Electrical properties of metallophthalocyanine thin films

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Sandwich structures devices of type $M_1/M_eP_c/M_2$ have been fabricated by successive vacuum deposition of M_1 (Ohmic hole injections contact: Au), MePc (ZnPc, NiPc) and M_2 (electrode with low work function: Al) thin films were thermally evaporate on glass substrates maintained at room temperatures under high vacuum (10^{-6}torr).The DC electrical parameters and conduction processes in M_eP_c (Φ_{ZnPc}=4.7 ev) films were investigated by studying the J (V) characteristics for two contacts such Au (Φ_{Au}=5.1 ev) and Al (Φ_{Al}=4.28 ev). The charge transport phenomenon in the M_eP_c films seems to depend highly on the electrode material and the temperature. The transport parameters, derived at room temperature are consistent with the values reported for some other authors on MePc's. The results indicate that the electrical properties of ZnPc films are affected by oxygen molecules where play the role of acceptor dopant. The addition of O_2 increases the conductivity of M_eP_c thin films by several orders of magnitude. The measurement of the current according to the tension reveals the transition between Ohmic conduction for weak tensions applied $(I_\Omega \; \alpha \; V)$ and space charge limited current $(I_{SCLC} \; \alpha \; V^m)$ for high tensions applied. Under forward bias and in the lower tension range structure exhibit an Ohmic conduction identified from current density-tension characteristics at room temperature. At high tension range, a transition from Ohmic comportment to space charge limited conduction (SCLC) has been observed. Also, a transition to exponential traps distribution mode is observed. The transport properties have been obtained from an analysis of the samples in the SCLC regime. The interaction of the charge injected with the localized states determines the behaviour of *J (V)*.

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1. Introduction

Organic semiconductors have recently become very attractive to replace inorganic semiconductors in the development of organic devices, such as OLED's [1] (organic light limiting diodes), OFET's [2] (organic thin field transistor), rectifiers (Schottky diodes), photovoltaic cells [3-4], organic switches... etc. The organic heterojunctions and the metal/organic semiconductors interfaces play a crucial role in device performance and elucidation of their electronic structure is therefore important to understand these devices.

The recent years small molecule organic semiconductors such as phthalocyanines (Pc's) have attracted great deal of attention due to their potential use in a wide range of technological applications. A large family of M_ePc can be chemically modified by attaching various peripheral groups to outer ring of isoindoles.

Eley and Vartanyan [5] were the first to observe semiconductivity in phthalocyanines (Pc's) where the impurities may have a role important in the semiconductivity of phthalocyanines. It is well established that among Pc's, H_2Pc and several MePc's as (NiPc, ZnPc,Pc$_2$Lu….etc) behave as p-type semiconductors and have the advantage of being sufficiently stable towards chemical and thermal treatment to form well-ordered thin films make them very attractive for applications of organic devices.

The metallophthalocyanines are a class of organic semiconductors which are chemically and thermally stable and may be deposited as thin films by vacuum evaporation without dissociation [6].

The electronic, electrical and structural properties in MePc's were found to be greatly dependent on the nature of the metallic contacts employed, including the phthalocyanines species (central metal: various synthetic modifications), the film thickness, the deposition temperature, the substrate temperature and the pression evaporation [7].

The effect of a superficial oxide layer at the interface is considered both to be responsible for the rectifying effect in MePc's layers. It has been confirmed that the space-charge region and corresponding rectifying effects are correlated with the presence of oxygen which acts as an acceptor centre and increases the conductivity in solid state [8].

The oxygen impurities, which are unavoidably introduced in the preparation of organic semiconductors appears to play the dual role of both acceptors and traps levels.

The DC electrical studies of thin films metal/organic semiconductors/metal have provided lots of information on the conduction processes and characteristics of metal/organic s/c interfaces. Various conduction processes have been proposed for charge transportation in metallophthalocyanines depending on types of electrical contacts.

Here we report on electrical properties of Au/ZnPc/Au (Al), Au/NiPc/Au (Al), sandwich structures devices. Electrical characterisation of these devices was performed

in-situ under high vacuum in order to eliminate any effect of oxygen absorption. Also, the effects of oxygen doping and thermal annealing on electrical properties are reported and analysed.

2. Experimental

Metallophthalocyanines (ZnPc and NiPc) powder (Aldrich chemicals ltd) were purified by successive sublimation under a steam nitrogen gas as a carrier. As results a needle-like shape crystals in the cooler region of the train sublimation.

Samples in the form of Au/ZnPc/Al (Au) and Au/NiPc/Al (Au) sandwich structures have been prepared using a fine powder of ZnPc and NiPc purified by sublimation in nitrogen gas.

Before to the deposition, all substrates were subjected to through cleaned to avoid contamination .A microscopic glass substrates plate carefully cleaned were ultrasonically cleaned with acetone, isopropyl alcohol, deionised water and then dried substrate in a vacuum oven.

The special geometric of the positions of the substrate, the quartz monitor and the evaporate sources was well defined, so that the evaporate film on the quartz monitor is the same that evaporate on the substrate.

The structures Au/ZnPc; NiPc/Al (Au) was obtained by:

1) A thin layer of Gold (Au) electrode was first deposited onto a pre-cleaned glass substrate using a tungsten spiral at an evaporation rate (10A/s). The Gold metallic contact (Au) was chosen in all structures because it is known to form Ohmic contact [9] (Φ_{Au}=5.1 eV) with most metallophthalocyanines (Φ_{ZnPc} = 4.78 eV).

2) The metallophthalocyanines layer was thermally evaporated on the thin film layer of gold under a pressure of order 10^{-6} torr, using an electrically heated tantalum boat at a deposition rate of 20A/s.The choice of this deposition rate is to limit the exposure time of substrate to heat of the crucible. The metallophthalocyanines is a polycrystalline layer (approximately 3 μm thick).

3) Finally, an aluminium (Al) and (In) thins layers were evaporating using another tungsten spiral at a deposition rate of 10A/s. The aluminium and indium forms bloquant contacts [10] (Φ_{Al}=4.28 eV) and (Φ_{In}= 4.1 eV) with MePc.

The three layers were made without any time the vacuum has been broken.

The thickness and the deposition rate were determined by using a quartz piezo-electric. The substrate is maintained at room temperature while the evaporation is carried out. The tantalum boat temperature is maintained constant during the all evaporation at the value inferior to 200 ^{o}C. In this condition the polycrystalline layer is therefore constituted of the α form of the metallophthalocyanines.

The effective cell area of each sample is defined by the overlap zone between the area of Gold (Au) contact and the area of the counter electrodes contacts. This area was measured approximativelly as 20 mm^2.

The electrical characteristics I(V) of the devices was studied in-situ under high vacuum (10^{-6} torr) by employing a Keithey electrometer (610C...) in a first step and after exposed the films to dry air in second step, for study the effects of doping films with oxygen molecular.

The temperature measurements were performed by utilising a Chromel-Alumel thermocouple placed in close proximity of the samples. Quartz crystal (6 MHz) with high temperature stability was used to follow the evaporation conditions. The rates of evaporation were adjusted by acting on the temperature of electrically heated containers.

3. Results and discussion

Detailed information about the transport mechanism through the organic (ZnPc; NiPc) thin film can be obtained from analysis of the forward current density-voltage J(V) characteristics of the junction.

Injection limited current transport in metal/organic semiconductor/metal structures is assumed to be controlled by the formation of the interfaces. The energy barriers that control the hole and the electron injection are estimated in first approximation successfully by knowledge the ionisation potential (IP), the electron affinity (EA) and the work function (Φ) of organic semiconductor and contact metallic by: Δ_h= IP- Φ_{Au} and Δ_e= Φ_{Al}- EA [11].

The gold metal (Au) as Ohmic hole injecting contact and the barrier height for holes from metal to organic semiconductor is calculated to be:

$$\Delta_h= IP \ (ZnPc) \ (5.28eV) – \Phi_{Au} \ (5.1eV) = 0.18eV$$

And the aluminium (Al) is used for creating the barrier for holes at the metal/ZnPc interface:

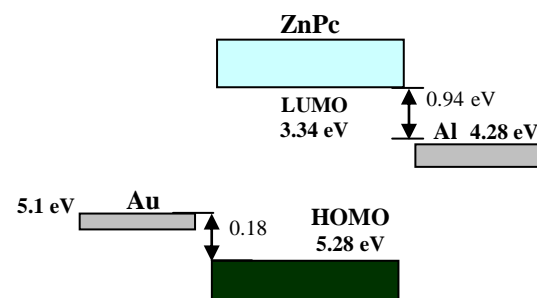$$\Delta_e=\Phi_{Al}(4.28eV)-EA \ (ZnPc) \ (3.34eV) =0.94eV \ Fig. \ (1).$$

Fig 1. Energy level diagram of the Au/ZnPc/Al.

In our devices, MePc is used as hole transport layer, Gold (Au) contact is acting as a Ohmic contact for hole injection and Aluminium (Al) is used as hole blocking contact [10].

The current-voltage J(V) characteristics of Au/ZnPc/Al device (3000 nm) are shown in Fig. 2. The

forward bias direction corresponds to the positive bias Au electrode and negative bias Al electrode of the device .In this case of the Al-ZnPc-Au a different behaviour of Log (J)-Log (V) characteristics is observed in Fig. 3. Two different regions may be identified in both of the forward and reverse bias:

A. The forward J (V) characteristics: shown in Fig. 3. There found to follow the power law dependence J α V^m At low voltages range the slopes of Log (J) Vs Log(V) is around unity (n=0.8) and (n=3.8) for voltages values higher. In such a dependence of the J (V) characteristics the current flowing through the structure is bulk controlled so that these slopes indicate an Ohmic region due to thermally generated carriers, satisfying the relation:

$$J=qp\mu V/d.$$

where p is the concentration of thermally activated holes in the valence band and d is the top and the bottom electrode spacing.

The typical of a space charge limited conduction (SCLC) mechanism controlled by the presence of traps distributed exponentially (n›2) (n = 3.8). This region represents some instability, probably originating from the interface between the organic layer and the electrode contact and the transition from Ohmic conduction to SCLC conduction. The current density for this particular case is described by Lampert [12].

$$J_{SCLC} = q\mu N_v (\frac{\varepsilon_r \varepsilon_0}{q P_0 k T_c})^l . (\frac{V^{l+1}}{d^{2l+1}})$$

where P_0 is the trap density per unit energy range at the valence band edge.

The term (l+1) represents the power law exponent where l=T_c /T with T_c represents a temperature parameter describing the exponential trapping distribution and describes how fast the defects fall off with the energy P(E) described as:

$$P (E) = P_0 exp(-E/kT_c).$$

The slope3.8 implies that l=2.8 and thus the temperature parameter T_c which characterizes the trap distribution is T_c = l*T where T is the room temperature and T_c = 2.8*293 = 820 k. The total concentration of traps N_t has been given by the evaluating the integer of:

$$N_t = \int P (E) dE = \int P_0 exp (-E/kT_c) = P_0 kT_c.$$

To estimate values for the hole concentration (p) and the parameters of the trap distribution (N_t and P_0), it is necessary to assume plausible values for the relative permittivity (ε_r) was derived from the zero capacitance measurements at high frequency, the mobility (μ) and the effective density of states in the valence band edge (N_v).In literature, the value of effective density of states in the valence band edge was $N_v = 10^{27}$ m^{-3}, corresponds to one

electronic state per molecular [13]. The values of ε_r derived from capacitance measurements were:

$$\varepsilon_{r \, ZnPc} = 3.2 \text{ and } \varepsilon_{r \, NiPc} = 2.7 \, [14]$$
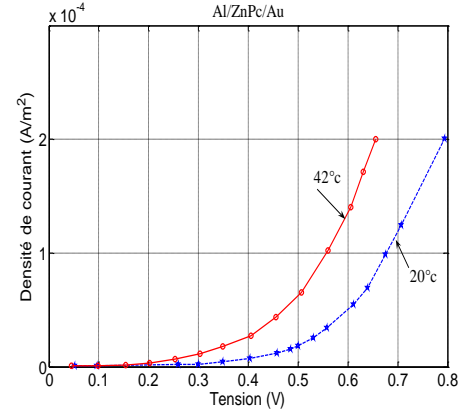

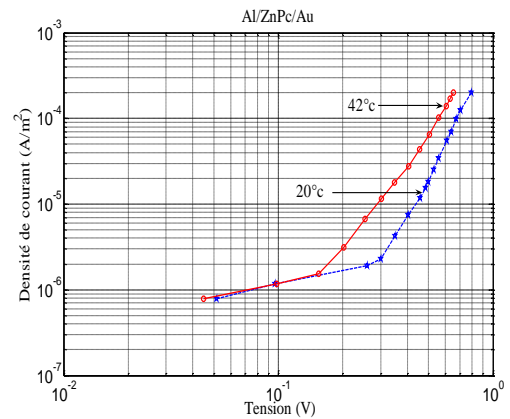*Fig. 2. Current density-voltage characteristics of Au/ZnPc/Al.*

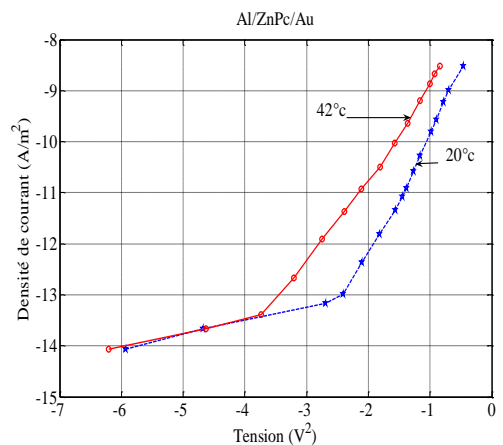*Fig. 3. Curves Log (J)-Log (V) of Au/ZnPc/Al.*

Fig. 4. Curves Log (J) on Voltage (V) of Au/ZnPc/Al.

Fig. 2 shows the dependence of current density J on the voltage V for Au/ZnPc/Al structure in the two values of temperature (42°c and 20°c). For each characteristic, there are two distinct voltages regions. At lower voltages, the slopes of the curves are approximately equal to unity,

while at higher voltages range, above the transition voltage $V_t=0.27v$, the slopes are approximately equal to 3.8.

In the lower voltages region is proportional to V and it may be described by ohm's law as:

$$J = qp\mu_h V/d.$$

An analysis of data of the Fig. 3 we obtain:
a) Below $V_t = 0.27V$ and using the mean value of $\mu_h = 1.12$ $10^{-9}m^2v^{-1}s^{-1}$, we obtain a mean value of holes concentration $p = 1.7\ 10^{17}m^{-3}$.
b) Above $V_t = 0.27V$, the current density law exponent $m = 3.8$ implies that $l = 2.8$ and $T_c = 820°k$ for measuring temperature of $293°k$.

From precedent equation giving J(V) a mean value of the traps density per unit energy range at the valence band edge of $P_0 = 1.5\ 10^{42}J^{-1}m^{-3}$ was derived and a value of $N_t = 1.7\ 10^{22}m^{-3}$ was obtained.

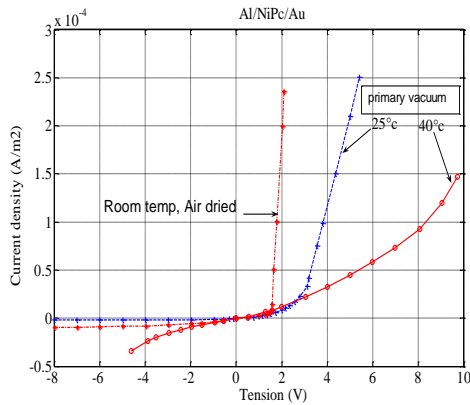All values obtained of p, P_0 and N_t are in the same order with the values deduced by other workers [12-16].

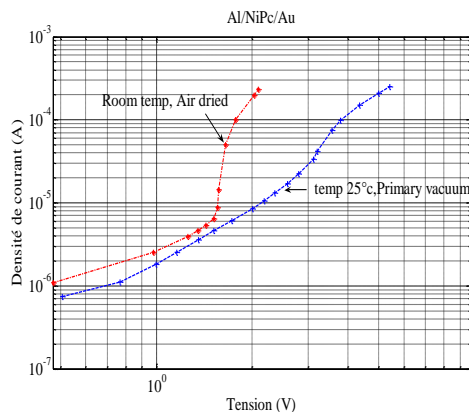*Fig. 5. Characteristics current density on voltages of Au/NiPc/Al structure.*

Fig. 6. Curves Log (J)-Log (V) of Au/NiPc/Al.

An analysis of data in Figs. 5 and 6 reported to Au/NiPc/Al structures give the values of parameters p, P_0, N_t as:

$$P_0 = 3.48\ 10^{43}J^{-1}m^{-3} \text{ and } N_t = 3.73\ 10^{23}m^{-3}.$$

B. In reverse bias current density characteristics

It can be observed that current density is lower compared with that under forward bias. Log (J) Vs $V^{1/2}$ shows the reverses bias characteristics. This linear plot can be analysed in terms of the two field lowering mechanisms, namely, Schottky effect and Poole-Frenkel effect. The general equations describing these comportments are given by Simmons:

$$J = A^*T^2 \exp\left(\frac{-\phi_s}{KT}\right) \exp\left(\frac{q\beta_s V^{1/2}}{KTV^{1/2}}\right)$$

For the Schottky type conduction, where $A^* = 1.2\ 10^{-6}$ Am^{-2} and Φ_s is the barrier height.

In the Poole-Frenkel type conduction the expression for the current density takes the form:

$$J = J_0 \exp\left(\frac{q\beta_{PF} V^{1/2}}{KTV^{1/2}}\right)$$

where $J_0 = \sigma_0 E$ is the low-field current density and σ_0 is the low-field conductivity.

β_s and β_{PF} are, respectively the Schottky and the Poole-Frenkel field lowering coefficients.

The theoretical values of β_s and β_{PF} are given by:

$$2\beta_s = \beta_{PF} = \left(\frac{q}{\pi\varepsilon_0\varepsilon_r}\right)^{1/2}$$

where $\beta_s = 2.29\ 10^{-5}$ eV $m^{1/2}V^{-1/2}$ and $\beta_{PF} = 4.58$ $eVm^{1/2}V^{-1/2}$.

The value of β calculated from the gradient of this plot is $1.2\ 10^{-5}eVm^{1/2}V^{-1/2}$. The observed variance of the experimental value of β_s with respect to the theoretical value of β_s is attributed to the fact that the entire thickness d of the film is not depleted.

Using the equation

$$J = A^*T^2 \exp\left(\frac{-\phi_s}{KT}\right) \exp\left(\frac{q\beta_s V^{1/2}}{KTV^{1/2}}\right)$$

and the value of J at the coordinate intercept, the barrier height at NiPc/Al interface was evaluated yielding a value of $\Phi_B = 0.93$ eV.

4. Conclusion

In summary, evaporate ZnPc and NiPc films shows a diodes kike asymmetric characteristics J (V). The curves J(V) shows the Ohmic conductivity at low voltages with holes concentration in order $10^{17}m^{-3}$ and space-charge-limited dominated by an exponential distribution of traps $P(E) = P_0 \exp(-E/kT_c)$ above the valence edge, where the of $P_0 = 1.5 \times 10^{42}J^{-1}m^{-3}$ and $N_t = 1.7 \times 10^{22}m^{-3}$ is obtained for

Au/ZnPc/Al and $P_0 = 3.48 \times 10^{43} J^{-1} m^{-3}$ and $N_t = 3.73 \times 10^{23} m^{-3}$ is obtained for Au/NiPc/Al structure.

References

[1] A. Fujii, Y. Ohmori, K. Yoshino; IEEE Trans. Electron Devices **14**, 1204 (1997).

[2] R. B. Chabane, G. Guillaud, M. Gamoudi, thin solid films, **269**, 145 (1997).

[3] A. K. Hassan, GOULD, phys stat sol (a), **132**, 91 (1992).

[4] Y. Shirota, Journal of Material Chemistry, **20**, 1 (2000).

[5] A. Wilson, R. A. Collins, Sensors and Actuators, **12**, 389 (1987).

[6] R. D. Gould, R. I. R Blyth, phys stat sol (a), **120**, K57 (1990).

[7] C. Haman, C. Tantzcher, Thin Solid Films, **36**, 81 (1976).

[8] F. R. Fam, L. R. Faulkner, J. Chem. Phys. **69**, 3334 (1978).

[9] J. J. Andre, J. Simon, G. Guillaud, B. Boudjema, M. Maitrot, Mol. Cryst. Liq. Cryst, **121**, 277 (1985).

[10] J. G. Simmons, J. Phys. **D4**, 6130 (1971).

[11] A. N. Sidorov, I. P. Kotlyer, Sov. Phys. Opt and Spectrosc, **11**, 92 (1961).

[12] M. A. Lampert, P. Mark: Current injection in solids, Acad. Press, N.Y (1970).

[13] T. D. Anthopoulos, T. S. Shafai, phys. status. solidi A **181**, 569 (2000).

[14] B. Boudjema, "Propriétés opto-électroniques des metallophtalocyanines " these d'etat lyon 1987.

[15] R. D. Gould, Coord. Chem. Rev, **156**, 237 (1996).

[16] T. G. Abdel-Malik, R. M. Abdel-Latif, Thin. Solid. Films, **305**, 336 (1997).

[17] S. Mammen, C. S. Menon, N. V. Unnikrisnan, Semicond. Sci. Technol, **21**, 677 (2006).

[18] A. S. Riad, Physca. B, **270**, 148 (1999).

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