

# Oxygen induced charge carrier generation and trapping in vacuum deposited phthalocyanine thin films\*

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Investigations of the temperature dependencies of the electrical conductivity and thermo-modulated space charge limited current spectroscopy measurements are carried out on metal-free phthalocyanine (H<sub>2</sub>Pc) thin films, in a gap sample configuration with interdigital gold electrodes in a controlled atmosphere. It was found that the influence of O<sub>2</sub> on the dark conductivity of H<sub>2</sub>Pc films is a thermally activated process at 360 K. The H<sub>2</sub>Pc-O<sub>2</sub> interaction is a two-stage process characterized by an activation energy ( $E_a$ )=0.36 eV of creation and  $E_a$ =0.60 eV of decay of charge transfer complexes and subsequent generation of free charge carriers, increasing the Ohmic current. The dependence of the Ohmic current on the O<sub>2</sub> concentration (for small O<sub>2</sub> concentrations) is linear. An increased concentration of traps, as a result of the oxygen influence upon a trap level of 0.52 eV depth, was observed.

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## 1. Introduction

The semiconducting behaviour of metal phthalocyanines (MPc's) was originally observed by Eley [1] and Vartanyan [2]. In spite of the long years of investigation, it is still difficult to control the Pcs' electrical properties, where charge carrier trapping plays an important role. There are some specific features concerning the traps, which cause problems in respect of the practical applications of the organic semiconductors.

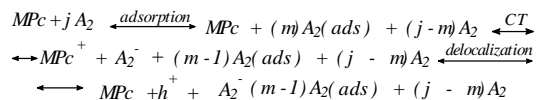
The polarisation of an MPc substance broadens any discrete trap level into a Gaussian distributed peak [3].

Due to the weak Van der Waals forces, traps with an exponential distribution in the electronic structure of polycrystalline or amorphous samples cannot be connected with the strong Coulombic potential, as often assumed in inorganic disordered substances.

One of the most characteristic features of organic molecular substances is the absence of dangling bonds on their surfaces. In spite of this fact, surface states are often observed, resulting from adsorption of gas molecules from the ambient. To measure the intrinsic properties of organic semiconductors, drastic precautions must be taken to avoid

the influence of gases, acceptors of electrons, such as BF<sub>3</sub>, BCl<sub>2</sub>, F<sub>2</sub>, Cl<sub>2</sub>, I<sub>2</sub>, NO<sub>2</sub>, O<sub>2</sub> [4].

A model of the gas/MPc interaction was proposed by Rella [5]. After the gas adsorption, the electrons are



transferred from the MPc to the adsorbed acceptor gas molecule (A<sub>2</sub>) and the holes residing in the film can be delocalised

where  $j$  is the number of acceptor gas molecules around the MPc ring,  $m$  is the number of adsorbed molecules from the MPc molecule, and  $h^+$  is the free hole responsible for the current. Then, the hole concentration results in an increase of the Ohmic current. The gas acceptor molecule creates negatively charged trapping centres on the film surface, capturing the electrons generated in the charge transfer process. In the literature, a trap level of about 0.51 eV depth was characterised as O<sub>2</sub><sup>-</sup> like Coulombic type for holes [6]. An increase in the free carrier concentration was indeed observed by Rella [5], in agreement with his

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model. However, his measurement did not detect the existence of  $O_2^-$  complexes.

Our previous measurements [7] of the oxygen influence on the parameters of copper phthalocyanine (CuPc) organic field effect transistors (OFETs) also support Rella's model. The drain current vs. gate voltage characteristics of an OFET measured in vacuum, after heating in vacuum at 420 K for 1 hr., were compared with those measured on the same sample after keeping it for three days under laboratory conditions (air and daylight). It was found that the influence of the air and daylight on the OFET increases both the conductivity and the threshold voltage. These effects, according to Rella's model, could be connected with the formation and decay of CuPc- $O_2$  charge transfer complexes (CTCs). The increased conductivity could result from the increased concentration of free holes after the decay of the CTCs, whereas the higher value of the threshold voltage was connected with  $O_2^-$  complexes. The sample properties were recovered after heating above 400 K in dark and vacuum.

In this work, metal-free phthalocyanine ( $H_2Pc$ ) films in a gap sample configuration are measured. Conventional measurements of the temperature dependencies of the electrical conductivity are combined with novel investigations using thermomodulated space-charge limited current spectroscopy (TM-SCLC).

## 2. Experimental

A commercially supplied  $\alpha$  form of  $H_2Pc$  powder (Tokyo Kasei Chemical Industry Co., Ltd.) was purified in a temperature gradient and vacuum of  $1 \times 10^{-3}$  Pa.

Samples in a coplanar electrode configuration (Fig. 1) with an inter-electrode gap ( $L$ ) of 0.7 and 0.013 mm were prepared for current vs. temperature and SCLC measurements, respectively. Before the electrode deposition, Corning 7059 glass substrates were cleaned in deionized water, ethanol and chloroform. Gold coplanar electrodes (2) of thicknesses about 50 nm were evaporated in vacuum, through a mask. The electrode area was about  $2.5 \times 5$  mm.

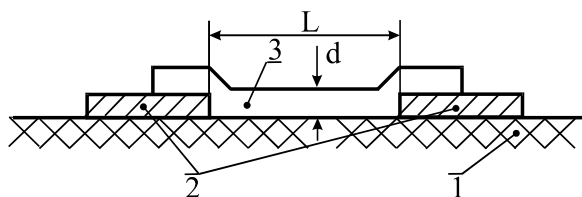


Fig. 1. Coplanar electrode sample: 1 - substrate, 2 - electrodes, 3 - active  $H_2Pc$  film,  $L$  - inter-electrode distance,  $d$  - film thickness.

$H_2Pc$  thin films (3) were deposited on the electrodes in a vacuum better than  $1 \times 10^{-3}$  Pa. During the deposition, the substrates were kept at room temperature, 20 cm away

from the evaporation source. The evaporation rate (typically 10 to 15  $nm\ min^{-1}$ ) and the film thickness ( $d = 50$  to 1200 nm) were controlled by a quartz oscillator thickness monitor.

The electrical measurements were carried out in a cryostat, using a Keithley 617 electrometer. A defined gas atmosphere was prepared by injecting gas with a syringe into the cryostat. The gas concentration was calculated by comparing the cryostat and syringe volumes.

Having  $L \gg d$  and neglecting the influence of the surface states on the distribution of the electric field for low concentrations of the  $O_2$  dopant, it could be assumed that the electric field inside the film is parallel to the substrate plane. This will allow us to use the SCLC models developed for sandwich type samples.

## 3. Results and discussion

### 3.1 Temperature dependence measurements

The temperature dependencies of  $H_2Pc$  films in the Ohmic conductivity region (electrode gap of 0.7 mm, film thickness of 200 nm and applied voltage of 50 V), measured in dark, initially in the presence of Ar, and then  $O_2$ , and then again Ar shown in Fig. 2.

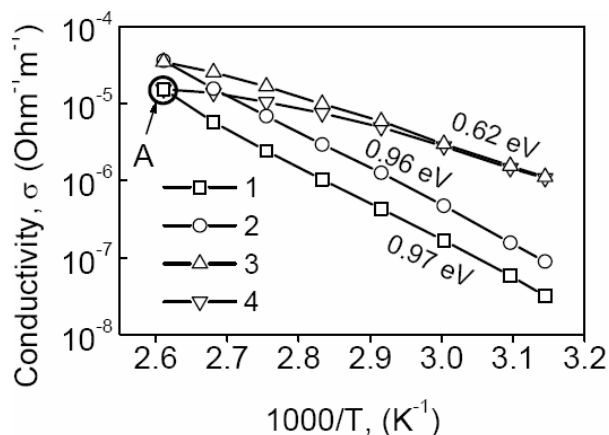


Fig. 2. Temperature dependencies measured in the dark, with cycled Ar and  $O_2$  atmospheres: 1 - in Ar decreasing  $T$ , 2 - in  $O_2$  increasing  $T$ , 3 - in  $O_2$  decreasing  $T$ , in Ar increasing  $T$ .

Curve 1 was measured in an Ar atmosphere by decreasing the temperature. The calculated value of the activation energy ( $E_a = 0.97$  eV) is close to half the band gap, related to the intrinsic conductivity of the material.

Curve 2 was measured after replacing the Ar by  $O_2$  and increasing the temperature. The electrical conductivity increases immediately after replacing the atmosphere, but the slope of the line remains almost the same ( $E_a = 0.96$  eV). This effect could be connected with an increase in the free charge carrier concentration.

Curve 3 was measured in an  $O_2$  atmosphere, with a decreasing temperature. The high temperature part of the curve is slight nonlinear, i. e. more than one process acts simultaneously. This nonlinearity could be connected with the creation and subsequent decay of  $H_2Pc-O_2$  CTCs,

according to Rella's model. The low temperature part of Curve 3 is linear using these scales. This could be related to a straightforward process of thermal generation of free charge carriers with  $E_a=0.62$  eV, as result of the CTCs decay. On the basis of this assumption, the energy of the formation of CTCs can be determined as a difference between the activation energies derived from Curves 2 and 3 –  $E_a$  CTCs = 0.96 - 0.62 = 0.34 eV. The value of  $E_a=0.36$  eV was reported misleadingly in the literature [8] as an oxygen induced trap level.

Curve 4 was measured after again replacing  $O_2$  with Ar. It is clearly seen that heating must be applied to remove the adsorbed oxygen from the film. A desorption process starts at about 350 K, which agrees with the literature data. The coincidence of point A from Curves 1 and 4 shows the reversibility of the process.

### 3.2 Thermomodulated SCLC spectroscopy

TM-SCLC (i. e. simultaneous measurement of the current-voltage ( $I-U$ ) and  $E_a-U$ ) characteristics, measured [9] in a  $N_2+O_2$  mixture on a 130 nm thick  $H_2Pc$  film, deposited at  $15 \text{ nm s}^{-1}$  are plotted in Fig. 3. Fig. 3a presents the  $I-U$  characteristics on a log-log scale. It can be separated into three sections, with slopes of approximately 1, 4 and 2.

At low voltages the Ohmic current increases with increasing oxygen concentration.

The Ohmic current measured at 1 V applied voltage ( $I_{1V}$ ) is plotted as a function of the  $O_2$  concentration in Fig. 4. The linear dependence suggests that one hole per adsorbed  $O_2$  molecule is created, according to Rella's model.

The  $E_a-U$  characteristics are presented in Fig. 3b. Generally the curves can be separated into two parts:

- the low voltage part of curves (almost parallel to the abscissa) is connected with the Ohmic conductivity. The reduced value of  $E_a$  with increasing  $O_2$  concentration indicates an increase in the free charge carrier concentration, according to Rella's model;

- in the high voltage part,  $E_a$  regularly decreases with the voltage, clearly indicating SCLC conditions. This effect is connected with the shift of the quasi-Fermi level, and allows us to scan the DOS.

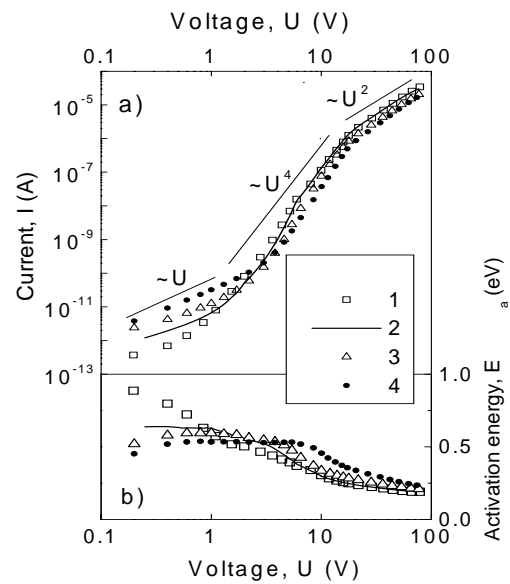


Fig. 3. (a) -  $I-U$  and (b) -  $E_a-U$  characteristics as a function of the  $O_2$  concentration; 1 -  $N_2$  only, 2 - 60, 3 - 180, 4 - 300 ppm (four points omitted between every two points plotted).

The first point of Curve 1, ( $E_a = 0.9$  eV) measured in a  $N_2$  atmosphere, agree with the value of  $E_a=0.91$  eV obtained from the temperature dependencies of the conductivity. It is very close to half the band gap of  $H_2Pc$ .

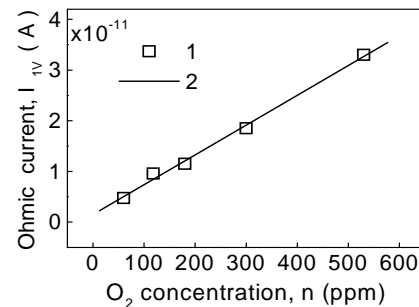


Fig. 4. Ohmic current at 1V applied voltage: 1 - measured data, 2 - linear fit.

The DOS function  $h(E)$  was reconstructed from the SCLC part of the  $I-U$  and  $E_a-U$  characteristics measured following a procedure explained elsewhere [9]. The curve smoothing and the derivative calculations were implemented by a cubic spline fitting procedure, producing from the experimentally measured data (Fig. 3.) 1000 points for DOS reconstruction.

The DOS spectrum ( $h(E)$  vs.  $E_d$ ) calculated from measurement in a  $N_2$  atmosphere (Fig. 3, Curve 1) is presented in the inset of Fig. 5.  $E_d$  stands for the dominant energy i. e. the energy position where the injected space charge is accepted [10]. The five peaks distinguished could be approximated with Gaussian functions, which

corresponds well to the molecular character of the organic substance [3].

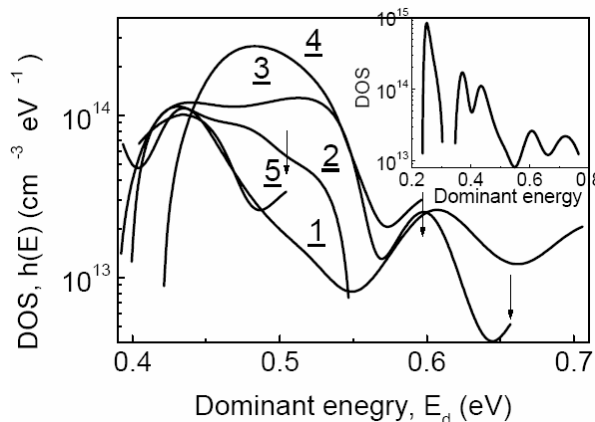


Fig. 5. Change of the spectra in the region 0.45-0.55 eV with oxygen concentration: 1 -  $N_2$ , 2-60, 3-180, 4-300, 5-530 ppm; inset – the full spectrum, reconstructed from measurement in a  $N_2$  atmosphere.

In the region 0.45-0.55 eV (Fig. 5.), a regular increase in the trap concentration as a result of the  $O_2$  influence takes place. The vertical arrows show the starting position of the scan, corresponding to the equilibrium position of the Fermi level (low voltage parts presented in Fig 3b). This change of the spectrum is expectable – it was indeed reported in the literature that traps at about 0.51 eV depth are characteristic of the  $O_2$ - like Coulombic type for holes [6].

Oxygen does not affect the other peaks. The peak energy positions are summarized from all measurements as follows - 0.72,  $0.59 \pm 0.010$ ,  $0.43 \pm 0.015$ ,  $0.37 \pm 0.007$  and  $0.25 \pm 0.0012$  eV.

It is seen that the peak at 0.37 eV does not depend on changes in the oxygen concentration. Therefore, the obtained activation energy from the temperature dependence measurements ( $E_a=0.36$  eV), connected with the adsorption, cannot be interpreted as an  $O_2$  induced trap level. It could be connected with the creation of CTCs, resulting in the shift of the transport band.

#### 4. Conclusions

The intrinsic conductivity ( $E_a=0.96$  eV) of the  $H_2Pc$  films investigated can be observed in an Ar atmosphere and after heating of the sample at 360-400 K.

The influence of  $O_2$  on the dark conductivity of  $H_2Pc$  films at 360 K is a thermally activated process.

The  $H_2Pc-O_2$  interaction is a two-stage process characterized by two activation energies:

i. energy of creation of CTCs  $E_a=0.36$  eV

ii. energy of CTC decay and generation of free charge carriers -  $E_a=0.60$  eV, connected with the Ohmic current.

The dependence of the Ohmic current on the  $O_2$  concentration (for small  $O_2$  concentrations) is linear, according to Rella's model.

An increased concentration of traps, connected with the oxygen influence for a Gaussian distributed trap level with a maximum  $E_t=0.52$  eV depth, was found.

#### Acknowledgements

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