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Oxygen induced *p*-doping of α-nickel phthalocyanine vacuum sublimed films: Implication for its use in organic photovoltaics

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The effects of oxygen doping on the charge transport and photovoltaic properties of α-nickel phthalocyanine (α-NiPc) based devices are investigated using *in situ* and *ex situ* $I-V$ measurements. $I-V$ characteristics for devices employing gold contacts indicate ohmic conduction at low voltages, followed by space-charge-limited conduction in higher fields. Upon exposure of NiPc to dry air an increase in the hole concentration (p_0) from 8.5×10^{10} to 2.6×10^{15} m^{-3} is observed. When the top gold ohmic cathode is replaced by lead, Schottky type behavior is evident with the junction exhibiting photovoltaic effect. The energy conversion efficiency of the cell increases following exposure to oxygen. These results suggest that fabrication of air stable electronic devices based on NiPc is feasible. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1559649]

Small molecule organic semiconductors such as phthalocyanines (Pcs) are currently under intense investigation due to their potential use in a variety of electronic and optoelectronic devices, such as field effect transistors,[1] organic light emitting diodes (OLEDs),[2] and photovoltaic (PV) cells.[3] In general, organic semiconductors posses several advantages over their inorganic counterparts, one of which is the processability they offer. They can be used for fabrication of large area devices such as flat panel displays and solar cells employing cost effective fabrication techniques like spin casting[4] and thermal evaporation.[1,3] In OLED applications, phthalocyanines have been used for improving device performance by acting as efficient hole-injecting layer between the indium tin oxide anode and the electroluminescent medium of the device.[2,5] However, due to the low dark conductivity encounter in most Pcs,[6] their application in practical OLEDs and PV is limited. An effective approach for overcoming this problem is doping Pcs with strong organic acceptor molecules. Indeed, examples of controlled doping of metal phthalocyanine layers by cosublimation of tetrafluorotetracynoquinodimethane have been demonstrated and a striking improvements on power efficiency of Alq_3 based OLEDs,[7] as well as PV cells[8] have been achieved. Despite promising results, the use of evaporated dopants still remains unattractive due to the need of complicated fabrication systems. Ideally, one would like to be able to dope the organic semiconductor employing simple techniques such as exposure of the sample to oxidizing gasses. From previously published work,[9] it occurred to us that air stable Schottky type junctions based on NiPc employing lead (Pb) as the cathode electrode could be fabricated. Although, the effects of incorporating Pb as the cathode electrode in phthalocyanine based devices has been reported,[9] yet no studies on the influence of oxygen on the photovoltaic performance of such cells has been published. In this letter, we report the effects of oxygen doping on the electrical properties of α-NiPc based devices. In particular, we show that by simple exposure of the as evaporated films to dry air, a large increase in the dark conductivity of α-NiPc is achieved. Furthermore, we fabricate Schottky type solar cells and we examine the effects of *p* doping on device performance.

Nickel phthalocyanine (Sigma-Aldrich Ltd.) was further purified by entrainer sublimation. NiPc was chosen because it is known to posses a relatively high hole mobility value.[10,11] Sandwich structure devices are prepared by thermal sublimation. Details of the fabrication method employed have been reported earlier.[9] The molecular structure of NiPc and a schematic diagram of a typical device employed are shown in the inset of Fig. 1. Freshly deposited NiPc films are studied by means of x-ray diffractometry employing Cu $K\alpha$ radiation. For measurement of dark conductivity of the as evaporated and oxygen doped NiPc films, gold ohmic contacts are employed.[12] In the case of Schottky devices, Pb as the low work function cathode is used.[9] The $I-V$ characteristics for freshly prepared devices are measured *in situ*. The

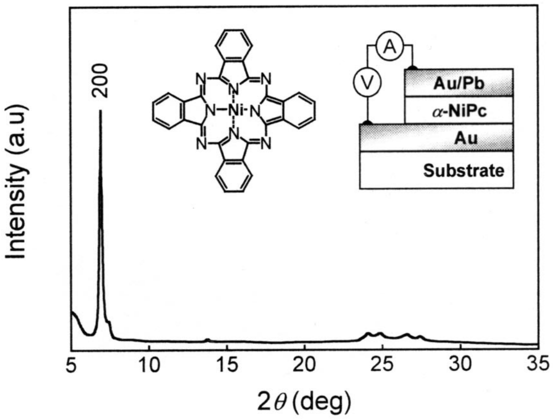

FIG. 1. X-ray diffraction patterns of as evaporated NiPc film. The inset shows the molecular structure of NiPc and a schematic diagram of the test device employed. For Schottky junction solar cells the top Au electrode is replaced by a semitransparent Pb contact.

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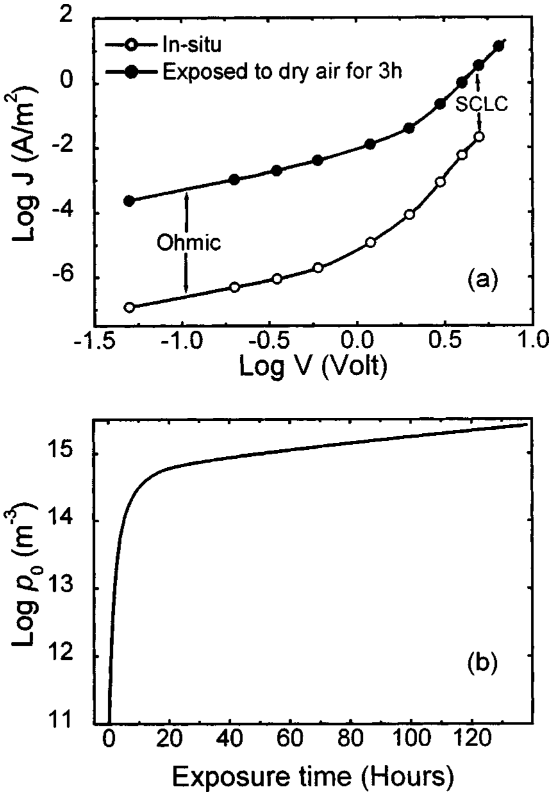

FIG. 2. The $J-V$ characteristics (a), and thermally generated holes concentration (p_0) as a function of exposure time in dry air (b), for hole only α-NiPc based device employing symmetric Au electrodes.

effects of oxygen on dark conductivity and photovoltaic performance of the solar cells are examined by introducing dry air into the chamber via a leak valve. Photovoltaic performance of the Schottky devices is assessed under white light illumination through the semitransparent top Pb electrode supplied by a 500 W halogen lamp.

TABLE I. Hole trapping parameters derived for a Au/α-NiPc/Au device tested under *in situ* conditions and after exposure to dry air for 3 h.

Experimental conditions	Parameter	
	$N_{t(e)}$ (m^{-3})	P_0 (J^{-1} m^{-3})
In situ	3.4×10^{24}	1.8×10^{44}
In dry air (3 h)	1.0×10^{24}	5.8×10^{43}

X-ray diffraction measurements (Fig. 1) indicate that the as evaporated NiPc are of the α form exhibiting a typical peak at $2\theta=6.92°$. From the literature[13] this peak is assigned to reflection from the 200 crystalline plane. From the full width and half maximum of this intense peak, the size for the crystalline cluster is calculated yielding a value of ~32.5 nm. In order to gain insight into the charge transport mechanism and the effects of oxygen doping in these films, we studied the dark current density ($J-V$) characteristics of hole only devices consisted of symmetric Au electrodes. Figure 2(a) displays a typical set of the $J-V$ characteristics obtained for an Au/α-NiPc (0.4 μm)/Au device prior and after exposure to dry air. In each of these traces two different conduction regimes are identified. At low voltages ($V_{\mathrm{bias}}<0.5$ V) current follows Ohm's law described by

$$J=p_0 e\mu F, \tag{1}$$

where p_0 is the concentration of thermally generated holes, e is the electronic charge, μ is the hole mobility, and F is the electric field strength. Upon exposing the sample to dry air, the hole current increases, which can be explained by the creation of additional acceptor states. Assuming a value for $\mu=7\times10^{-5}\ \mathrm{m}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-111}$ in Eq. (1) the variation of p_0 as a function of exposure time is calculated. These results are presented in Fig. 2(b) where p_0 is plotted as a function of exposure time. Concentration of holes saturate with time and seem to reach a near equilibrium value of approximately $2.6\times10^{15}\ \mathrm{m}^{-3}$. A distinct characteristic of this trace is the drastic effect of oxygen absorption during the first 5 h. At higher applied voltages ($V_{\mathrm{bias}}>2.5$ V), current increases and in both cases follows a relationship of the type $J\propto V^m$, with $m\sim5.5$. This behavior is characteristic for space-charge-limited conduction (SCLC) governed by exponentially distributed trapping levels.[14,12] In this regime J is described by

$$J_{\mathrm{SCLC}}=e\mu N_V\left(\frac{\epsilon}{eP_0kT_t}\right)^l\frac{V^{l+1}}{d^{2l+1}}, \tag{2}$$

where N_V is the effective density of states at the valence band edge ($\sim10^{27}\ \mathrm{m}^{-3}$, one state per molecule),[15] ϵ is the permittivity of NiPc ($2.42\times10^{-11}\ \mathrm{F\,m}^{-1}$),[12], P_0 is the trap concentration per unit energy range at the valence band edge, k is the Boltzmann's constant and d the α-NiPc film thickness. The term $(l+1)$ represents the power law exponent, where $l=T_t/T$, with T_t being a temperature parameter characterizing the exponential trap distribution. The total concentration of traps $N_{t(e)}$ is given by[16]

$$N_{t(e)}=P_0kT_t. \tag{3}$$

From the slope of the SCLC region in Fig. 2(a), the temperature parameter $T_t=1336$ K is calculated at $T=297$ K. Furthermore, the values for P_0 and $N_{t(e)}$ are also determined, according to Eqs. (2) and (3). Derived results are summarized in Table I. To investigate the effects of oxygen doping on the photovoltaic properties of α-NiPc based cells, Schottky junctions were realised employing Pb cathode electrode. The thickness of α-NiPc was 90 nm. Figure 3 shows the $J-V$ characteristic (dark) of such device after exposure to dry air for few minutes demonstrating the good rectification of the junction. Doping is found to be homogeneous throughout the α-NiPc layer (determined by capacitance–

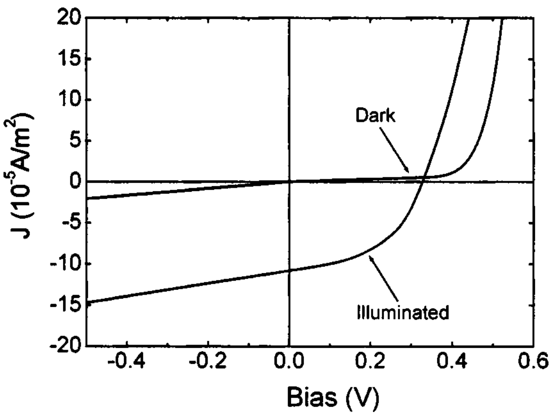

FIG. 3. Dark and illuminated (75 mW/m^2), $J-V$ characteristics of an α-NiPc/Pb Schottky junction after exposure to dry air for few minutes.

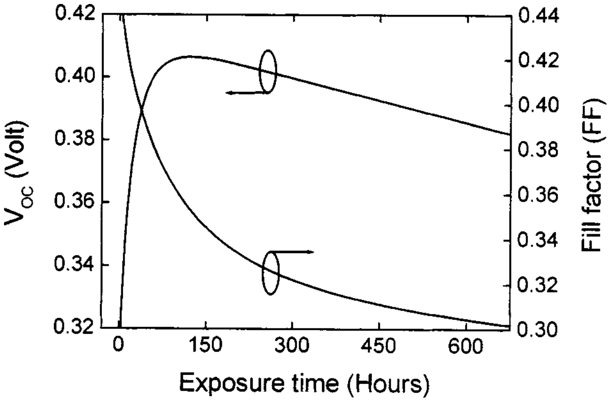

FIG. 4. Exposure time dependence of the V_{OC} and FF for a α-NiPc/Pb Schottky junction under white light illumination (30 mW/m^2).

voltage measurements). The hole injection barrier at the α-NiPc/Pb interface is found to vary from 0.95 to 1.1 eV for the cells exposed to air for few minutes and one month, respectively. For the cell under illumination in Fig. 3 (illuminated), a photovoltaic effect is observed. It is worth mentioning that when cells are tested *in situ* non/or very small photovoltaic response is evident. This can be explained in terms of low intrinsic carrier concentration as suggested in Fig. 2(b). However, photovoltaic behavior of the cell is improved considerably upon exposure to dry air. Figure 4 shows the open circuit voltage (V_{OC}) and fill-factor (FF) as a function of exposure time to dry air. The increase of V_{OC} is consistent with the increase in p_0, which increases the electrostatic field across the Schottky barrier, resulting to more efficient exciton dissociation and charge collection from the corresponding electrode. The energy conversion efficiency (corrected for the transmittance of the semitransparent Pb contact) is enhanced from 0.001% (exposed to air for 2 min) to 0.058% upon exposure for 24 h and under white light illumination (30 mW m^{-2}). The reduction in the value of V_{OC} (for exposure time $>$110 h) and FF may be ascribed to interaction of oxygen at the Pb electrode. The latter is believed to be the main reason responsible for the cell's degradation and the loss in energy efficiency after prolonged period of exposure to dry air. It is believed that doping of the organic layer prior to Pb deposition will lead to better device stability.

In summary, the present results demonstrate that simple exposure of α-NiPc films to dry air results to efficient p-type doping. *In situ* and *ex situ* $I-V$ measurements show an increase by more than four orders of magnitude in the value of p_0 suggesting that oxygen act as electron acceptor. In the case of Schottky type solar cells, oxygen doping was found to have a profound effect improving cell's performance. It is believed that by optimizing film thickness and doping process in these devices, as well as incorporating lower work function materials as the cathode, might lead to development of more efficient solar cells. Furthermore, the ability of doping NiPc by using such a simple method is making it more attractive for applications in the area of OLEDs.

[1] Z. Bao, A. J. Lovinger, and A. Dodabalapur, Appl. Phys. Lett. **69**, 3066 (1996).
[2] M. Ishii and Y. Taga, Appl. Phys. Lett. **80**, 3430 (2002).
[3] Rudiono, S. Okazaki, and M. Takeuchi, Thin Solid Films **334**, 187 (1998).
[4] P. W. M. Blom, M. J. M. de Jong, and J. J. M. Vleggaar, Appl. Phys. Lett. **68**, 3308 (1996).
[5] Y. Qiu, Y. Gao, P. Wei, and L. Wang, Appl. Phys. Lett. **80**, 2628 (2002).
[6] J. Simon and J.-J. Andre, in *Molecular Semiconductors*, edited by J. M. Lehn and Ch. W. Rees (Springer, Berlin, 1985), p. 7.
[7] J. Blochwitz, M. Pfeiffer, T. Fritz, and K. Leo, Appl. Phys. Lett. **73**, 729 (1998).
[8] M. Pfeiffer, A. Beyer, B. Plonnigs, A. Nollau, T. Fritz, K. Leo, D. Schlettwein, S. Hiller, and D. Wohrle, Sol. Energy Mater. Sol. Cells **63**, 83 (2000).
[9] T. D. Anthopoulos and T. S. Shafai, Phys. Status Solidi A **186**, 89 (2001).
[10] T. G. Abdel-Malik, R. M. Abdel-Latif, A. E. El-Samashy, and S. M. Khalil, Thin Solid Films **256**, 139 (1995).
[11] T. D. Anthopoulos and T. S. Shafai, J. Vac. Sci. Technol. A **20**, 1 (2002).
[12] T. D. Anthopoulos and T. S. Shafai, Phys. Status Solidi A **181**, 569 (2000).
[13] S. Nakamura, H. Amatatsu, T. Ozaki, S. Yamaguchi, and G. Sawa, Jpn. J. Appl. Phys., Part 1 **26**, 1878 (1987).
[14] M. Lampert and P. Mark, in *Current Injection in Solids*, edited by H. G. Booker and N. DeClaris (Academic, New York, 1970), p. 27.
[15] A. Sussman, J. Appl. Phys. **38**, 2738 (1967).
[16] R. D. Gould and M. S. Rahman, J. Phys. D **14**, 79 (1981).