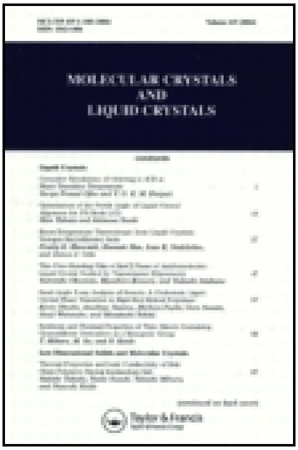

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Role of Oxygen in the Space Charge Layer Formation in Organic-Metal Junctions: Trans-Polyacetylene and Metallo-Phtha-Locyanine

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ROLE OF OXYGEN IN THE SPACE CHARGE LAYER FORMATION IN ORGANIC-METAL JUNCTIONS: TRANS-POLYACETYLENE AND METALLO-PHTHALOCYANINE

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Abstract Junctions based on trans-polyacetylene and different metallo-phthalocyanines have been studied. The dark conductivity as a function of the frequency and of the applied voltage of sandwich cells of the type $M_1/t\text{-}(CH)_x/M_2$ or $M_1/MPc/M_2$ demonstrate that these different organic materials present very similar properties. If all these compounds show an apparent Schottky behavior, the standard model cannot be applied. The properties of the space charge region below the surface charge layer are dramatically different from those found in monocrystalline inorganic semiconductors (constant thickness, constant capacity and variable equivalent resistance on applied voltage). The O_2 adsorption is clearly shown to be responsible of the formation of the depletion layer. Indeed O_2 not only acts as a dopant of $t\text{-}(CH)_x$ and MPc but is also responsible for the formation of the space charge region near blocking electrodes with trapped charge carriers. The I-V relationship seems to indicate Frenkel Poole mechanism of charge detrapping.

INTRODUCTION

As well known oxygen drastically influences the electrical properties of most of the organic semiconductors. The effect of O_2 are visible on the dc electrical conductivity, on the photoelectrical properties, on the magnetic characteristics and also on the dark rectification ratio and the photovoltaïc behavior of junctions based on organic materials.

This study is an experimental approach of the understanding of the mechanisms involved in such junctions i.e. the role of O_2 in the formation of a space charge region in the vicinity of the interface organic material/metal, the nature of the action of O_2, the specificity of this action for different molecular material.

To answer these questions, experiments have been made on two very different materials:

- narrow band semiconductors: the metallo-phthalocyanine (MPc)[1-6]. This choice is linked to its purity, the possibility to obtain evaporated thin films and to perform devices in ultrahigh vacuum without breaking the vacuum at any stage. The undoped MPc have an intrinsic dc conductivity of 10^{-15} $\Omega^{-1}cm^{-1}$. Two central metals have been used: Ni with which no coordination with O_2 can take place and Zn which may have an axially coordinate extraligands such as O_2 or H_2O;
- a broad band semiconductor: the trans-polyacetylene[6-8]. For polyacetylene short exposures to air are unavoidable during the making of the devices and unfortunately this material is known to be strongly sensitive to O_2 or water. The undoped trans-$(CH)_x$ samples used had a dc conductivity of nearly 10^{-10} $\Omega^{-1}cm^{-1}$ (probably a value still much higher than the intrinsic conductivity).

For both materials sandwich devices of the type M_1/organic SC/M_2 have been made in different conditions. For both cases *ohmic contacts* may be formed with metals having a high work function such as Au and *rectifying contacts* with metals having lower work functions such as Al or In. The devices are then the following succession: a metal M_1 having an ohmic contact, the organic semiconductor films and a second metal M_2 forming or not a rectifying contact. The characterization of these devices have been made by studying the the rectification ratios, the photovoltaic effects, and the dielectric response in large frequency range (10^{-4} - 10^5 Hz).

I-V CURVES

The space charge region is formed by ionization of impurities present in the semiconductor near one of the interfaces. The existence of a space charge region is detected in the I-V plots by giving rise to a rectification effect. Such plots have been already reported for metallo-phthalocyanine derivatives[2]. In a complete absence of air exposure of the organic layer, the sandwich device Au/PcZn/Al shows a curve almost perfectly symmetrical. After an air exposure for 10 minutes, the rectification ratio is 82 (at ± 0.5 V). For polyacetylene, although it is not possible to work in such an absence of oxygen, the same effect is observed (Fig. 1). For samples only accidently doped before deposition of the last electrode, a very small rectification ratio is observed. After an air exposure for a longer time, this rectification ratio is increased. This effect is at least partly reversible.

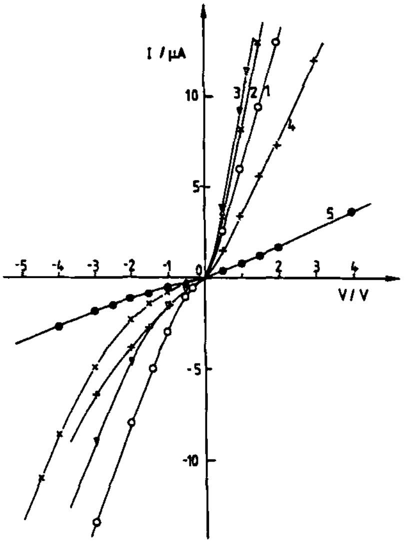

FIGURE 1 I-V curves for Au/t-$(CH)_x$/In cells at room temperature (1): one day under vacuum after contacts evaporation; (2): 30 min. in air and measurements under ambient pressure; (3): one hour under reduced pressure; (4): one day under reduced pressure; (5): five days under reduced pressure. (For details see reference 7).

At that point, a first conclusion may be drawn: *the space charge region and the corresponding rectifying effect are correlated with the presence of O_2. O_2 is indispensable to observe a high rectification ratio.*

This point found a confirmation in the fact that the open-circuit voltage is correlated with the work function of the metal M_2 when the depletion layer is formed (i.e. after air exposure) whereas no correlation is found for the junctions prepared under vacuum[2].

The eventual role of an oxide layer formation at the interface has been checked by realization of devices of the type Al/Al_2O_3/PcM/Au.[2] Since a rectification ratio around unity is found, it is possible to assert that *the space charge region develops within the organic semiconductor, interfacial oxide layers do not play a dominant role in its formation process.* That point may found a confirmation on results of dielectric response of Au/t-$(CH)_x$/Al junctions for which a well separeted contribution of the interfacial oxide layer and the space charge region is observed.[7]

DIELECTRIC SPECTRA

a deeper insight into the chemical mechanisms involved in the space charge region formation may be obtained by studying the whole dielectric properties of the devices over a wide frequency range. That has been made for metallo-phthalocyanines[4] and trans-polyacetylene.[7]

Au/PcNi/Au for which no rectification is observed has a strictly ohmic behavior and no space charge region develops within the metalloorganic semiconductor: nearly constant G_p in the low frequency range, monotonous decrease of the loss factor with frequency, no effect of the superimposition of a constant dc voltage.[4]

Au/PcZn/In,[4] Au/PcZn/Al (Fig. 2), Au/t-$(CH)_x$/In (Fig. 3) and Au/t-$(CH)_x$/Al [7] devices show a very different electrical behavior. G_p varies strongly with frequency and with bias. At high frequencies G_p shows a plateau correlated with the bulk material (the most conductive part of the organic layer) and another at low frequencies which may be attributed to the space charge layer. The tg δ shows a broad maximum near 10^2–10^3 Hz (with tg δ in the range 1 - 15 depending on the system). The superimposition of a forward dc voltage reveals the presence of a second maximum in tg δ at the lowest fre-

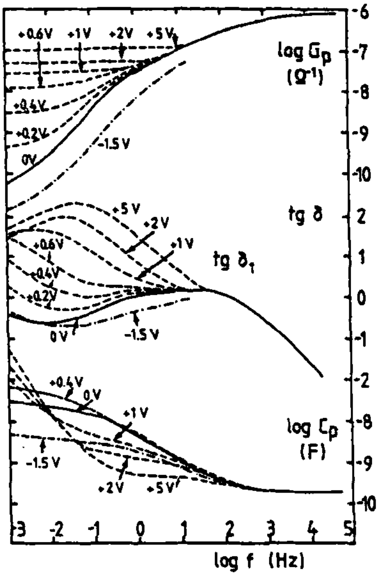

FIGURE 2 Dielectric spectrum of Au/PcZn/Al at room temperature under reduced pressure (10^{-3} Torr) as a function of forward and backward dc voltages. Solid line: no bias; dashed lines: forward bias; dot-dashed lines: backward bias. For reasons of clarity, the experimental points have been omitted.

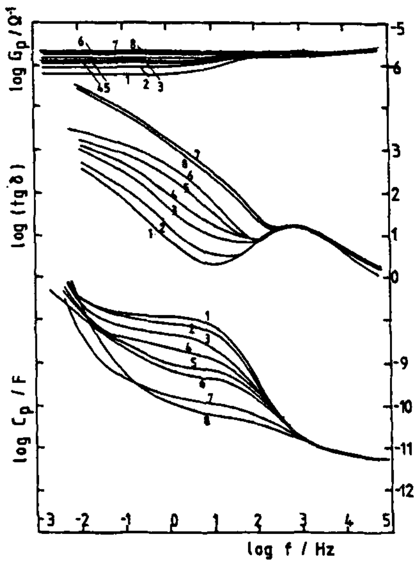

FIGURE 3 Dielectric spectrum of Au/t-$(CH)_x$/In at room temperature under reduced pressure (10^{-3} Torr) as a function of forward dc voltages. (1): no bias; (2): +0.1 V; (3): +0.2 V; (4): +0.3 V; (5): +0.4 V; (6): +0.6 V; (7): +1.0 V; (8): +1.5 V.

quencies without any modification of the first one. This first maximum is also nearly insensitive to the nature of the counter electrode and, for MPc, to the nature of the central metal. The second maximum well visible for MPc devices is only suggested by the slope modification of the loss factor in the low frequency range for t-$(CH)_x$.

EQUIVALENT CIRCUIT

A satisfactory approach of the dielectric behavior may be obtained by considering a simple equivalent circuit[4] which allows to ratio-

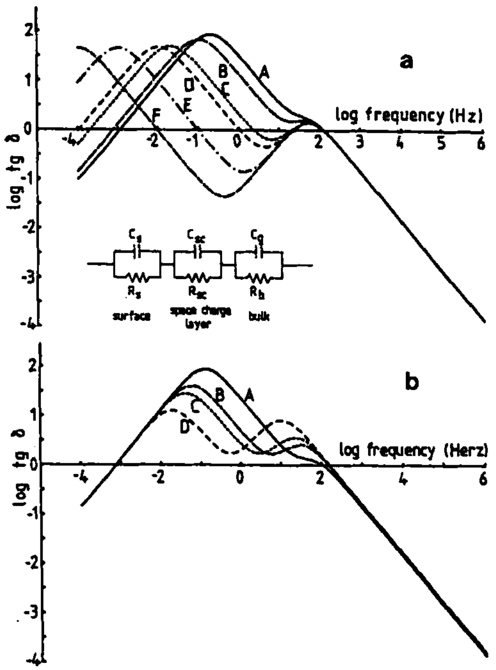

FIGURE 4 Variation with frequency of tg δ for the equivalent circuit shown in the insert. The following values of the parameters are taken: $R_s=10^{10}$ Ω, $C_s=1.4\ 10^{-5}$F, $R_b=10^6$ Ω, $C_g=2\ 10^{-9}$F. The different curves have been drawn for:
a) $C_{sc}=1.7\ 10^{-9}$F and different values of R_{sc}: $5\ 10^6$Ω (A); 10^7Ω (B); $5\ 10^7$Ω (C); 10^8Ω (D); 10^9Ω (E); 10^{10}Ω(F);
b) $R_{sc}=10^7$Ω and different values of C_{sc}: 10^{-9}F (A); $5\ 10^{-9}$F (B); 10^{-8}F (C); $5\ 10^{-8}$F (D).
(Taken from reference 4)

nalize all the ac electrical properties of the devices involving either metallo-phthalocyanine or trans-polyacetylene. The organic (or metalloorganic) layer is divided in three regions (see insert in Fig. 4): (1) At the very surface of the semiconductor, a surface charge layer characterized by the parameters R_s and C_s is postulated (2) The space charge region (C_{sc}, R_{sc}) extends within the semiconductor below the previous surface layer. (3) Finally, the bulk semiconductor - whose properties may be independently determined - constitutes the rest of the layer (C_g, R_b).

Such an equivalent circuit, as far as the conditions $C_s > C_{sc} > C_g$ are fulfilled, shows two maxima in the loss factor variation as observed experimentally with the following relationships:

$$\left.\begin{aligned}\omega_{max,1} &= R_b^{-1}\,(C_g\,C_{sc})^{-1/2}\\ \mathrm{tg}\ \delta_{max,1} &= 1/2\,(C_{sc}\,/\,C_g)^{1/2}\end{aligned}\right\}\ \begin{aligned}&\text{for the maximum at}\\ &\text{at high frequencies}\end{aligned}$$

$$\left.\begin{aligned}\omega_{\max,2} &= R_{sc}^{-1}\,(C_{sc}\,C_s)^{-1/2}\\ \mathrm{tg}\,\delta_{\max,2} &= 1/2\,(C_s\,/\,C_{sc})^{1/2}\end{aligned}\right\}\quad \text{for the maximum at at low frequencies}^{9}$$

Therefore the position and the intensity of both maxima allow a rapid determination of the characteristics of the depletion layer (see Table I). The variations of the loss factor spectra with the different parameters have been calculated. A variation similar to that observed experimentally for different bias may easily be simulated by varying the space charge resistance R_{sc} (Fig. 4a). The modification of any other parameters gives very different variations of tg δ (as shown for the most important parameter C_{sc} in Fig. 4b).

These results have three consequences:

(1) The apparent variation of the overall capacity with voltage is in fact due to a variation of the *resistance* of the space charge region and not of its *capacity*. The usual interpretation of the $1/C^2$ versus V plots are then highly questionable.

(2) A plot of $\log(V/R_{sc})$ vs V yields a straight line indicating that a Poole-Frenkel type mechanism of detrapping of the charge carriers is probably effective.

(3) The spatial extension of the different space charge layers may be roughly estimated (for a discussion see reference 7). An evaluation of the space charge region depth l_{sc} is given in Table I.

TABLE I Adjusted parameters for space charge layer and bulk.

	R_{sc} (10^9 Ω)	C_{sc} (10^{-9}F)	R_b (10^6Ω)	C_g (10^{-10}F)	l_{sc} (Å)
Au/PcZn/In	1.25	2	5	2	∿2000
Au/PcZn/Al	10	2	5	2	∿2000
Au/PcZn/Au	—	—	1	2	—
Au/PcNi/In	10	—	500	1	—
Au/PcNi/Au	—	—	—	1	—
Au/t-$(CH)_x$/In	—	8	1	0.05	∿500
Au/t-$(CH)_x$/Al	—	2	0.8 → 8	0.05	∿500

MECHANISMS

As obtained from the I-V plots in different conditions and in the light of the dielectric behavior, two contributions must be invoked.[4,7] O_2 acts as a dopant in the bulk of the semiconductor:

$$\mathrm{PcM}\ ,\ O_2 \rightleftharpoons \mathrm{PcM}^{\dot{+}}\ ,\ O_2^{\dot{-}} \rightleftharpoons h^{+} + \mathrm{PcM}\ ,\ O_2^{\dot{-}}$$

$$(\mathrm{CH})_x\ ,\ O_2 \rightleftharpoons (\mathrm{CH})_x^{\dot{+}}\ ,\ O_2^{\dot{-}} \rightleftharpoons S^{+} + (\mathrm{CH})_x^{\cdot}\ ,\ O_2^{\dot{-}}$$

Near the blocking electrode, there is the formation of a space charge layer following:

$$\mathrm{PcM}\ ,\ \overset{\curvearrowleft}{O_2\ /\ \mathrm{metal}} \rightleftharpoons \mathrm{PcM}\ ,\ O_2^{\dot{-}}\ /\ \mathrm{metal}$$

$$(\mathrm{CH})_x\ ,\ \overset{\curvearrowleft}{O_2\ /\ \mathrm{metal}} \rightleftharpoons (\mathrm{CH})_x\ ,\ O_2^{\dot{-}}\ /\ \mathrm{metal}$$

The depletion layer depth is mainly determined by the electrostatic interactions i.e. it depends only a little on the nature of the organic material. The case of polyacetylene is complicated by the other chemical reactions which may take place between the polymer and oxygen and by the inhomogeneity of films.

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9. Note an error in the expression (14) of the reference 4.