

Electrical and optical properties of vacuum deposited MnPc thin films

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Received 24 February 2005 / Received in final form 22 May 2005

Published online 11 October 2005 – © EDP Sciences, Società Italiana di Fisica, Springer-Verlag 2005

Abstract. Sandwich and planar structures were fabricated using manganese phthalocyanine (MnPc) as active layer and gold (Au) as electrodes by thermal evaporation method. The permittivity ε of MnPc was determined from the dependence of capacitance on film thickness. J - V characteristics of Au/MnPc/Au structure at room temperature were performed. Thermally generated hole concentration p_0 , hole mobility μ_p , total trap concentration N_t and depth of the trap level were estimated. The activation energies of MnPc films were determined from the Arrhenius plots of $\ln \sigma$ versus $1000/T$. The absorption and reflectance spectra of MnPc thin film deposited at room temperature were recorded in the spectral range 300–900 nm. The optical band gap of MnPc thin film was determined from the α^2 versus $h\nu$ graph. The optical constants n and k were found. The real and imaginary parts of the optical dielectric constant ε_1 and ε_2 were calculated.

PACS. 72.80.Le Organic semiconductors – 73.61.-r Electrical properties of specific thin films – 78.20.-e Optical properties thin films

1 Introduction

Molecular electronic materials such as dyes, conjugated polymers, and small molecules are gaining interest for applications in solar cell technology. Attractive features are the possibility of device processing, compatibility with flexible substrates, and the low materials consumption for ultrathin molecular films, all of which offer the prospect of cheaper photovoltaic energy generation. Large-scale production is easier than for inorganic materials. The greatest peculiarity of organic material is that they can be tuned chemically, in order to adjust separately the band gap, valence and conduction band energies, charge transport, as well as the solubility or other structural properties. The research into the behavior of these materials is normally carried out in two ways, optically and electrically. In optical method usually optical absorption measurements are performed. While the conductivity properties are explored in electrical method. The electrical conductivity measurements can be carried out either using planar or sandwich devices. Planar devices consisting of thin films with electrodes deposited at the ends are primarily use as gas sensors and also to observe the materials response to various gases by d.c. electrical characteristics. The sandwich configuration is used in thin film diodes and transistors [1,2]. The mechanism of carrier transport in organic semiconductors and carrier injection from metal electrodes becomes the most important subject to be elucidated for

high performance organic thin film devices. Phthalocyanines (Pc) are a class of highly stable organic compounds which are classified as p-type semiconductor characterized by low mobility and low carrier concentration [3]. Pc's have potential to applications to organic electronic devices such as gas sensors [4,5] and optoelectronic devices [6,7] because of their ease of synthetic modification, high chemical and thermal stability [8] long π -electron conjugated system and absorption bands which extends from ultraviolet to infrared region. It is necessary to investigate the intrinsic electrical properties prior to their utilization. Relatively few studies have conducted on manganese phthalocyanine (MnPc) thin films. In the present investigation d.c. electrical measurements are carried out in the planar and sandwich configuration as a function of temperature to study the electronic structure of MnPc thin films and to identify the conduction mechanisms operating under different conditions. Also we have determined the optical parameters and dielectric constants of MnPc thin films from their absorption measurements.

2 Experimental

The powdered MnPc procured from Aldrich Inc. USA is purified by entrainer method. Thin films are deposited at room temperature and at different substrate temperature at a base pressure of 10^{-6} Torr onto pre-cleaned glass substrates using the Hind Hivac 12 A4 coating plant by

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thermal evaporation technique. For deposition of films, highly polished and thoroughly cleaned substrates are used. First the substrates are cleaned using liquid detergent. Then it is kept in dilute nitric acid. After this, they are cleaned using distilled water and agitated ultrasonically in acetone. They are then dried in hot air. Subsequently the substrates are subjected to ionic bombardment for five minutes as a final cleaning before deposition. The ions are produced by high tension (HT) discharge. Evaporation of the material is carried out with a molybdenum boat of dimensions $2.9 \times 1.2 \times 0.5$ cm used as the resistive heating element. During evaporation, substrates are placed at a distance of 11 cm from the source and the deposition rate is kept at 0.5 nms^{-1} . The thicknesses of the films are measured using the Tolansky's multiple beam interference technique [9]. Film thickness is typically 204–630 nm. The film is sandwiched between two evaporated gold electrodes. Most of the devices had an active area of $1.2 \times 10^{-5} \text{ m}^2$. In the planar configuration gold electrodes are deposited at the ends of the MnPc film. Electrical contacts are made using copper strands and are fixed to the specimen with a colloidal suspension of silver in aqua or alkadag. Sample currents are measured using a stabilized power supply and a Keithley electrometer (model No. 617). Capacitance measurements are made at 1 KHz using a Hioki. To avoid contamination, measurements are performed in a subsidiary vacuum of 10^{-3} Torr. Electrical conductivity studies are done in the temperature range 300–384 K for the sandwich structures and 322–537 K for the planar devices. The samples are shielded from incident light to avoid photoelectric effect. UV-VIS-NIR absorption spectra of the films are recorded using the Shimadzu 160A spectrophotometer. Reflectance spectra are recorded using a Hitachi E330 spectrophotometer.

3 Results and discussion

3.1 Electrical properties – sandwich configuration

Studies such as ohmic and space charge limited conductivity (SCLC) are applied on Au/MnPc/Au structures. These studies are capable of providing considerable insight into the charge transport mechanism and carrier trapping in MnPc. Figure 1 shows the I - V characteristics of MnPc thin film of thickness 500 nm. The graph is almost linear. In this structure Au electrode forms an ohmic contact with MnPc layer. This behaviour is explained by high work function of Au and p-type conduction of MnPc.

Figure 2 shows the dependence of capacitance C on the reciprocal film thickness, $1/d$. The linearity of the plot can be analyzed in terms of the capacitance of a parallel plate capacitor

$$C = \epsilon A/d \quad (1)$$

where ϵ is the permittivity of MnPc, A is the area ($1.2 \times 10^{-5} \text{ m}^2$) and d is the thickness of the sample. The value of ϵ is estimated from Figure 2 and found to be $2.89 \times 10^{-11} \text{ Fm}^{-1}$. Detailed information about the transport mechanism through the MnPc film can be obtained

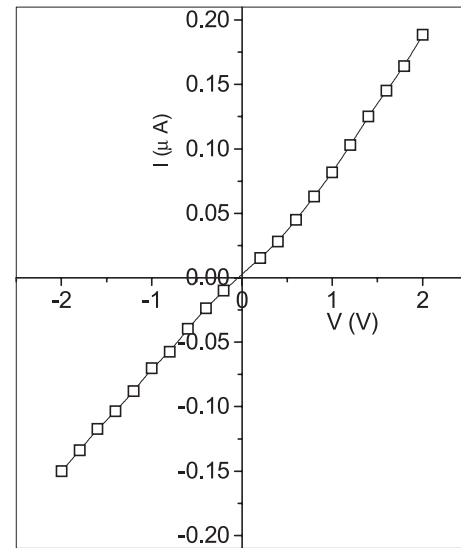


Fig. 1. I - V characteristics of Au/MnPc/Au structure.

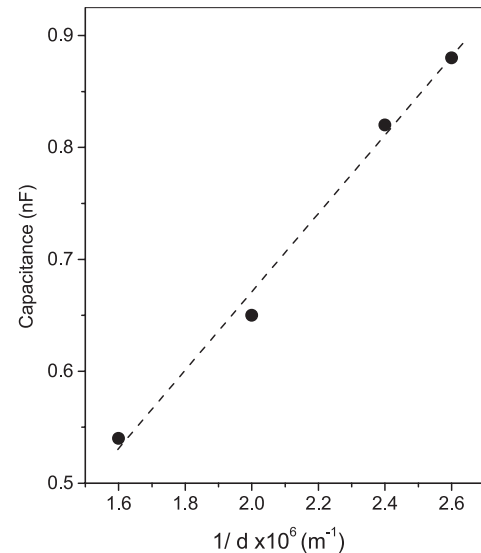


Fig. 2. Dependence of capacitance C on the reciprocal of film thickness.

from the analysis of current density (J) – voltage (V) characteristics. The J - V characteristics of Au/MnPc/Au structure are shown in Figure 3. In the J - V characteristics, there are two distinct regions. At low voltages, the slope of $\ln J$ versus $\ln V$ plot is approximately unity. These plots suggest ohmic conduction at low voltages. Assuming conduction is via holes, the current flow may be expressed in the form [10]

$$J = e p_0 \mu_p (V/d) \quad (2)$$

where p_0 is the concentration of thermally generated holes in the valance band, e is the electronic charge, μ_p is the hole mobility and d is the thickness of the film. The concentration of holes at thermal equilibrium is given by

$$p_0 = N_v \exp[-(E_f - E_v)/kT] \quad (3)$$

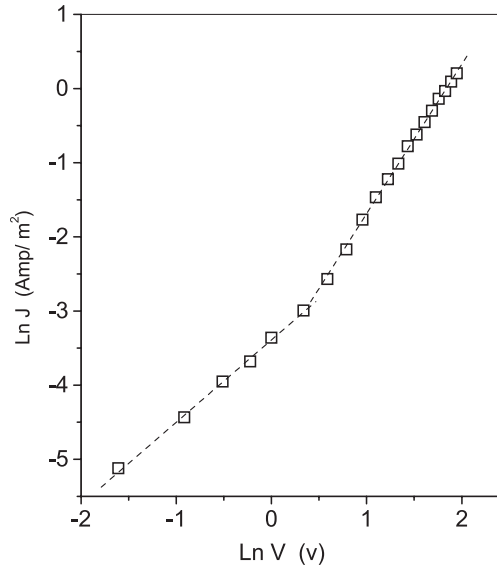


Fig. 3. $\ln J$ vs. $\ln V$ for the Au/MnPc/Au structure at room temperature.

where N_v is the effective density of state in the valance band, $(E_f - E_v)$ is the separation of Fermi level from the valance band edge, k is the Boltzmann constant and T is the absolute temperature. Now with equation (4), the current density in the ohmic region becomes

$$J = e\mu_p N_v (V/d) \exp[-(E_f - E_v)/kT]. \quad (4)$$

By plotting $\ln(J/V)$ against $1000/T$ (Fig. 4), the values of $(E_f - E_v)$ and $\mu_p N_v$ have been calculated from the slope and intercept at $1/T = 0$. Taking $N_v = 10^{27} \text{ m}^{-3}$ which correspond to one state per molecule [11] and $d = 500 \text{ nm}$, the values of $(E_f - E_v)$, μ_p and p_0 are calculated for MnPc. $(E_f - E_v)$ and μ_p are found to be 0.61 eV and $1.016 \times 10^{-6} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. The concentration of thermally generated holes, p_0 is determined to be 3.43×10^{18} and $6.34 \times 10^{18} \text{ m}^{-3}$ for the low voltage and high voltage regime. These values suggest that the MnPc is a p-type organic semiconductor with low mobility and relatively high thermal activation energy. In the higher voltage regime of the $J - V$ characteristics (Fig. 3), the slope of $\ln J$ versus $\ln V$ plot is approximately equal to 2, which shows that current is SCLC controlled by the relationship [12]

$$J = (9/8)\varepsilon\mu_p\theta(V^2/d^3) \quad (5)$$

where ε is the permittivity of MnPc and is equal to $2.89 \times 10^{-11} \text{ Fm}^{-1}$ and θ is the ratio of free to trapped charge carrier density or trapping factor given by [13]

$$\theta = (N_v/N_t) \exp[-(E_t - E_v)/kT] \quad (6)$$

where N_t is the total trap concentration at the energy level, $E_t - E_v$ is the activation energy of hole traps, k is the Boltzmann constant and T is the absolute temperature. Using the above expression current density in the SCLC becomes

$$J = (9/8)\varepsilon\mu_p(N_v/N_t)(V^2/d^3) \exp[-(E_t - E_v)/kT]. \quad (7)$$

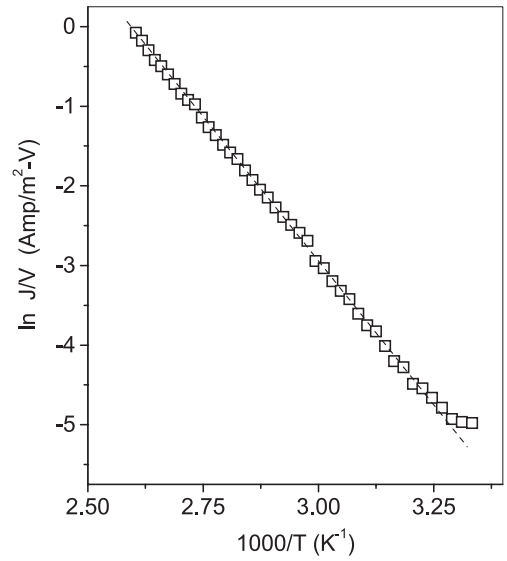


Fig. 4. $\ln(J/V)$ vs. $1000/T$ for the Au/MnPc/Au structure in the ohmic region.

From the above expression it is evident that $\ln(J/V^2)$ versus $1000/T$ should be a straight line. The slope and intercept at $1/T = 0$ on the current axis give $E_t - E_v$ and N_t respectively. $E_t - E_v$ and N_t , are determined to be 0.67 eV and 8.7×10^{22} from the $\ln(J/V^2)$ versus $1000/T$. Using these values in equation (6) the trapping factor θ is estimated to be 4.2×10^{-7} . Thus a total trap concentration $N_t = 10^{22} \text{ m}^{-3}$ is obtained at about 0.67 eV above the valance band edge.

3.2 Electrical properties – planar configuration

Electrical conductivity studies on MnPc thin films are used to determine thermal activation energy and to study the effect of substrate temperature on the activation energy. In inorganic semiconductors the semiconducting properties are brought about by thermal excitation, impurities, lattice defects and nonstoichiometry. Holes in the valance band and electrons in the conduction band contribute to the electrical conductivity. If we assume that the variation of mobility of the electrons and holes in an electric field with temperature is small, then conductivity σ , which is proportional to the number of carriers has a variation of the form

$$\sigma = \sigma_0 \exp(-E_a/2kT) \quad (8)$$

where σ_0 is a constant. Such an exponential variation of electrical conductivity is known for semiconductors. Multiple donor levels exist within the forbidden energy gap and the deeper levels can be frozen out as the temperature is increased. Conductivity in phthalocyanines is due to both hopping of holes and charge transport via excited states. In such a case, the conductivity is given by

$$\sigma = A \exp(-E_1/kT) + B \exp(-E_2/kT) + C \exp(-E_3/kT) + \dots \quad (9)$$

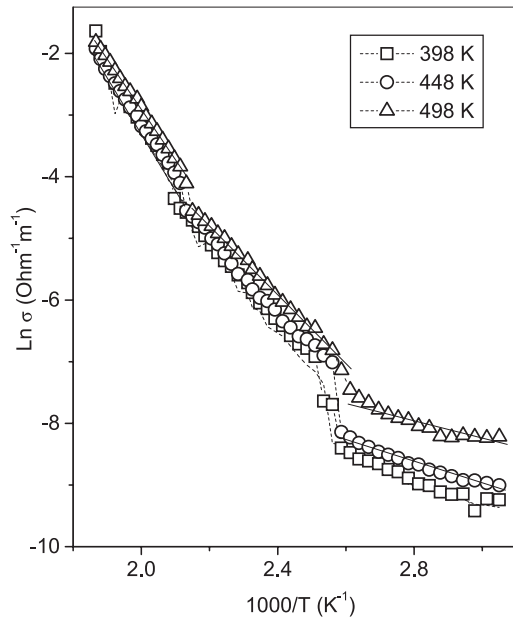


Fig. 5. $\ln \sigma$ vs. $1000/T$ for MnPc thin film deposited at different substrate temperature.

where E_1 is the intrinsic energy gap and E_2, E_3, \dots are the activation energy needed to excite the carriers from the corresponding trap levels to the conduction band. A, B, C are constants. k is the Boltzmann's constant.

Arrhenius plots of $\ln \sigma$ vs. $1000/T$ of MnPc thin films are made to study the dependence on substrate temperature of the conduction mechanism and are given in Figure 5. Three activation energies are obtained and are given in Table 1. Error bar associated with activation energy is ± 0.02 eV. The thermal activation energy E_1 is associated with an intrinsic generation process. This corresponds to the process observed in inorganic semiconductors. It is based on the assumption of electron hole pair production via thermal transition from a valence band to the conduction band, and may occur in several organic solids. The assumption of an intrinsic excitation process explains the dependence of electrical conductivity of phthalocyanine compounds on the constitution of the molecules. This type of excitation provides the applicability of the electron gas model to the conduction process and the increase of conductivity with the number of π -electrons in the individual classes of compounds. The phthalocyanines owe their intrinsic conductivity to the partial charge transfer from phthalocyanine ring to the central ion. E_2 and E_3 are the activation energy needed to excite the carriers from the corresponding trap levels to the conduction band and are associated with the impurity conduction [14]. The activation energies of MnPc films are found to decrease with the substrate temperatures. Higher substrate temperature leads to an increase in the size of the critical nucleus and hence a decrease in the value of the activation energy [15].

Table 1. Variation of activation energy for MnPc thin film deposited at different substrate temperatures.

Temperature (K)	Activation energy (eV)		
	E_1	E_2	E_3
398	0.72	0.50	0.12
448	0.72	0.48	0.14
498	0.70	0.47	0.13

Error bar ± 0.02 eV.

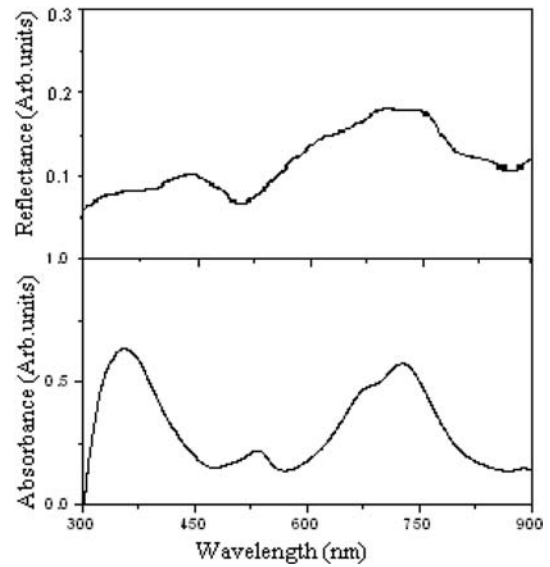


Fig. 6. Absorption and reflectance spectra of MnPc thin film deposited at room temperature.

3.3 Optical properties

The UV-NIR absorption and reflectance spectra of MnPc thin film of thickness 204 nm deposited at room temperature are given in Figure 6. The distinct characterized peaks in the visible region are generally been interpreted in terms of π - π^* excitation between bonding and antibonding molecular orbitals. The absorption peak at higher energy region (383 nm) and low region results from B (Sorret) band and Q-band respectively. Both Q and B bands arise from π to π^* transitions [16,17]. To obtain information about direct or indirect inter band transitions the fundamental absorption edge data is analyzed within the frame work of one electron theory of Bardeen et al. [18]. This theory has been used to analyze the absorption edge data of molecular solids such as phthalocyanine [19]. The absorption ($\alpha \geq 10^4$ cm $^{-1}$) is related to direct band transitions [20]. The absorption coefficient α is related to the band gap E_g and photon energy $h\nu$ according to the relation [21,22]

$$\alpha = \alpha_0(h\nu - E_g)^n \quad (10)$$

where $n = 1/2$ for direct allowed transitions. Figure 7 shows the plots of variation of α^2 with $h\nu$ for MnPc thin film deposited at room temperature. Satisfactory fit is obtained for α^2 versus $h\nu$ indicating the presence of a direct band gap. A band gap of 2.88 ± 0.01 eV is obtained. The absorption at the lower energy side is related to singlet

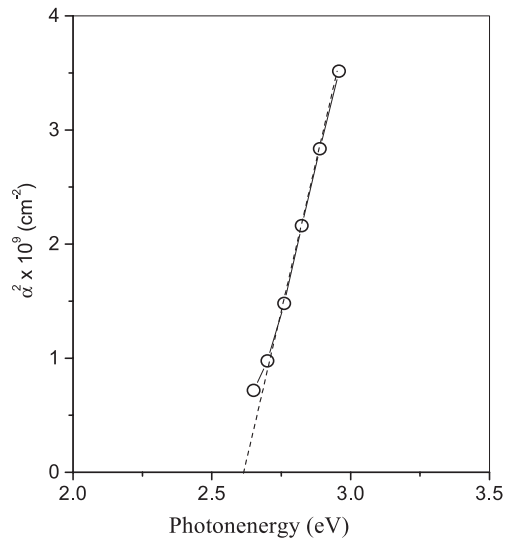


Fig. 7. α^2 vs. $h\nu$ for MnPc thin film.

excitons and has been confirmed for many other phthalocyanines [23–25]. Arshak et al have reported a band gap energy of 2.59 eV for the as-printed MnPc thick film [26]. The extinction coefficient k is calculated using equation

$$k = \frac{\alpha\lambda}{4\pi} \quad (11)$$

where α is the absorption coefficient, λ is the wavelength

The reflectivity of an absorbing medium of indices n and k in air for normal incidence is given by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \quad (12)$$

Figure 8 shows the variation of refractive index n and extinction coefficient k with photon energy for the MnPc thin film. The optical properties of the medium are characterized by a complex refractive index ($N = n - ik$) and complex dielectric constant ($\epsilon = \epsilon_1 - i\epsilon_2$). The real part generally relates to dispersion, while the imaginary part provides a measure of the dissipative rate of the wave in the medium.

The real and imaginary parts of the optical dielectric constant ϵ_1 and ϵ_2 are calculated using the expressions

$$\epsilon_1 = n^2 - k^2 \quad (13)$$

$$\epsilon_2 = 2nk. \quad (14)$$

The variation of ϵ_1 and ϵ_2 with photon energy for MnPc thin film is given in Figure 9. The refractive index n has a maximum value of 2.44 at 1.76 eV for the MnPc thin film. The extinction coefficient k has a maximum value 0.39 at 1.70 eV. The real part ϵ_1 shows a maximum value of 5.81, at 1.76 eV while the imaginary part ϵ_2 has a maximum value of 1.86 at 1.71 eV.

4 Summary

The current density voltage and temperature dependence of current density for MnPc sandwiched between gold

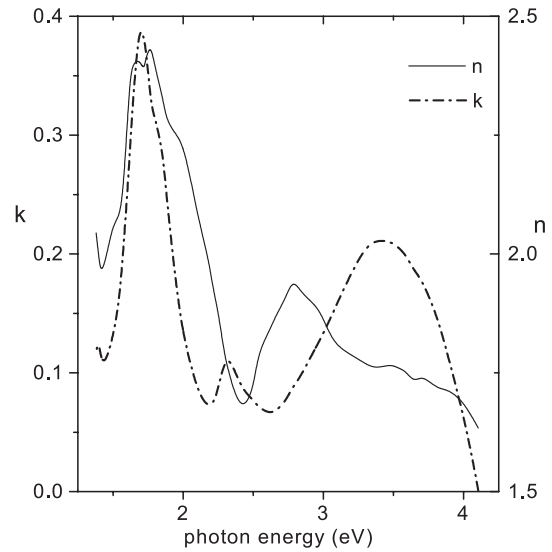


Fig. 8. Variation of n and k with photon energy.

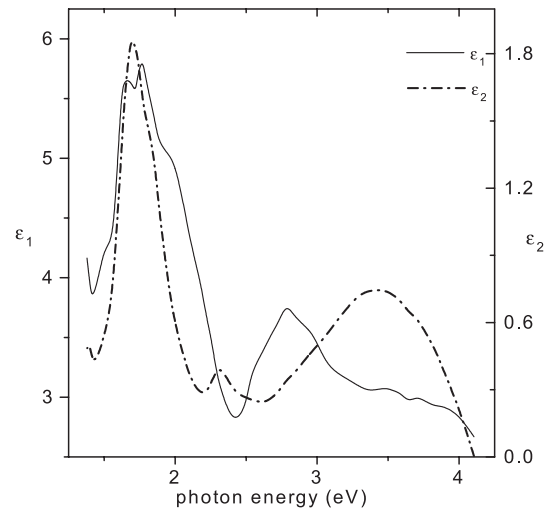


Fig. 9. Variation of ϵ_1 and ϵ_2 with photon energy.

ohmic electrodes are studied. These characteristics show ohmic conductivity at low voltages and space charge limited at high voltages. Thermally generated hole concentration p_0 , and mobility μ_p are estimated. These measurements confirm the p-type semiconductivity of MnPc. Also the mobility of MnPc is obtained to be sufficiently high compared with that reported for other metal-phthalocyanines. This is an advantage in almost all the application. For example in Photovoltaic devices, since transport of optically excited carriers to their respective electrodes is expected to be much faster, thus reducing carrier recombination and subsequently increasing power conversion efficiency of the device. The SCLC process has been observed with a single dominant trap level. The effect of substrate temperature on the electrical conductivity is investigated. The existence of trap levels is confirmed by the presence of more than one linear portion in the $\ln \sigma$ versus $1000/T$ plots. From the slopes of the linear portions of the graphs, the activation energies are determined. The

activation energy E_1 corresponding to the high temperature region is identified as due to intrinsic carriers. This intrinsic activation energy arises from the intrinsic majority carriers whereas that in the extrinsic regions depend on the extrinsic conduction due to impurity states. An extrinsic to intrinsic cross-over for the activation energy is found in MnPc. The conduction process is found to be controlled by different trapping levels present in the forbidden energy gap. Change in substrate temperature results in change in intrinsic activation energy.

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