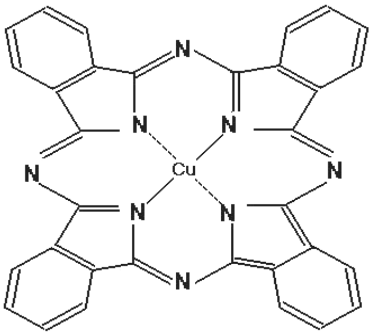

Fig. 1. Molecular structure of CuPc.

The CuPc films were deposited by using a centrifugal machine (Fig. 2), from CuPc 5 wt% solution in benzene on Ni substrates at room temperature at gravity conditions of 123g, 277g and 1107*g*; where *g* is acceleration due to gravity. The substrate was placed inside an aluminum vessel which was mounted on the centrifugal machine. The machine had an 11 cm arm and provides acceleration up to 1107*g* at its maximum rotation speed of 3000 rpm. For each film growth two symmetrically installed aluminum vessels filled with solution of equal volume (0.6-0.9 ml) were used. The 10-30 minutes processing time was required to evaporate the solvent completely and to get the films deposited on the substrate. Optical examination showed that the films deposited at 1107 *g* were homogeneous and of uniform morphology and those deposited at 1g, 123g and 277g were not uniform and had visible cracks. Therefore in the current article only the results obtained on CuPc films deposited at 1107g have been presented. The nominal thicknesses of the CuPc films (10 μm) were estimated by measurement of capacitance. The relative dielectric constant ε_d at dark conditions was equal to 4 at T=20 °C and at a frequency of 1 kHz [16].

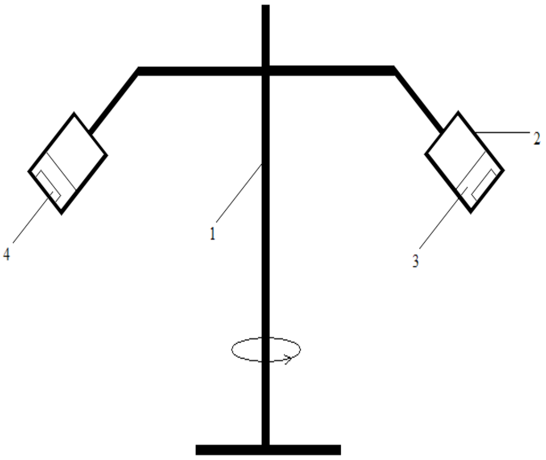

Fig. 2. Schematic diagram of a table-top centrifuge apparatus used for the growth of organic films. (1-support,2-glass vessel,3-solution,4-substrate).

Unlike spin casting or solution casting, in centrifugation the solution is rotating with respect to substrate during the film growing process which results usually in more uniform deposition of the film. On CuPc films aluminum films (transparency was equal to 15 %) were deposited, by vacuum evaporation, to form Schottky junction and by this way Al/p-CuPc/Ni samples were fabricated (Fig. 3). Droplets of liquid gallium, at room temperature, were deposited on the Al film and Ni foil to provide contacts with terminals. *I-V* characteristics were then evaluated by using a dc measurement station with temperature adjusting facility. The measurements were carried out in the temperature range of 24 to 64 °C with an experimental error of ±0.5 °C.

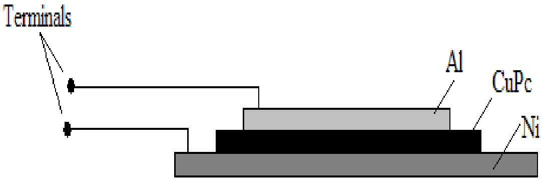

Fig. 3. Cross sectional view of the Al / p-CuPc / Ni sample.

3. Results and discussion

Fig. 4 shows the *I-V* characteristics of the Al/p-CuPc/Ni sample measured under dark condition at T=24 °C and 64 °C. It is seen that the currents increased with increase of temperature. The characteristics exhibit slightly a rectification behavior. Rectification ratio RR defined as a ratio of forward to reverse current at the same voltages (here ± 30 V) was equal to 2.2 and 2.9 at 24 °C and 64 °C respectively. In the forward bias the "+" voltage of power supply was applied to Ni electrode.

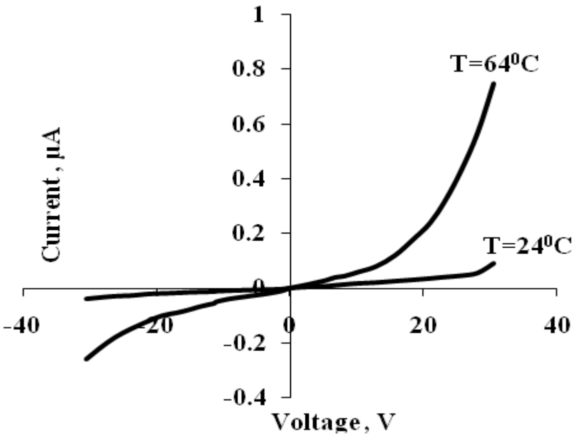

Fig. 4. Dark I-V curves of the Al / p-CuPc/ Ni sample at T=24°C and 64 °C.

The forward bias current *(I_f)* is non-linear and its dependence on the voltage, *V* is given by [17]:

$$I_f = cV^B \tag{1}$$

where *c* is the proportionality factor and *B* is the nonlinearity coefficient that may be determined from the following expression [17]:

$$B = \frac{(\ln I_2 - \ln I_1)}{(\ln V_2 - \ln V_1)} \tag{2}$$

where I_1 and I_2 are currents measured at voltages V_1 and V_2 respectively. It was found that *B* depends on voltage and is in the range of 1-4.0.and 1-3.0 at 24°C and 64°C respectively. It is known that CuPc/Al junction forms Schottky barrier [16]. As work function of Ni (5.15 eV) is larger than that of Al (4.28 eV), we may assume that CuPc/Ni junction is ohmic or tunneling, unlike CuPc/Al junction. The decrease in the nonlinearity coefficient with increase in the temperature may be firstly due to increase of conduction of depletion region formed in CuPc and Al interface and CuPc bulk region and secondly due to the increase of mobility of charge carriers (hopping mechanism of conduction). To explain the electrical behavior and the charge transport mechanism in organic semiconductor materials, the trapping model with a space-charge-limited current (SCLC) was used [18]. Traps at locations arise from disorders, dangling bonds, impurities, etc., and are called localized states that very often capture free charge carriers. Most frequently, an exponential distribution of traps in the energy band is assumed [18]. For the trapping model of SCLC Lamberts theory was used [19]:

$$J = 9\, \varepsilon_s\, \theta\, \mu\, V^2 / 8\, d^3 \tag{3}$$

where *J* is the current density, ε_s, θ, μ and *d* are permittivity, trap factor, mobility and film's thickness respectively. Trap factor θ is defined as the ratio of free carrier density (p_o) to total carrier density:

$$\Theta = p_o / (po + p_t) \tag{4}$$

where p_t is trapped carrier density, and may be calculated as:

$$\theta = J_1 / J_2 \tag{5}$$

where J_1 and J_2 are current densities at the beginning and at the end of square law region, where B = 2 or 1<B<2 (in the first approximation), of the logarithmic plot of the current and voltage characteristics (Fig. 5). From these characteristics we can find θ = 0.27 and 0.33 at 24 °C and 64 °C respectively. When majority of traps are filled a large increase in current takes place (Fig. 5), here ***B*** is more than 2 (4 and 3 at 24 °C and 64 °C respectively).

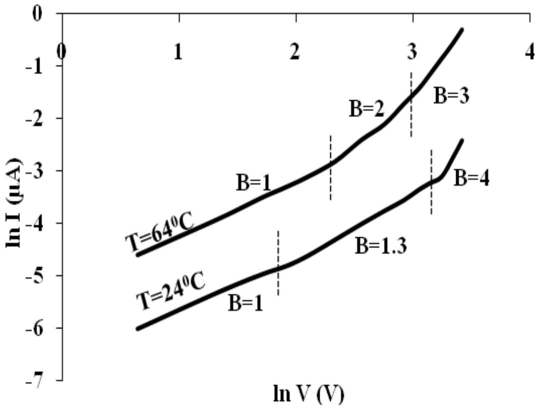

Fig. 5. Dark I-V curve of the Al / p-CuPc/ Ni sample with the current and voltage plotted on the logs.

Conductivity (effective) in a linear part of *I-V* curve may be determined by using:

$$\sigma = J\, d / V \tag{6}$$

where *J* is current density, *V* is voltage, *d* is film thickness: σ is equal to $3 \times 10^{-11}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ and $13 \times 10^{-11}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 24 °C and 64 °C, respectively.

From Eq. 3 the mobility μ can be determined: μ is equal to $2 \times 10^{-5}\ \mathrm{cm}^2 / \mathrm{V\ s}$ and $10 \times 10^{-5}\ \mathrm{cm}^2 / \mathrm{V\ s}$ at 24 °C and 64 °C respectively. Intrinsic concentration of charge carriers:

$$n_o = \sigma / e\, \mu \tag{7}$$

is equal to $1 \times 10^{13}\ \mathrm{cm}^{-3}$ and is the same at 24 °C and 64 °C. Here *e* is elementary charge. In [16] CuPc films were deposited by vacuum evaporation and electrical properties of the SnO_2/CuPc/Ag samples were investigated: room temperature conductivity, mobility and concentration were $2 \times 10^{-8}\ \Omega^{-1}\mathrm{cm}^{-1}$, $2 \times 10^{-5}\ \mathrm{cm}^2/\mathrm{V\ s}$ and $3 \times 10^{15}\ \mathrm{cm}^{-3}$ respectively. For the CuPc films deposited from solution by centrifugation we obtained the same values of mobility, but conductivity and concentration are lower. It may be due to relatively higher concentration of traps in our samples. It confirmed by lower room temperature trap factor in our samples (θ=0.27), with respect of θ=0.33 in [16]. It seems that the "pure" hopping mechanism of conductivity takes place in Al/p-CuPc/Ag samples: charges are carried by hopping from one potential well to another by thermal excitation, where the activation energy of conductivity is actually the activation energy of mobility rather than the concentration of charges [13, 14].

I-V characteristics in Fig.5 show linear or ohmic region (B=1), space-charge limited current region (B=1-2) and traps region (B>2). Actually in space-charge limited current region shallow traps exchange by charge carriers from valence band (in the case of p-type semiconductor) and in transition from this region to trap region, deep traps are filled by charges causing a steep rise in the current [20]. Taking into account that the I-V characteristics are asymmetric (Fig. 4) we may assume that in the Al/p-CuPc/Ni sample double or bipolar injection takes place: in forward bias holes are injected from Ni electrode into valence band of CuPc and electrons are injected by Al electrode into conduction band of CuPc [20] .

Taking into account the data presented in [11] concerning absorption spectrum of the CuPc films (maximum absorption of the CuPc spectrum corresponds to the energy of 1.5 eV), Fig. 4 and considering the concepts related to heterojunction properties [21], an energy-band diagram of the Al/*p*-CuPc metal-semiconductor junction was developed (Fig. 6). In this diagram the eV_n is Schottky barrier, i.e. potential barrier seen by electrons in the metal trying to move into the semiconductor, and eV_{bi} is built-in potential barrier seen by holes [21], E_c, E_v and E_g are bottom of conduction band, top of valence band and band gap respectively. Mobility of the majority charge carriers of CuPc is equal to $10^{-3}\ \mathrm{cm}^2 / \mathrm{V\ s}$. [7]. Therefore in the CuPc side of the junction, unlike the delocalized states in the Al side, there are localized states because in CuPc mobility of charge carriers is much less than $1\ \mathrm{cm}^2 / \mathrm{V\ sec}$ [6].

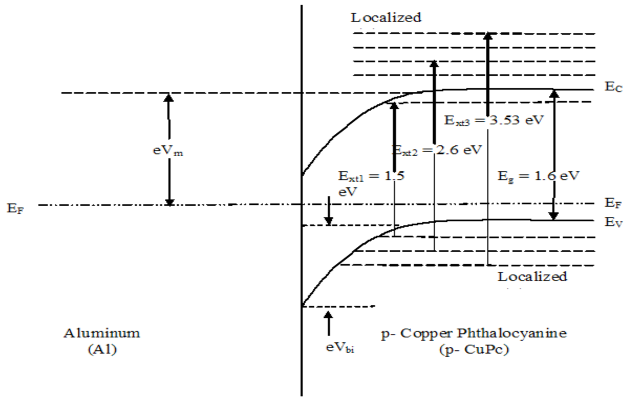

Fig. 6. Energy-band diagram of the Al/p-CuPc metal-semiconductor junction.

4. Conclusions

Thin films of copper phthalocyanine were grown on Ni substrates by employing centrifugal machine at 1107g and then by vacuum deposition of Al films Al/p-CuPc/Ni samples were fabricated. *I-V* characteristics of the Al/p-CuPc/Ni samples were evaluated at 24°C and 64°C. Rectifying characteristics were found as a function of temperature: rectification ratio, unlike to conventional p-n junction, increased with temperature. This can be associated with the generation of free carriers, detrapping of charges at elevated temperatures and with enhanced temperature assisted hopping in the organic films that decreases bulk resistance of the films. It is further observed that *I-V* characteristics of the samples follow space charge limited conduction model. With increase of temperature linear (ohmic) part of *I-V* characteristics extended into higher voltages, nonlinear part decreases in voltage scale and nonlinearity coefficient decreases as well. It was shown that trap factor, mobility and conductivity increase with temperature whereas the intrinsic concentration was approximately constant.

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*Corresponding author: imran_murtaza11@yahoo.com