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Influence of iodine on the electrical properties of nickel phthalocyanines thin film devices

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The electrical properties of pure Nickel Phthalocyanine (Ni Pc) thin films and iodine doped Ni Pc thin films with Gold and Aluminium electrode sandwiched devices have been investigated. The electrical properties and the various electrical parameters of the pure and iodine-doped films have been estimated and compared from the analysis of the current density characteristics. From our study we find that the iodine doping enhanced the electrical conductivity compared to pure Nickel Phthalocyanine and the conduction mechanism is much improved with the iodine doping. Interestingly these films after iodine doping showed remarkably increased electrical conductivity nearly ten times that of pure Phthalocyanine. This may be accounted for by the decrease in the metal-metal bond distance. At low voltages the film shows an ohmic conduction whereas at higher voltage levels the conduction is dominated by space charged limited conduction. Further the reverse conduction mechanisms have also been investigated for this sandwiched device. From the current limitations in the reverse condition a strong rectifying behaviour is evident. © *2006 Springer Science + Business Media, Inc.*

1. Introduction

Phthalocyanines are a class of stable organic semiconductors, which have attracted considerable interest during the past few years because of its low cost, high thermal and chemical stability. In the last two decades there has been considerable interest in the study of the electrical and optical properties of Phthalocyanines [1–4]. Phthalocyanine are widely used as gas sensors [5–8], liquid crystal colour display systems and photovoltaic devices [9–12]. The light absorbing properties of the Phthalocyanine in the visible and in the infrared regions have attracted considerable attention in recent years because of the present interest in the conversion of solar to electrical energy [13]. The electrical, optical and structural properties of many of these thin films depend on several factors such as the substrate temperature, nature of substrate, evaporation rate, annealing, and film thickness and prepared from different techniques have already been reported [14–16]. Further the conduction mechanism in organic semi conducting thin films also depends on the metallic contact to the semiconductor, which may behave either as an ohmic or blocking electrode. Gold and Silver electrodes have proved to be an effective ohmic contact to this type of materials whereas Aluminium and Lead were found to form blocking electrodes to many Phthalocyanines [17, 18]. The order of applied voltages across the film, doping and its concentrations [19–21] also influence the conduction process in the organic thin films. Many of the impurities diffuse into the films acting as acceptor impurities and considerably change the conduction mechanisms. In the present work the electrical properties of sandwiched device of Nickel Phthalocyanine with gold and aluminium electrodes doped with iodine vapour have been investigated. From the analysis of the current–voltage characteristics the various electrical parameters of the device has been discussed in detail. An evaluation and a comparison were made for different electrical parameters of the pure and iodine doped films of almost same dimensions.

2. Experimental details

Nickel Phthalocyanine powder from Sigma–Aldrich Co Ltd is the base material for the present study. Nickel Phthalocyanine is thermally evaporated from a tantalum boat at a pressure of about 10^{-5} torr using a high precision thin film-coating unit. Thin films of Ni Pc are deposited onto a pre cleaned glass substrate, which is previously deposited with a Gold film of about 50 nm thickness as one electrode.

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During the evaporation process of Ni Pc the pressure is kept steady by a diffusion pump backed by oil sealed rotary pump. The evaporation rate and the evaporation time are well monitored to get the different sample films with almost uniform thickness. Iodine is doped in to the organic layer by releasing iodine vapour from another boat containing pure iodine crystal. A separate power supply is used for this purpose. The device fabrication is completed with an aluminium top contact layer that is also deposited from a tungsten coil. The thickness of this aluminium electrode is later measured as approximately 60 nm. The active area of the organic layer is found to be 1.5×10^{-4} m^2 and a thickness of approximately 600 nm. Electrical conductivity measurements have been performed by a stabilized power supply and a Kethley programmable electrometer in a subsidiary vacuum system at a pressure of approximately 10^{-3} Torr. Keeping the gold electrode as positive for the forward bias condition, current is measured for the different values of applied voltage ranging from 0 to 10 V. Dependence of current in the forward bias and reverse bias for different applied voltage at room temperature has been measured. The forward current at a constant voltage of 0.3 , 3.0 and 6.0 V have also been measured in the 300–350 K temperature range. Temperature is measured by means of chromel/alumel thermocouple. Using the same technique samples of pure Ni Pc thin films are also prepared and the different electrical parameters are estimated from the current-voltage characteristics. In order to find the permittivity of the organic layer the capacitance of the device for different film thickness are also measured using an LCZ meter.

3. Results and discussion

The absolute permittivity of the Ni Pc film is a factor, which is necessary for the calculation of the various the electrical conductivity parameters. To find the permittivity of the organic film the capacitance of a sandwich layer of the Ni Pc films of different thickness are measured. The effective value of the capacitance C of the device is given by

$$C = \frac{\varepsilon_0 \varepsilon_r A}{d} + C\mathrm{p} \tag{1}$$

where ε_0 is the permittivity of free space and ε_r is the permittivity of organic layer C_p is a constant capacitance due to the instrument or the edge effects. The graph of capacitance C against (1/d) yield a linear plot and the slope of the curve is equal to ε_0 ε_r A. Fig. 1 shows the variation of capacitance of the films with the inverse of thickness at a constant frequency of 1 kHz. From the slope of the curve the absolute permittivity of Ni Pc is calculated as 1.2×10^{-11} F/m. This value is slightly lower but comparable with the values reported earlier by Saleh [22]. The lower value of the permittivity may be due to the lack of non-uniformity and low packing density of films. There are various conduction methods and hence their corresponding theories depend upon the different materials used as the electrical contacts to the organic layer. Fig. 2 is the current density (J)-voltage (V) characteristics of the sandwiched device of pure and iodine doped Gold-Ni Pc-Aluminium sample measured in the voltage range of 0.1 to 10 V. Slope of the graph implies that the conduction mechanisms are different in the different voltage levels. From the order of the slopes it is concluded that there are two distinct conduction processes involved. In the low voltage range nearly up to 1 V the slope of the J-V characteristics is in the order of unity and hence can be considered as an ohmic conduction between the organic layer and the electrodes. The current density J within the ohmic region is described by

$$J = P_0 e \mu \frac{V}{d} \tag{2}$$

where e the electronic charge, μ the hole mobility, V the applied voltage, d the thickness of the organic film and P_0 is the concentration of thermally generated holes in the

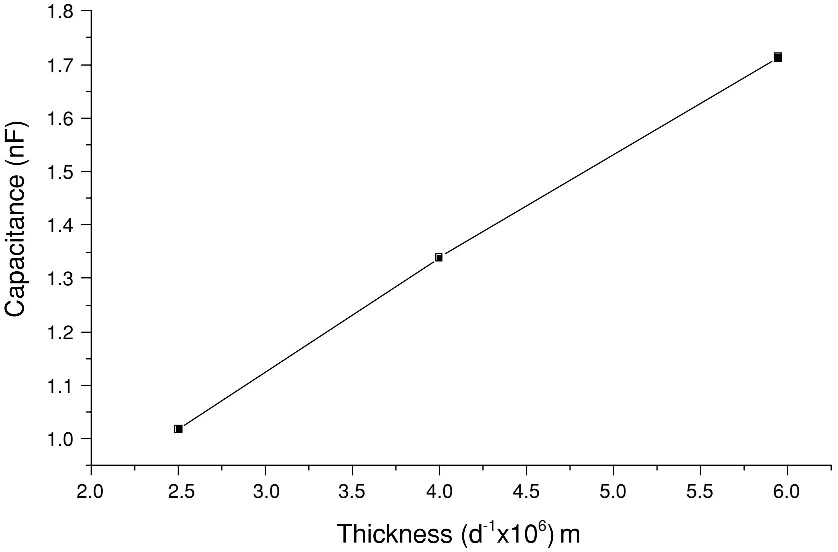

Figure 1 Varation of capacitance with inverse thickness.

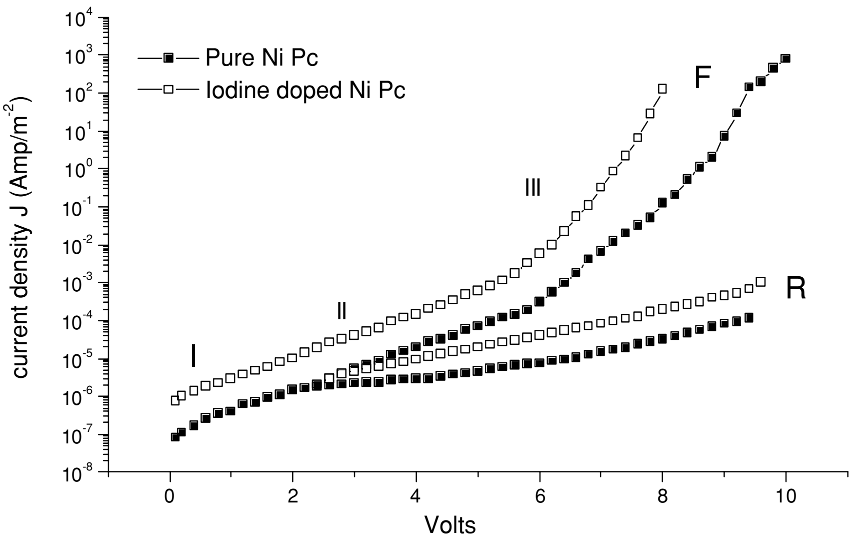

Figure 2 J-V characteristic pure and I_2 doped Ni Pc F-Forward R-Reverse.

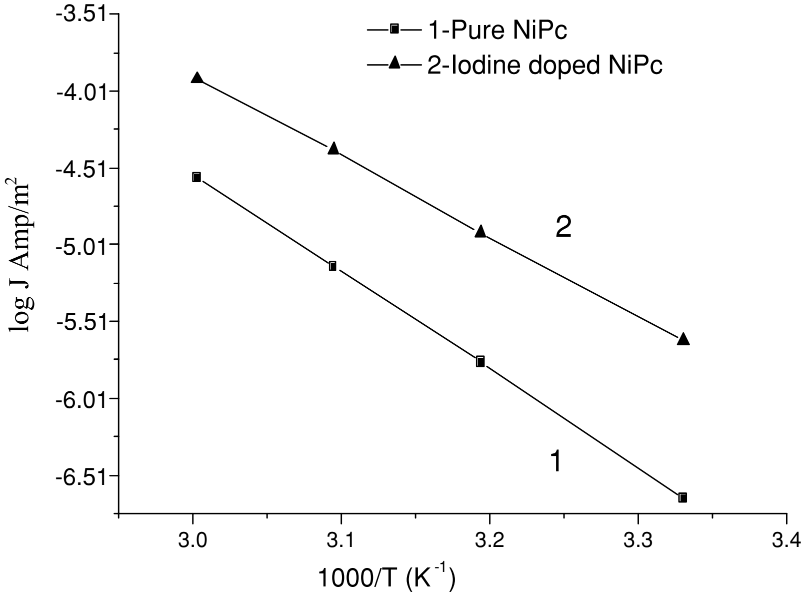

Figure 3 Variation of log J with 1000/T in the ohmic region for pure and I_2 doped Ni Pc.

valance band which given by

$$P_0 = N_v \exp\left(-\frac{E_f}{kT}\right) \quad (3)$$

where E_f is the position of the Fermi level above the valance band edge and the N_v the density of states in the valance band. Substituting for P_0 in Equation 2

$$J = N_v e\mu \frac{V}{d} \exp\left(-\frac{E_f}{kT}\right) \quad (4)$$

The value of N_v is taken as 10^{27} m^{-3} for Ni Pc [23, 24] which corresponds to approximately one electronic state per molecule. Fig. 3 is the plot of Log J against 1000/T for the pure and iodine doped Ni Pc films for the ohmic region in the 300–350 K-temperature range at 0.3 V. The slope of the graph (Fig. 3) yields the value of E_f, and the intercept will provide the value of μ the mobility of holes. These values are calculated and listed in Table I.

Fig. 4 is the J-V forward characteristics of the pure and doped samples in the ohmic region that are re plotted. From the slope this graph (Fig. 4) and using Equation 2 the value P_0 for the pure and iodine doped Ni Pc are calculated

TABLE I Electrical parameters of pure and I_2 doped Ni Pc in the ohmic region.

Parameters	Pure Au/Ni Pc/Al	Au/I_2 doped Ni Pc/Al
E_f eV	0.52	0.41
μ m^2 V^{-1} s^{-1}	1.21×10^{-13}	9.16×10^{-14}
P_0 m^{-3}	2.61×10^{18}	2.01×10^{18}

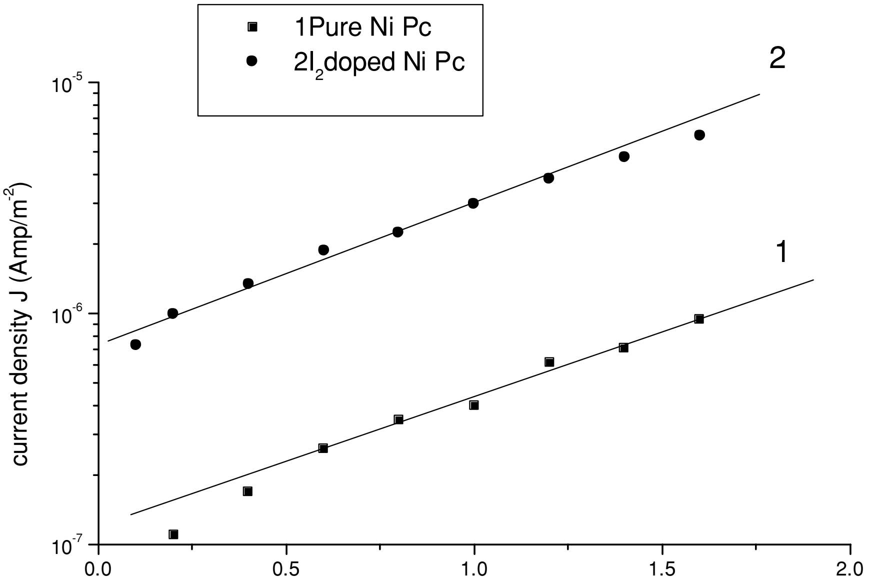

Figure 4 J-V characteristic pure and I_2 doped Ni Pc in the ohmic region.

and are tabulated in Table I. These parameters in the ohmic region fall within the range of previously reported values phthalocyanines thin films by Gould [25].

At higher voltages the slope of the J-V characteristics in Fig. 2 for the segment (II) and segment (III) are 2 and more suggesting the conduction mechanism is that of a space charged limited conduction (SCLC), which is characterized by power law dependence in the form

$$J \alpha V^{\mathrm{n}}$$

where '*n*' is an index which has the values ≥2. The numerical value of this index was found to be associated with the nature of traps within the forbidden gap, the sample temperature and the bias direction. For the segment II in Fig. 2 the slope is found to be nearly 2 which suggesting that the conduction is an SCLC charactistized by a single trap level situated at an energy level E_t above the valance band edge. The current density in this region is described by

$$J = \frac{9}{8}\varepsilon\mu\theta\frac{V^2}{d^3} \tag{5}$$

where θ measure of the ratio of free charges to trapped charges and

$$\theta = \frac{N_{\mathrm{v}}}{N_{\mathrm{t(s)}}}\exp\left(-\frac{E_t}{kT}\right) \tag{6}$$

where $N_{\mathrm{t(s)}}$ is the total trap concentration at the energy level E_{t}.Hence

$$J = \left(\frac{9}{8}\right)\varepsilon\mu\frac{N_{\mathrm{v}}}{N_{t(s)}}\frac{V^2}{d^3}\exp\left(-\frac{E_t}{kT}\right) \tag{7}$$

where ε and μ are the permittivity and the carrier mobility of the Nickel Phthalocyanines. Fig. 5 is the plot of Log *J* with 1000/T at a constant potential difference of 3.0 V in the first SCLC region, the slope and the intercept of this graph yield the values of E_t and $N_{\mathrm{t(s).}}$ Using the values of N_v, ε and μ in Equation 7 the values of E_t and $N_{\mathrm{t(s)}}$ are calculated and listed in the Table II. For the higher voltage region in segment III of the Fig. 2 in the SCLC mechanism is governed by the equation

$$J = e\mu N_{\mathrm{v}}\left(\frac{\varepsilon}{eP_{\mathrm{t}}kT_{\mathrm{t}}}\right)^{l}\frac{V^{l+1}}{d^{2l+1}} \tag{8}$$

Besides the terms defined earlier P_{t} is the trap concentration per unit energy range at the valance band edge, *d* the film thickness and the term $(l + 1)$ represents the power exponent factor and $l = T_{\mathrm{t}}/T$ where T_{t} is the temperature parameter measuring the exponential trap distribution given by 1

$$P(E) = P_{\mathrm{t}}\exp\left(\frac{-E}{kT_t}\right) \tag{9}$$

where $P(E)$ is the concentration of traps per unit energy range and is a function of energy *E* above the valence

TABLE II Electrical parameters in the SCLC region of pure and I_2 doped Ni Pc.

Parameters	Au/NiPc/Al	Au/I_2 doped Ni Pc/Al
E_{t} eV	0.44	0.33
$N_{\mathrm{t(s)}}$ m^3	2.23×10^{23}	1.3×10^{22}
P_{t} $\mathrm{J}^{-1}\,\mathrm{m}^{-3}$	5.76×10^{44}	1.64×10^{44}
$N_{\mathrm{t(e)}}$ m^{-3}	8.06×10^{23}	3×10^{25}

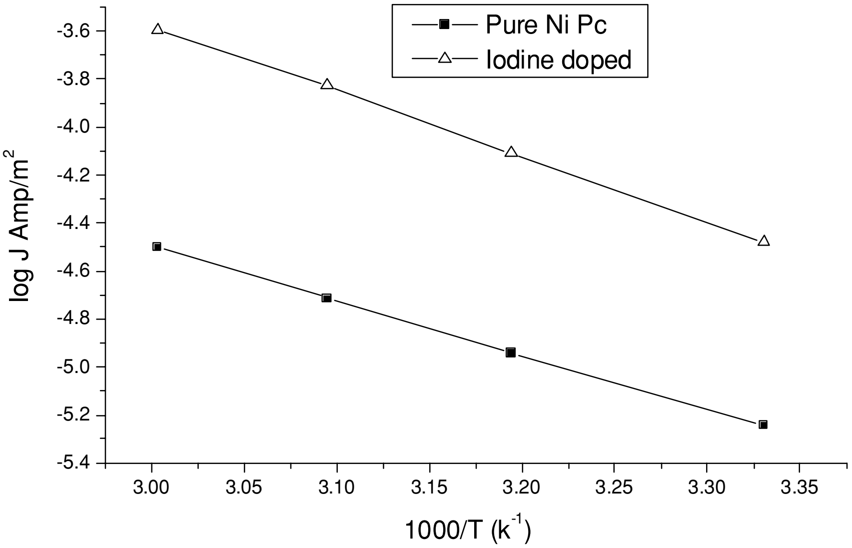

Figure 5 Variation of log J with 1000/T in the SCLC region segment(II) at 3.0 V.

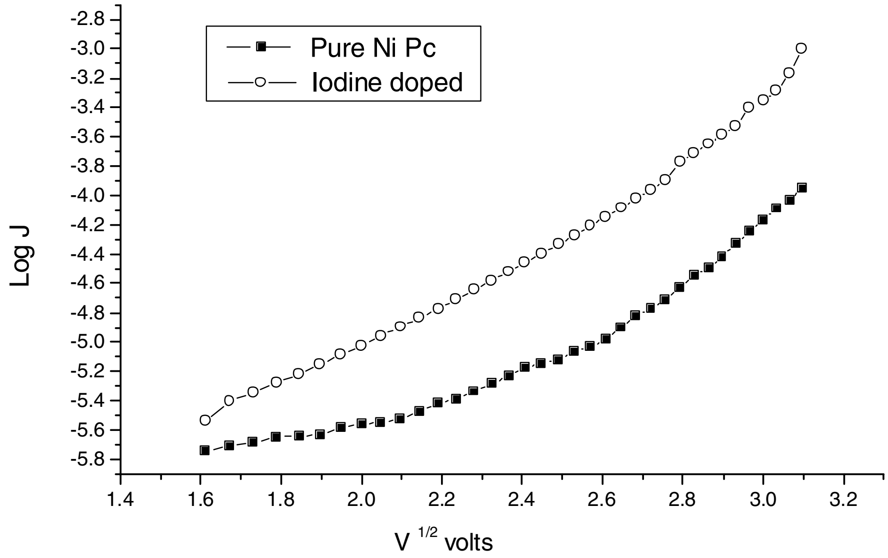

Figure 6 Plot of log J vs. V$^{1/2}$ in the reverse bias for the pure and I$_2$ doped Ni Pc films.

band edge. The total concentration of traps $N_{t(e)}$ has been given by

$$N_{t(e)} = P_t k T_t \tag{10}$$

The slope of line segment (III) of the graph in Fig. 2 is found to be 4 and hence the value of $l = 3$ and the temperature parameter $T_t = 1014$ K for $T = 300$ K. Assuming the value of the density of states $N_v = 10^{27}$ m$^{-3,}$ permittivity of the Ni Pc $\varepsilon = 1.2 \times 10^{-11}$ F/m, mobility $\mu = 1.21 \times 10^{-13}$ m^{-1} V^{-1} s^{-1} and using Equations 8 and 10 the values of P_t and $N_{t(e)}$ for the pure and doped Ni Pc films are calculated and listed in Table II.

From the analysis of the forward current graph an exponential increase in forward current with applied voltage in the low voltage range is evident. The exponential dependence of current in the lower voltage range can be attributed to the formation of a depletion region between gold electrode and organic layer. It can be also observed that the Schottky barrier disappears when the applied voltage is above 0.6 V and 1.0 V for devices of pure Ni Pc and the iodine doped devices. But beyond this applied voltage the current is mainly due to the bulk series resistance of the organic layer rather than the electrode interface. In the reverse bias condition the order of current is much lower than the forward current indicating a current limitation that can be explained as a Schottky or Poole-Frenkel type of conduction. The general equations [26] describing the reverse current density under these circumstances is given by

$$J = A^{**} T^2 \exp\left(-\frac{\Phi_s}{kT}\right) \exp\left(\frac{\beta_s V^{1/2}}{kT d^{1/2}}\right) \tag{11}$$

where $A^{**} = 1.3 \times 10^5$ A m^{2}K^2 is the Richardson Constant and Φ is the Schottky barrier height at the injecting

TABLE III Electrical constants of pure and I_2 doped Ni Pc in the reverse region

	Pure Ni Pc		Doped Ni Pc	
Parameter	Low voltage	High voltage	High voltage	Low voltage
β_{PF} eVm$^{1/2}$ V$^{-1/2}$	6.74×10^{-5}	3.37×10^{-5}	1.43×10^{-5}	3.6×10^{-5}

electrode interface, βs is the Schotty field lowering coefficient. For the Schottky effect which is a field lowering of interfacial barrier at the injecting electrode, the current voltage relation is defined by

$$J = J_0 \exp\left(\frac{\beta_{PF} V^{1/2}}{kT d^{1/2}}\right) \qquad (12)$$

where Jo is the low field current density and β_{PF} Poole-Frenkel field lowering coefficient The two coefficients β_S and β_{PF} are related by the equation

$$2\beta_s = \beta_{PF} = \left(\frac{e^3}{\pi \varepsilon}\right)^{1/2}$$

substituting the values of the permittivity $\varepsilon = 1.12 \times 10^{-11}$ F/m, the theoretical values of the field lowering coefficients are calculated as $\beta_{PF} = 6.75 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$ and $\beta_s = 3.375 \times 10^{-5}$ eV m$^{1/2}$ V$^{-1/2}$.

In order to find the experimental values of these coefficients a graph of log J against V$^{1/2}$ is plotted in Fig. 6. This plot is having two linear portions and correspondingly there are two slopes. Hence there are two values of these coefficients such as β_{PF} in the lower voltage range and β_{PF} in the higher voltage region. The values of β_{PF} in the two voltage regions are listed in Table III. In the low voltage region the current conduction is originated from the contact interface rather than from the bulk material.The experimental values of β_{PF} n the high voltage region is in reasonable agreement with the theoretically calculated values β_{PF}. The variation of β_{PF} in the low voltage region may be due the non uniformity of the doping process.

4. Conclusion

From the investigations of the current density characteristics of the doped Ni Pc films we find that at low voltage the current conduction is ohmic where as at higher voltage the conduction mechanism is a space charge limited conduction. For the doped films there is a considerable shift in the Fermi level. This may be accounted for by the decrease in the metal-metal bond distance. The low value of E_f suggests that I_2 doped Ni Pc is more efficient in conduction because of the increased electrical conductivity compared with the pure Ni Pc. The reverse current is found to be much lower from the forward current indicating a semi conducting behaviour of gold-I_2 doped Ni Pc -aluminium device.

Reference

1. K. P. KRISHNA KUMAR and C. S. MENON, *J. Solid State Chem.* **128** (1997) 27.
2. S. AMBILY and C. S. MENON, *Thin Solid Thin Films* **347** (1999) 284.
3. G. B. KAMATH, C. M. JSEPH and C. S. MENON, *Mater. Lett.* **57** (2002) 730.
4. K. R. RAJESH and C. S MENON, *Materials letters* **58** (2002) 329.
5. M. C. Petty, *Bio Sensors and Bio Electronics* **10** (1995) 129.
6. A. COLE, R. J. MCLLROU, THORPE and S. C.COOK, *Sensors and Actuators* **13** (1993) 416.
7. M. E. AZIM ARAGHI and A. KRIER, *App. Surf. Sci.* **119** (1997) 260.
8. R. RELLA, A. SERRA, P. SICILLIANO and A. TEPORE *Thin Solid Films* 286 (1996) 256.
9. S. ANTOHE, N. TOMOZEU and S. GOGONEA, *Physics Status Solid* (1991) 397.
10. M. PFEIFFER, A. BEYER, T. FRITZ and K. LEO, *Appl. Phys. Lett.* **73** (1998) 3202.
11. Q. ZHOU and R. D. GOULD, *Thin Solid Films* **317** (1998) 436.
12. H. YAMAGI, H. KATAURA and YUEDA, *J. Appl. phy.* **75** (1994) 568.
13. T. G. ABDEL-MALIK, A. A. AHEMED and J. SIMON, *ibid.* **54** (1990) 507.
14. K. N. NARAYANAN UNNI and C. S. MENON, *J. Mater. Sci. Lett.* **20** (2001) 1207.
15. M. M. EL-NAHAS, Z. EL-GOHARY and H. S. SOLIMAN, *Optics and Laser Technol.* **35** (2003) 523.
16. A. M. SALEH, A. K. HASSAN and R. D. GOULD, *J. Phy. Che. Solids* **64** (2003) 1297.
17. T. G. ABDEL-MALIK and R. M. ABDEL-LATIF, *Physica* **B205** (1995) 59.
18. T. S. SHAFAI and T. D. ANTHOPOULOS, *Thin Solid Films* **398** (2001).
19. M. S. ROY, G. D. SHARMA and S. G. SANGODKAR, *Synthetic Metals* **81** (1996) 159.
20. V. R. ZAKAMOV, V. A. PANTELEEV, L. G. PAKHOMOV and G. L. PAKHOMOV, *High Energy Chem.* **36** (2002) 80.
21. W. Y. GAO and A. KAHN, *Appl. Phys. Lett.* **79** (2001) 4040.
22. A. M. SALEH, A. O. ABU-HILAL and R. D. GOULD, *Curr. Appl. Phys.* **3** (2003) 345.
23. T. D. ANTHOPOULOS and T. S. SHAFAI, *Thin Solid Films* **64** (2003) 1217.
24. T. G. ABDEL MALIK, R. M. ABDEL-LATIF, A. E. EL-SAMAHY and S. M. KHALIL, *Thin solid Films* **256** (1995) 139.
25. R. D. GOULD and A. K. HASSAN, *Thin solid Films* **193/194** (1990) 895.
26. J. G. SIMMONS, *J. Phys.* **D4** (1971) 613.

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