

# The implication of Meyer-Neldel behaviour for oxidising gas detection in phthalocyanine thin-films

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The dark conductivity of phthalocyanine thin-films are often sensitive to the presence of oxidising gases such that changes in conductivity magnitude are accompanied by shifts in the associated thermal activation energy for conduction. It is noted that the conductivity pre-factor and activation energy are invariably related by the Meyer-Neldel rule so that the conductivity becomes independent of the oxidising gas concentration at a finite temperature  $T_0$ . Data illustrating such a relationship are presented for evaporated metal-free phthalocyanine films containing various amounts of absorbed oxygen where  $T_0$  is estimated to be about 1161 K. Independent work has proposed that  $T_0$  may be related to the energetic width of localised band tail states that are exponentially distributed and it is therefore argued that the  $T_0$  magnitude for a particular phthalocyanine will dictate its potential application as a gas-sensing medium. Phthalocyanines that exhibit a low  $T_0$  may thus offer low threshold detection possibilities at the expense of response speed, whereas high  $T_0$  materials should be considered for situations demanding the rapid detection of high concentrations of oxidising gases. © 2002 Kluwer Academic Publishers

## 1. Introduction

Phthalocyanines (Pcs) deposited in a thin-film form have been extensively studied as an alternative photoconductor to commercially important inorganic materials such as hydrogenated amorphous silicon, and have potential large-area electronic applications including solar cells and electrostatic imaging devices [1, 2]. The intrinsic semiconducting properties of Pcs are often difficult to characterise, however, due to the sensitivity of deposited films to oxidising gases which generally act as a p-type dopant [2, 3]. Many Pcs are particularly sensitive to oxygen present in the ambient environment and it is therefore essential to conduct electrical measurements under controlled, high-vacuum conditions, in order to elucidate true fundamental parameters such as the majority carrier type, the dark Fermi energy location and the photogeneration efficiency [4]. The problems encountered in the experimental measurement of intrinsic semiconductivity have suggested that Pcs may nevertheless prove appropriate as the active sensing medium for a variety of oxidising gases including carbon monoxide (CO) and oxides of nitrogen (NO and NO<sub>2</sub>). Considerable effort has accordingly been devoted to the development of thin-film Pc gas detectors that exploit the sensitivity of the Pc conductivity to oxidising environments [3]. The majority of the proposed sensors operate at elevated temperatures between 100°C and 300°C in order to improve the speed of response, and the Pcs employed range from metallo-

phthalocyanines (MPcs) to more complex substituted phthalocyanines. Gas detection in these systems normally involves monitoring the resistance of a patterned gap-cell metal electrode structure deposited on the Pc thin-film surface. Such sensors are often found to display a linear electrical response with the oxidising gas concentration that has been shown to reflect an increase in the majority (hole) carrier concentration as the Fermi energy is displaced towards the (valence) band edge [5]. Enhanced conductivities should thus be accompanied by a progressive reduction of the activation energy for conduction as the concentration of oxidising gas is increased. Comparatively little work has been devoted to examining the changes that accompany the conductivity activation energy with gas exposure, however, with most reports only showing the performance of the Pc film at the fixed operating temperature of the sensor. An exception is the comprehensive study conducted by Sadaoka and co-workers [6] who measured the conductivity of a variety of Pc thin-films between 100°C and 300°C both before and after exposure to NO<sub>2</sub> diluted in air. These authors noted a correlation between the conductivity ( $\sigma$ ) at 150°C and the corresponding activation energy ( $\Delta E$ ) and attempted to interpret their results in terms of a simple Arrhenius expression involving a fixed conductivity prefactor term  $\sigma_0$  according to;

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (1)$$

where  $k_B$  is Boltzmann's constant and  $T$  is the temperature. For many of the Pcs studied by Sadaoka *et al.*, the slopes of the correlation graphs drawn between  $\sigma(T = 150^\circ\text{C})$  and  $\Delta E$  are significantly smaller (and in no instance ever greater) than the value of  $27.4 \text{ eV}^{-1}$  predicted by Equation 1. This observation suggests that the dark conductivity for these materials would be better described by an expression of the form;

$$\sigma = \sigma_0 \exp\left[\frac{\Delta E}{k_B} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \quad (2)$$

Here,  $T_0$  represents a reduced temperature where the measured conductivity of the Pc material becomes independent of  $\Delta E$  and is consequently insensitive to the oxidising gas concentration.

The activated form of Equation 2 is often applicable for the description of physical quantities displaying Arrhenius behaviour and is known as the Meyer-Neldel (MN) rule [7]. Several theories have been proposed to explain the underlying physical origin of observed MN phenomena, and for macroscopic transport in amorphous semiconducting materials it has been shown that the existence of exponentially distributed band-tail states will result in a correlation between  $\sigma_0$  and  $\Delta E$  as embodied in Equation 2 [8]. If the distribution  $g(E)$  of localised band-tail states varies with energy  $E$  according to  $g(E) = g_0 \exp(-E/E_0)$ , the MN reduced temperature parameter  $T_0$  is then expected to correspond to the characteristic band-tail energy  $E_0$  according to  $k_B T_0 = E_0$  [8]. For Pc materials deposited in a thin-film form by vacuum sublimation, the existence of exponential band-tails has traditionally been deduced from space-charge-limited current studies. A more recent experimental technique that involves the measurement of transient photoconductivity [9] has also concluded that the band-tail states for Pcs dispersed in polymeric binders decay exponentially with energy below the delocalised band edge. MN behaviour should therefore be commonly observed in dark conductivity studies of Pc materials as the Fermi energy is shifted upon exposure to oxidising gases.

## 2. Experimental results

To illustrate the MN response typically observed for Pcs upon exposure to oxidising gases, dark conductivity measurements were performed for metal-free phthalocyanine ( $\text{H}_2\text{Pc}$ ) films exposed to varying amounts of oxygen. The  $\text{H}_2\text{Pc}$  material was obtained from a commercial supplier and used in the as-received form without further purification. The films were deposited by vacuum sublimation onto unheated glass substrates from a heated quartz crucible under a pressure below  $3 \times 10^{-6}$  mbar. Film thicknesses were measured using a surface profilometer and were approximately  $0.82 \mu\text{m}$ . Gold gap-cell electrodes, having a width of 0.2 cm and a separation of 0.1 cm, were finally deposited onto the surface of the  $\text{H}_2\text{Pc}$  films by thermal evaporation. The electroded films were placed on a heated stage in a sealed vacuum chamber and connected to a stabilised voltage supply and electrometer

unit to allow current-voltage profiling of the gap-cell to be performed. The air pressure inside the vacuum chamber was controllable between atmospheric pressure and  $10^{-2}$  mbar using a zeolite powered sorption pump, and specimen temperatures were monitored with a type K thermocouple. For all conditions of air pressure and film temperature encountered during the course of the measurements, the gap-cell electrodes gave an ohmic response across the entire range of applied voltage (1 V–30 V). The dark conductivity of the  $\text{H}_2\text{Pc}$  film was accordingly calculated from the measured film resistance and gap-cell geometry. It was generally observed that the room-temperature ( $T = 294 \text{ K}$ ) conductivity could be reversibly varied over 6 orders of magnitude by controlling the amount of absorbed oxygen in the film. Oxygen absorption was conveniently achieved by annealing the films under atmospheric pressure at temperatures above  $150^\circ\text{C}$  for 1 hour before cooling the specimen to room temperature. Progressive desorption of oxygen could subsequently be controlled by annealing the films under vacuum ( $\sim 10^{-2}$  mbar) for selected times and temperatures. The room temperature conductivity was noted to decrease as oxygen was desorbed from the films, and the associated activation energy for conduction was observed to increase. Similar behaviour has been reported to occur during the interaction between oxygen and thin-film CuPc samples [10].

A summary of the data obtained is given in Fig. 1 where the dark conductivity is plotted logarithmically against reciprocal temperature. For each of the data sets presented in Fig. 1, the  $\text{H}_2\text{Pc}$  film contains a particular amount of absorbed oxygen which is expected to

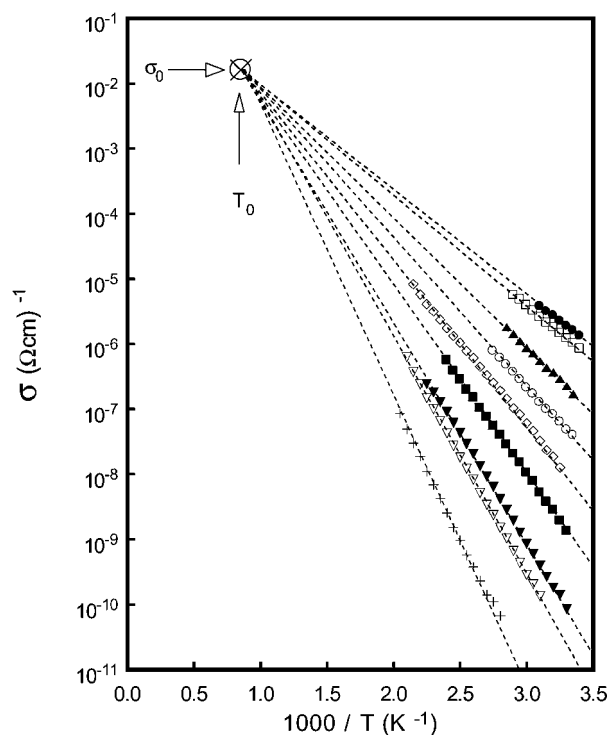


Figure 1 The dark conductivity of an evaporated  $\text{H}_2\text{Pc}$  thin-film as a function of reciprocal temperature. The various data sets as represented by different symbols correspond to different amounts of oxygen absorbed in the films. The solid lines through the data points are the lines of best fit given by Equation 2 where  $\sigma_0 = 0.016 (\Omega \text{ cm})^{-1}$ ,  $T_0 = 1161 \text{ K}$  and  $\Delta E$  is an adjustable parameter. Film thickness is  $0.82 \mu\text{m}$ .

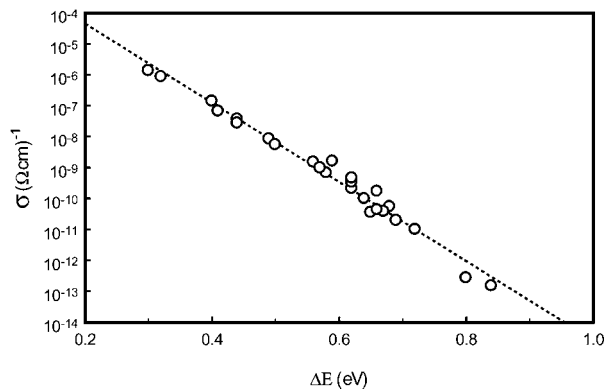


Figure 2 The MN correlation observed between the dark conductivity at 294 K and the corresponding energy of activation for evaporated H<sub>2</sub>Pc thin-films. The dashed line through the data is represents the best fit to Equation 2 and yields  $\sigma_0 = 0.016 (\Omega \text{ cm})^{-1}$  and  $T_0 = 1161 \text{ K}$ .

act as a p-type dopant. The measured activation energies therefore indicate that, by controlling the amount of absorbed oxygen using the present experimental approach, it is possible to shift the Fermi energy between approximately 0.3 eV and 0.8 eV below the transport band edge. To verify whether the complete set of data points plotted in Fig. 1 may in fact be described by Equation 2, a MN correlation plot of the room temperature conductivity against the corresponding activation energy  $\Delta E$  was produced as shown in Fig. 2. From Equation 2, the gradient and extrapolated  $\sigma$  magnitude at  $\Delta E = 0$  for the best fit line shown in Fig. 2 were used to obtain fitting parameters  $\sigma_0 = 0.016 (\Omega \text{ cm})^{-1}$  and  $T_0 = 1161 \text{ K}$ . Using these values as fixed constraints, individual  $\sigma$  data sets shown in Fig. 1 were finally analysed according to Equation 2 where  $\Delta E$  was the only adjustable parameter. As evidenced by the solid lines drawn in Fig. 1, the fits obtained are excellent across the entire range of  $\Delta E$  magnitudes encountered. It may therefore be concluded that the dark conductivity of our H<sub>2</sub>Pc films exposed to oxygen is controlled by the MN rule and that the characteristic energy of the band-tail states for the majority (hole) carriers is  $E_0 = 100 \text{ meV}$ .

### 3. Discussion and conclusions

It is instructive to survey the MN  $T_0$  magnitudes that may be derived from other published data. From the results presented by Sadaoka and co-workers [6] (originally analysed by these authors using Equation 1) it is possible to calculate  $T_0$  magnitudes for their Pc films both before and after exposure to NO<sub>2</sub> in air. The results are summarised in Table I where it is noted that the H<sub>2</sub>Pc  $T_0$  magnitude is somewhat larger than the value obtained in the present work. For the MPcs not containing aluminium, it is intriguing that exposure to NO<sub>2</sub> in air results in a pronounced reduction in  $T_0$ , implying that for these materials,  $E_0$  falls with NO<sub>2</sub> absorption and the band-tail states become sharper. Such a shift in  $E_0$  magnitude may be attributable to a change in the density and distribution of ionised centres involving mono-electronic transfer from MPc to O<sub>2</sub>. The resulting distribution of MPc<sup>+</sup> and O<sub>2</sub><sup>-</sup> ions is expected to result in long-range electrostatic potential fluctuations

TABLE I Reduced temperatures  $T_0$  deduced from published conductivity data [6] for thin-film phthalocyanines

| Material          | $T_0$ (K)<br>(before NO <sub>2</sub> exposure) | $T_0$ (K)<br>(after NO <sub>2</sub> exposure) |
|-------------------|--|---|
| H <sub>2</sub> Pc | 1733   | 1733  |
| PbPc              | 1330000  | 503   |
| ZnPc              | 25000  | 751   |
| CuPc              | 1300000  | 592   |
| AlPcCl            | 1227   | 1227  |
| AlPcF             | 17000  | 17000   |
| AlPcO             | 1048   | 1048  |

throughout the MPc films, and these fluctuations have been argued to be the origin of the exponential band-tails in amorphous semiconducting solids [9, 11].

Pc materials that exhibit comparatively low  $T_0$  magnitudes are likely to be less favourable for gas sensing applications, however, as they will produce a smaller dynamic range of response at typical elevated operating temperatures. To illustrate this, it is sufficient to consider the conductivity increase ( $\Delta\sigma$ ) that would occur as a result of the conductivity activation energy being reduced by an amount  $\delta E$  due to oxidising gas exposure at an operating temperature  $T$ . From Equation 2 it may be shown that  $\Delta\sigma = \exp[-\delta E/k_B(1/T_0 - 1/T)]$  and in order to simultaneously maintain an acceptable speed of response (by working at minimum temperature of say  $T_{\min}$ ), and continue to deliver a sensitive output (corresponding to  $\Delta\sigma_{\min}$ ), it is therefore essential that  $T_0$  exceeds a critical value  $T_{00}$  where;

$$T_{00} = \left[ \frac{1}{T_{\min}} - \frac{k_B}{\delta E} \ln(\Delta\sigma_{\min}) \right]^{-1} \quad (3)$$

The dependence of  $T_{00}$  upon  $\Delta\sigma_{\min}$  is shown in Fig. 3 for selected operating temperatures  $T_{\min}$  of 100°C, 200°C and 300°C. The curves were produced for a fixed  $\delta E$  of 0.5 eV which would appear to represent the maximum obtainable Fermi energy shift from the Pc conductivity data presented in this and other work [2, 3, 6]. The Fig. 3 data indicates that  $T_{00}$  must exceed a minimum value of about 500 K and that in order to produce an acceptable  $\Delta\sigma_{\min}$  response,  $T_{00}$  magnitudes approaching 1000 K are required.

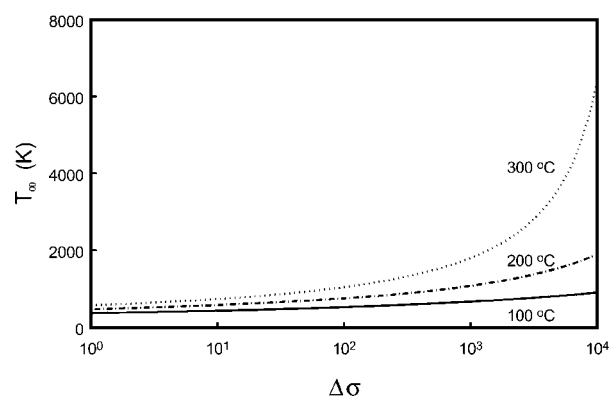


Figure 3 Calculated dependence of the minimum MN reduced temperature  $T_{00}$  upon required minimum conductivity ratio  $\Delta\sigma$  for Pc gas sensors operating at fixed temperatures of 100°C, 200°C and 300°C. The change in activation energy associated with  $\Delta\sigma$  was taken to be 0.5 eV in all cases.

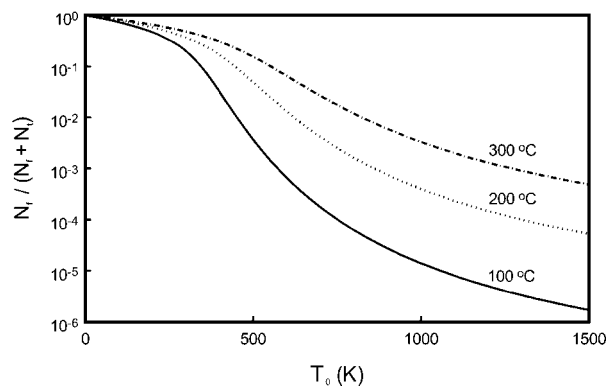


Figure 4 Calculated ratio of free ( $N_f$ ) to total ( $N_f + N_t$ ) charge as a function of  $T_0$  for operating temperatures of 100°C, 200°C and 300°C. The Fermi energy was chosen in the calculations to lie at  $\Delta E = 0.5$  eV from the transport edge.

It should be noted, however, that although Equation 3 implies that a greater dynamic range of response may be achieved by using materials with a higher  $T_0$ , the associated increase in the density of band-tail states will diminish the density of excess charge carriers created by oxidative absorption which are actually free to conduct at the transport band edge. The amounts of free ( $N_f$ ) and trapped ( $N_t$ ) band tail charge may be calculated using simple Fermi occupation statistics so that the fraction of the total extrinsic carrier population generated by oxidative absorption that contributes to the measured conductivity may be estimated from the ratio  $N_f/(N_f + N_t)$ . The effect of the band tail width on the ratio  $N_f/(N_f + N_t)$  is depicted at several operating temperatures in Fig. 4 for a Fermi energy position corresponding to  $\Delta E = 0.5$  eV. As  $T_0$  is increased, the proportion of generated carriers that are free to conduct is suppressed due to trapping. To displace the Fermi energy towards the band edge by a desired amount, it is consequently necessary to enhance the amount of oxidising gas absorbed. A low detection threshold would therefore appear to demand that the density of band tail states and hence  $T_0$  is minimised. The existence of MN behaviour would thus appear to preclude

the detection of oxidising species at low concentrations whilst offering an acceptable dynamic range of response at the elevated temperatures where conductivity changes will be rapid. The band tail energy  $E_0$  associated with a particular Pc is accordingly likely to dictate how the material should be considered for oxidising gas detection with low  $T_0$  materials offering a sensitive, low threshold possibility at the expense of response speed, whereas high  $T_0$  materials should be better employed in environments where high concentrations of oxidising gas need to be quickly identified.

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