

Influence of O₂ on rectification properties of Nickel Phthalocyanine thin film devices

T. D. Anthopoulos and T. S. Shafai
Staffordshire University, School of Engineering and Advanced Technology,
Beaconside, Stafford,
ST18 0DF, UK.

Abstract. Thin sandwich film structure devices of Gold/Nickel Phthalocyanine/Lead (Au/NiPc/Pb) were fabricated employing a novel in-situ method. Electrical measurements were performed prior to, and after exposure of the samples to dry air. Under forward bias and for low applied voltages an ohmic conduction was evident, followed by SCLC in the higher voltage range. In the reverse bias, devices were found to exhibit weak rectifying properties originated mainly from the bulk of the NiPc layer. After exposure of the sample to dry air for five days a strong rectifying effect at the NiPc/Pb interface was evident. The phenomenon is believed to be associated with a change of NiPc work function as result of O₂ adsorption on the NiPc layer. To verify this a second sample of the type Au/NiPcO₂/Pb was fabricated. Electrical characterization of the sample showed stronger rectifying properties providing further experimental evidence on the influence of O₂ adsorption on the organic layer. Potential barrier height and diode ideality factor for both NiPc/Pb, and NiPcO₂/Pb interfaces after exposure to dry air, were also calculated.

1. Introduction

Organic semiconducting compounds such as Phthalocyanine (Pc) and its metal derivatives (MPc's) have been studied for some time with regard to their electronic properties. In general Pc and its metal derivatives are classified as p-type semiconductors [1]. Their thermally stable nature makes them suitable for fabrication of various electronic devices utilizing the relatively simple technique of thermal vacuum sublimation. Previous studies have shown that this particular class of organic compounds can be used in a wide range of electronic devices including solar cells and organic light emitting diodes (OLED) [2,3]. Most of the devices investigated so far have been of schottky type in sandwich configuration utilizing suitable electrode materials [3,4]. Schottky barrier devices incorporating phthalocyanine as the active layer appears to be sensitive to oxygen adsorption as well as the adsorption of water vapor [5,6]. It has been previously demonstrated that presence of oxygen enhances the energy conversion efficiency of phthalocyanine based solar cells [7]. Despite the numerous reports on the effects of oxygen on the electronic properties of phthalocyanines, still many questions concerning its effects on Pc/Metal electrode interfaces are remaining unanswered. The reason is mainly due to fabrication processes employed, where oxygen was almost unavoidably introduced into the phthalocyanine layer. Thus a fuller understanding of the oxygen adsorption mechanism and its effect on contact properties between Metal/Pcs is of vital importance. In the present paper we report $I - V$ measurements obtained in-situ and under light-tight conditions for two different thin film samples. The first set of results is concerned with an un-doped sample based on Au/NiPc/Pb, while the second set obtained from an oxygen doped sample consisting of Au/NiPcO₂/Pb. Influence of prolonged exposure to dry air under atmospheric pressure is also reported for both set of devices.

2. Experimental Details

Nickel phthalocyanine (NiPc) powder obtained from Sigma-Aldrich Co. Ltd., was further purified utilizing a three zone entrainer sublimation apparatus using nitrogen gas as carrier. Multilayer sandwich devices of Au/NiPc/Pb and Au/NiPcO₂/Pb have been fabricated in-situ utilizing a relatively simple technique of sequential thermal vacuum sublimation. Details on the sequential turret source

masking system used in this experiment are reported elsewhere [8]. The substrates employed were corning 7059 borosilicate glass substrates, and were subjected to thorough cleaning prior to deposition to avoid contamination. To allow uniform doping of O₂ in NiPc film for the Au/NiPcO₂/Pb sample, all devices were exposed to dry air for three days prior to Pb electrode deposition under in-situ conditions. Gold (known to provide ohmic contact to most Pc's [9,10]) and lead (as the low work function material) electrodes were evaporated using molybdenum boats at an evaporation rate of 0.4 nm/sec. The typical final electrode thickness was approximately 80 nm. For evaporation of NiPc a tantalum boat was utilized with evaporation rate maintained approximately to 0.45 nm/sec, to a final thickness of 1 μm. Both deposition rate and film thickness were monitored in-situ using a calibrated IL 150 quartz crystal thickness monitor. Each of the final sandwich devices measured to have an effective conduction area of $A = 1.2 \times 10^{-5} \text{ m}^2$. Electrical characterization was performed using a conventional DC technique utilizing a Thurlby PL320 TGP stabilized power supply, a Keithley 414S Picoammeter and a HP 3478A voltmeter. Prior and during each test the devices were stored under light tight conditions to avoid any photoelectric effect.

3. Results and discussion

The forward and reverse dark $I - V$ characteristics for the Au/NiPc/Pb test sample are shown in Fig. 1. The forward bias corresponds to Au electrode being positively biased, while reverse bias corresponds to the Pb being positively biased. For low voltages and under forward bias an ohmic conduction region is evident. For higher voltages a current increase is observed following a relationship of the type

$$I \propto V^n \quad (1)$$

In the reverse bias, current does not follow such a simple relation, and has lower magnitude for the same applied voltage when compared to that measured under forward bias. This kind of behavior may be attributed to the existence of a current limitation mechanism, arising either from the bulk of the NiPc layer (Poole-Frenkel effect), or from the injecting electrode (NiPc/Pb) interface (Schottky effect). Current density expressions for both mechanisms are given respectively by [11] as

$$J = A^{**} T^2 \exp\left(\frac{-\phi_s}{kT}\right) \exp\left(\frac{\beta_s V^{1/2}}{kTd^{1/2}}\right) \quad (2)$$

for Schottky effect and

$$J = J_o \exp\left(\frac{\beta_{PF} V^{1/2}}{kTd^{1/2}}\right) \quad (3)$$

for Poole-Frenkel effect. Where A^{**} is the effective Richardson constant ($1.3 \times 10^5 \text{ Am}^2\text{K}^{-2}$ [12]), ϕ_s the Schottky barrier height at the injecting electrode interface, $J_o (= \sigma_o F)$ is the low-field current density, V the applied voltage across the device, d is the NiPc layer thickness, T is the absolute temperature, and β_s & β_{PF} are respectively the Schottky and Poole-Frenkel field lowering coefficients. Theoretical values of β_s & β_{PF} are given by

$$2\beta_s = \beta_{PF} = \left(\frac{e^3}{\pi\epsilon}\right)^{1/2} \quad (4)$$

where e is the electronic charge, and ϵ the permittivity of NiPc ($2.425 \times 10^{-11} \text{ Fm}^{-1}$ [13]). Following Shafai and Gould [14], analysis of the reverse $I - V$ characteristics yields field-lowering coefficient values closer to theoretical value for β_{PF} , suggesting the existence of a current limitation mechanism originated from the bulk of the NiPc layer rather than the NiPc/Pb interface. Similar observations have also been reported for Pb/CuPc/Au samples [15]. From the results presented up to this point the first conclusion may be drawn:

- I. In-situ fabrication of Au/NiPc/Pb structures leads to an ohmic NiPc/Pb contact under forward bias, while under reverse bias a current limitation mechanism owing to the bulk of NiPc layer is evident

In order to examine the effects of air in this particular set of devices, the sample has been exposed to dry air for five days under atmospheric pressure. A typical set of $I - V$ characteristics obtained from this particular sample is shown in Fig. 2. As can be observed presence of O_2 gives rise to a rectification effect with the current under forward bias ($0.2\text{V} \leq V_F \leq 0.4\text{V}$) following the diode equation [16], given as

$$I = I_s \left(\exp\left(\frac{eV_F}{mkT}\right) - 1 \right) \quad (5)$$

where V_F is the applied voltage across the device, k is the Boltzmann's constant, m is the diode ideality factor, and T is the absolute temperature. I_s is the saturation current and can be expressed as

$$I_s = AA^{**} T^2 \exp\left(-\frac{e\phi_b}{kT}\right) \quad (6)$$

where A is the effective conduction area, and ϕ_b the barrier height at the NiPc/Pb interface. Analysis of the forward $I - V$ curve together with equations 5 & 6, yields the barrier height $\phi_b = 0.96 \text{ eV}$, and the diode ideality factor of $m = 3.6$. This set of results permits to draw the second conclusion:

- II. Presence of O_2 plays the dominant role in the creation of the rectifying effect observed at the NiPc/Pb interface

Although, the effect might either be induced by O_2 adsorption on phthalocyanine layer or due to oxidation of the Pb electrode. To answer this question two assumptions are made. In the first we consider the case in which O_2 reacts with the Pb electrode: Reaction of O_2 with the Pb electrode most

probably would increase the work function of Pb leading to a decrease of the barrier potential (if any) rather than the observed creation of the barrier. And the second case, where adsorption of O₂ close to NiPc/Pb interface is taking place: More likely the latter will lead to an increase in the work function of NiPc causing an equivalent increase to the barrier height. In order to verify this a sample of the type Au/NiPcO₂/Pb has been fabricated. Prior to deposition of the top electrode the sample has been exposed to dry air for three days and then followed by in-situ deposition of the top Pb electrode. The forward and reverse bias characteristics obtained from this particular sample are shown in Fig. 3. As it can be seen the current flowing in the forward direction is higher in magnitude than that observed for the un-doped sample for the same applied voltage, while under reverse bias the opposite is observed. Comparing the results obtained from the Au/NiPcO₂/Pb with that of Au/NiPc/Pb, after exposure to air indicates a lower rectifying effect from the latter. A possible explanation is that O₂ is adsorbed only on the surface of the NiPc and held by rather weak van der Waals type forces with energies rarely exceeding 0.2 eV [17]. Thus during the deposition of the top (Pb) electrode under high vacuum, the majority of the O₂ molecules are removed. The small fraction of O₂ molecules remaining adsorbed on the surface of the NiPc layer will have a measurable influence in its electronic properties, in agreement with our observations. Therefore a third conclusion may be drawn

- III. Adsorption of O₂ on the NiPc microcrystalline structure is the dominant mechanism responsible for the creation of the rectifying effect observed at the NiPcO₂/Pb interface.

Incorporation of O₂ may be related to either change of NiPc work function giving rise to the potential barrier at the NiPc/Pb interface or to a space-charge region arising from an oxide layer between NiPc/Pb, enhancing the rectifying properties of the junction. The electrical characteristics of Metal/Oxide/MPc (Al/Al₂O₃/MPc) structure have been examined by Martin et al [18]. Their work led to the conclusion that, formation of interfacial oxide layers between M/MPc systems do not play a dominant role to the creation of the rectifying effect at the M/S interface. Therefore a change of NiPc work function upon O₂ adsorption is the most likely dominant mechanism that taking place, giving rise to the diode behavior. Although a possible two-step O₂ dependent contribution mechanism between NiPc and Pb electrode should not in any case be completely disregarded. The *I* - *V* characteristics for the O₂ doped sample after has been re-exposed to dry air for five days at atmospheric pressure is shown in Fig. 4. As it can be seen the device exhibits strong rectifying properties. Analysis of the data obtained under forward bias, together with equation 5 & 6, yields values of the barrier height $\phi_b = 1$ eV, and ideality factor $m = 2.6$. The higher values of ϕ_b and lower value for m , compared with values obtained from the un-doped sample, correlates well with the O₂ adsorption process on the NiPc layer.

4. Summary and Conclusions

Current - voltage characteristics have been obtained for an Au/NiPc/Pb sample fabricated and tested in-situ. Under forward bias conditions and within low applied voltages an ohmic conduction region was evident, followed by SCLC in the higher voltage range. In the reverse bias current flow was found to be dominated by a current limitation mechanism originated from the bulk of the NiPc layer. On exposure of the device to dry air a strong diode behavior has been identified. Analysis of *I* - *V* characteristics allowed calculation of barrier height and diode ideality factor yielding values of $\phi_b = 0.96$ eV and $m = 3.6$ respectively. The effect of O₂ doping on the NiPc work function was also investigated. For this purpose a sample of the type Au/NiPc O₂/Pb has been fabricated. Formation of the NiPcO₂/Pb contact found to exhibit stronger rectification effect in comparison to that observed for the Au/NiPc/Pb sample. This behavior was attributed to a change of NiPc work function. Re-exposure of the sample to dry air for a period of five days revealed an even stronger rectifying behavior. Barrier

height and diode ideality factor, were also calculate yielding values of $\phi_b = 1\text{ eV}$ and $m = 2.6$ respectively. The improved rectifying effect was correlated with O₂ adsorption on NiPc layer.

References

- [1] R. G. Gould., 'Structure and electrical conduction properties of phthalocyanine thin films', *Coordination Chemistry Reviews*. 156 (1996) 237.
- [2] J. B. Whitlock, P. Panayotatos, G. D. Sharma, M. D. Cox, R.R. Sausers, and G.R. Bird., 'Investigations of materials and device structures for organic semiconductor solar cells', *Opt. Eng.* 32(8) (1993) 1921.
- [3] J. Blochwitz, M. Pfeiffer, T. Fritz, and K. Leo., 'Low voltage organic light emitting diodes featuring doped phthalocyanine as hole transport material', *Appl. Phys. Lett.* 73 (1997) 729.
- [4] G. D. Sharma, S. G. Sangodkar, and M. S. Roy., 'Influence of iodine on the electrical and photoelectrical properties of zinc phthalocyanine thin film devices', *Material Sci. Eng.* B41 (1996) 222.
- [5] G. A. Chamberlain., 'Organic solar cells: A review', *Solar Cells*. 8 (1983) 47.
- [6] F. R. Fan, and L. R. Faulkner., 'Photovoltaic effects of metal free and zinc phthalocyanines. II. Properties of illuminated thin-film cells', *J. Chem. Phys.* 69 (1978) 3334.
- [7] R. O. Loutfy, J. H. Sharp, C. K. Hsiao, and R. Ho., 'Phthalocyanine organic solar cells. Indium/x-metal free phthalocyanine Schottky barriers', *J. Appl. Phys.* 57 (1981) 5218.
- [8] T. Anthopoulos, and T. S. Shafai., 'Sequential turret source masking system for fabrication of multilayer structures', *J. Vac. Sci. Technol. (A)*. 18 (2000) 2595.
- [9] A. Sussman., 'Space-Charge-Limited Currents in Copper Phthalocyanine thin films', *J. Appl. Phys.* 38(7) (1967) 2738.
- [10] R. D. Gould, and R. I. Blyth., 'Conductivity and absorption measurements in nickel phthalocyanine thin films', *Physica Status Solidi (a)*. 120 (1990) K57.
- [11] J. G. Simmons., 'Conduction in thin dielectric films', *J. Phys. D.* 4 (1971) 613.
- [12] T. Anthopoulos, and T. S. Shafai., 'Junction properties of nickel phthalocyanine thin sandwich film structures using dissimilar electrodes', Submitted for publication in *Physica Status Solidi (a)*. July 2000.
- [13] T. Anthopoulos, and T. S. Shafai., 'SCLC Measurements in nickel phthalocyanine thin films', *Physica Status Solidi (a)*. 181(2) (2000) page number not available at the time.
- [14] T. S. Shafai, and R. D. Gould., 'Observations of Schottky and Poole-Frenkel emission in lead phthalocyanine thin films using aluminium injecting electrodes', *Int. J. Electronics*. 73(2) (1992) 307.
- [15] A. K. Hassan, and R. D. Gould., 'High field electronic conduction process in copper phthalocyanine thin films using lead and gold electrode combinations', *Thin Solid Films*. 193/194 (1990) 895.
- [16] M. S. Sze., 'Physics of Semiconductor devices', 1981. 2nd edition. New York: Wiley.
- [17] J. Oudar., 'Physics and Chemistry of Surfaces. 1975. Backie, London.
- [18] M. Martin, J. J. Andre, and J. Simon., 'Influence of dioxygen on the junction properties of metallophthalocyanine based devices', *J. Appl. Phys.* 54(5) (1983) 2792.

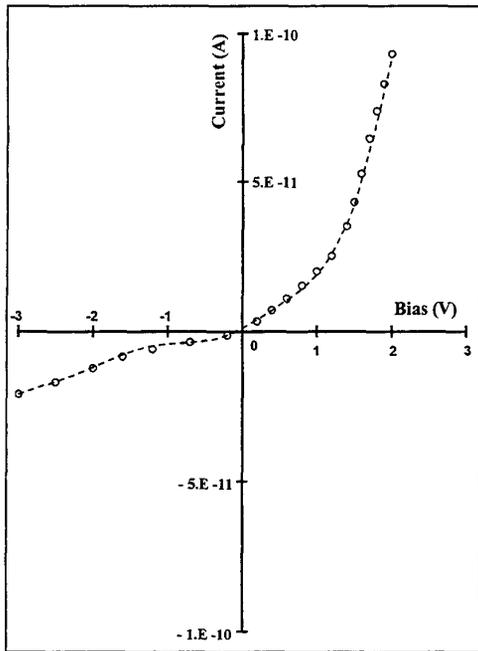


Figure 1. Dark conductivity I-V characteristics for an Au/NiPc/Pb sample fabricated and tested in-situ.

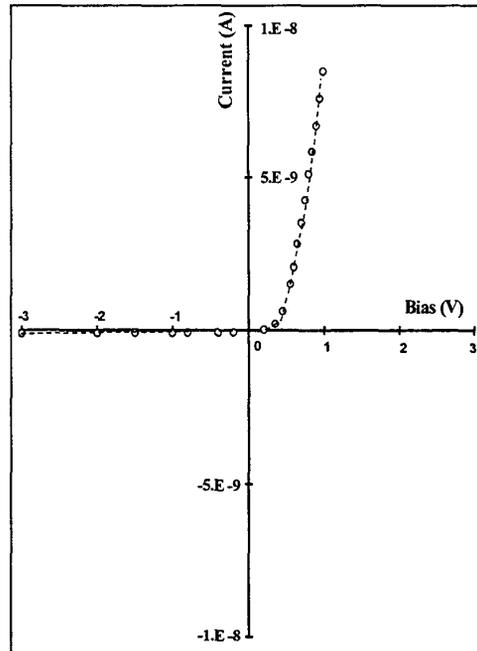


Figure 2. Dark conductivity I-V characteristics for an Au/NiPc/Pb sample obtained after exposure to dry air for five days.

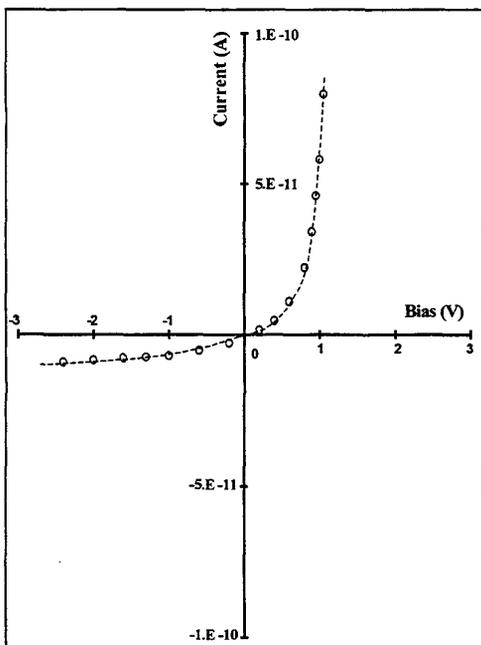


Figure 3. In-situ dark conductivity I-V characteristics obtained for an Au/NiPcO₂/Pb sample.

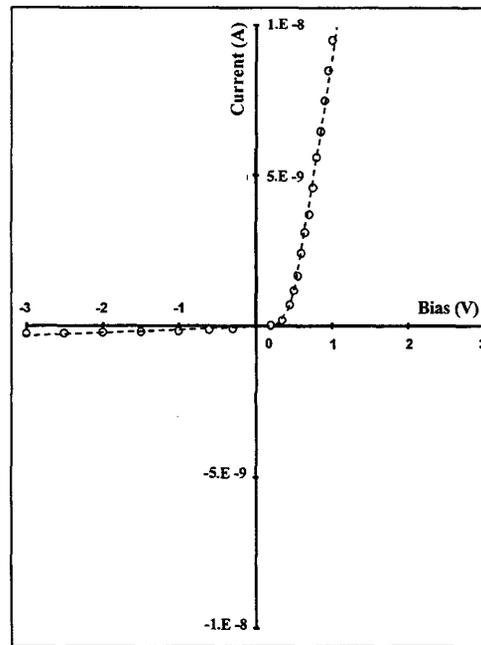


Figure 4. Dark conductivity I-V characteristics obtained for an Au/NiPcO₂/Pb sample after exposure to dry air for five days.