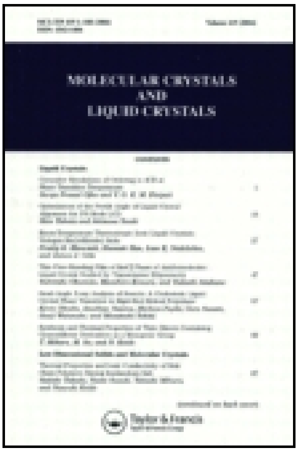

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Photoconduction in Vacuum-Evaporated Films of Phenothiazine

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PHOTOCONDUCTION IN VACUUM-EVAPORATED FILMS OF PHENOTHIAZINE

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Abstract Steady-state photoconduction characteristics have been measured for the system vacuum-evaporated film of phenothiazine contained between aluminum semitransparent electrodes. Three spectral regions of the action spectrum are distinguished: (i) (200-300) nm with near-surface charge generation and its subsequent injection into the bulk; (ii) (300-370) nm dominated by the surface injected current; and (iii) > 370 nm characterized by a superposition of the surface and bulk generated carriers. A weak feature between 400 and 420 nm corresponds to the low energy charge-transfer excitons suggested previously to yield a large photoconduction peak at ≅ 410 nm in phenothiazine single crystal.

INTRODUCTION

Photoconductivity in crystalline organic materials may have several origins. Single photon excitation in model aromatic single crystals in the near UV leads predominantly to the formation of neutral molecular excitons. These excitons can interact with electrodes or chemical and structural defects to give rise to carriers (usually holes).[1] A photo-enhanced conductivity is observed if their interactions with trapped charge carriers predominates.[1-3] Of great interest is the mechanism of single photon generation of intrinsic carriers (bulk generation) in organics. Degeneracy of molecular and charge-transfer (CT) states with quasi-continuous or continuous free carrier bands leads to a strong variation in the charge generation quantum yield and, consequently, to different photoresponse of organic materials. Of particular interest is photo-genertion via CT states located within or even below the first molecular absorption transition in single component organic materials. It can appear under special relations between ionization potential and electron affinity of their molecules,[4] and has been recently suggested to take place in phenothiazine single crystal.[5] However the thickness of the crystal samples, grown by the Bridgman technique, restricted the measurements, performed on

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sandwich-type arrangement, to the lower-absorption region of the active light and to surface-type electroabsorption experiments. In order to avoid this restrictions we have performed photoconduction experiments on thin (< 20 μm) phenothiazine films prepared by a vacuum-evaporation technique. This allowed us to obtain broad range (200-500 nm) action spectra and to observe high-field (> 3x10^5 V/cm) photoresponse behaviour of polycrystalline phenothiazine.

EXPERIMENTAL

The present study reports photoconductivity measurements on polycrystalline layers of phenothiazine prepared by evaporation under vacuum (≅ 10^{-4} Pa) at a rate of 0.3 nm/s. They were contacted with semitransparent (≅ 80% transmission in visible) Al electrodes in a sandwich-type arrangement and mounted in a vacuum (≅ 0.1 Pa) chamber or nitrogen (≅ 10^5 Pa) atmosphere. A high-power (1000 W) Xenon lamp combined with a high-intensity Hilger & Watts (grating) monochromator served as a light source. The absorption spectrum was measured with a Perkin-Elmer (Lambda 5) UV/VIS spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows the steady-state photocurrent action spectra measured under vacuum

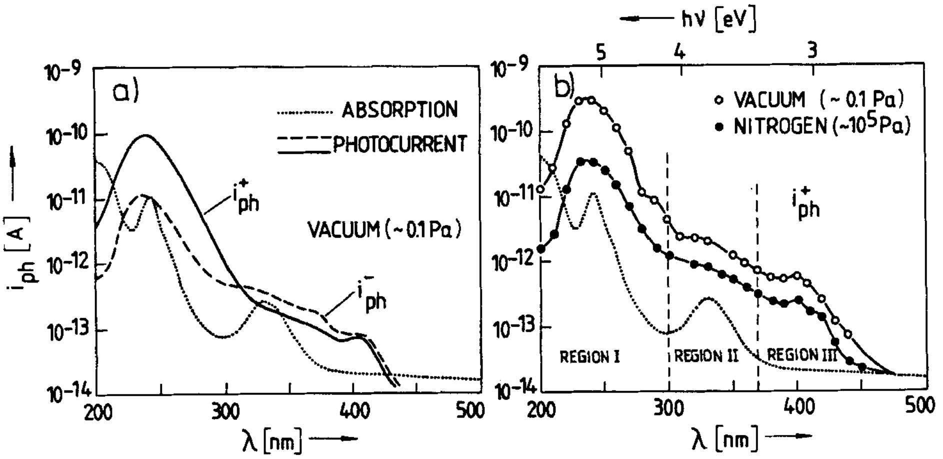

FIGURE 1 Action spectra of the photocurrents measured in a polycrystalline sandwich cell for different electric fields: (a) F = 4.3x10^4 V/cm; (b) F = 1.7x10^5 V/cm. Influence of the ambient is shown in part (b). Film thickness is d = 11.5 μm.

and neutral gas conditions. By convention, the photocurrents are denoted i^+_{ph} or i^-_{ph}, depending upon whether the illuminated side was at positive or negative potential, respectively. The maxima of the photocurrents are shifted with respect to the maxima of the absorption spectrum. Besides i^-_{ph} exhibits stronger antibatic behaviour than i^+_{ph}. However, both i^+_{ph} and i^-_{ph} exhibit a weak long-wavelength feature between 400 and 420 nm.

Three spectral regions can be distinguished: (200-300) nm range (quantal energy $4.1 < h\nu < 6.2$ eV) with the penetration depth of the exciting light $l_a < 1\mu m << d$ and $i^+_{ph} >> i^-_{ph}$ (Region I); the (300-370) nm range ($3.4 < h\nu < 4.1$ eV) with $l_a \cong 1\mu m << d$ and $i^+_{ph} < i^-_{ph}$ (Region II); the $\lambda > 370$ nm range ($h\nu < 3.4$ eV) with $l_a > 1\mu m$ (up to $\cong 10\ \mu m$ at 410 nm) (Region III) where $i^+_{ph} \cong i^-_{ph}$ (see Figure 1). Characteristic is no absorption features in Region III. These observations are compatible with superposition of bulk-generated carriers and those produced at the surface. i_{ph} is thus controlled by both electron-hole recombination and injection conditions in the generation region. Due to different contributions of these mechanisms in the above spectral regions, one would expect different current-voltage (i-V) dependences: from linear for predominant bulk generation to S-shaped for surface (+trap)-limited currents.[6] It is evident from Figure 2 that Regions I and II are dominated by the surface injection (straight line plots of $\log(i^+_{ph})$ versus $(aU^{1/2}\text{-}bU^{-1/2})$) but Region III by bulk generation ($i^+_{ph} \sim U^n$ with $n \cong 1$) of the carriers. Since the experimental values of parameter

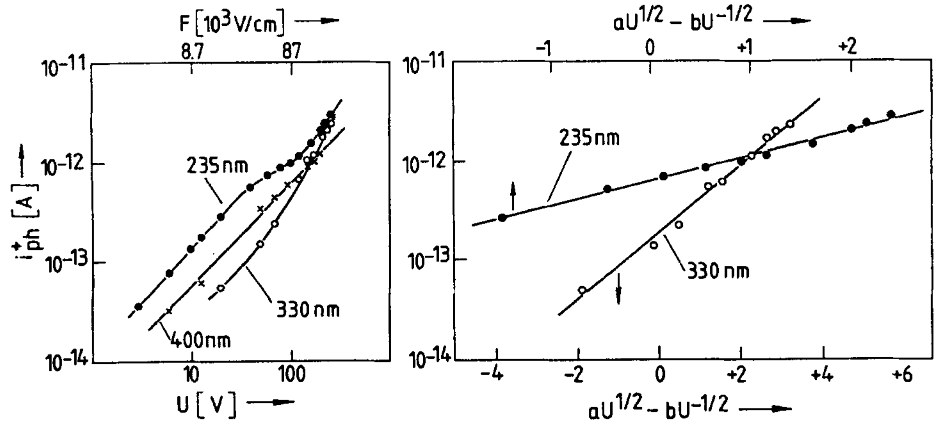

FIGURE 2 Photocurrent-voltage dependence plotted in two different scales: (a) $\log(i^+_{ph})$-logU and (b) $\log(i^+_{ph})$-$(aU^{1/2}\text{-}bU^{-1/2})$ with a and b standing for the model parameters in the surface-trap-limited injection currents (STLIC)[6]. $a = 0.26\ V^{-1/2}$, $b = 13.7\ V^{1/2}$ for $\lambda = 330$ nm; $a = 0.2\ V^{-1/2}$, $b = 12.9\ V^{1/2}$ for $\lambda = 235$ nm. Sample: the same as in Fig.1.

$a < a_{Schottky} = (e/kT)(e/4\pi\varepsilon_0\varepsilon d)^{1/2} = 0.26\ V^{-1/2}$ (ε=4) and $a < a_{Poole\text{-}Frenkel} = 2a_{Schottky}$, production of charge carriers via autoionization of excited states must be affected by local, most probably, macrotrap potentials which modify the electric field separating the carriers. Consequently, the charge separation mechanism cannot be resolved in Region I and II. In Region III, however, carriers diffusion in their mutual Coulombic field may be the main separation mechanism, since the low-field approximation of the Onsager model of dissociation predicts a linear dependence of the separation yield (see e.g. ref. 7).

The injection ability of the illuminated surface increases under residual ambient atmosphere (vacuum $\cong$ 0.1 Pa) as compared with nitrogen-ambient results (see Figure 1). $i^+_{ph}/i^-_{ph} \gg 1$ in the strong absorption Region I in vacuo (Figure 1(a)), and $i^+_{ph}(\text{Vacuo})/i^+_{ph}(\text{Nitrogen}) > 1$ in the whole spectral range used in the experiment (Figure 1(b)). It is probable that oxidation products of phenothiazine form surface generation centres, which also are active in the dark (see Figure 3). The larger values and straight-line plot $\log(i_{dark})$-$(aU^{1/2}\text{-}bU^{-1/2})$ for the dark current in the vacuum support the surface origin of the currents; linear dependence of i_{dark} above 10 V in the nitrogen atmosphere suggests its bulk origin. Strong support for this interpretation comes from the light intensity dependence of the photocurrent in different regions of the action spectrum (Figure 4).

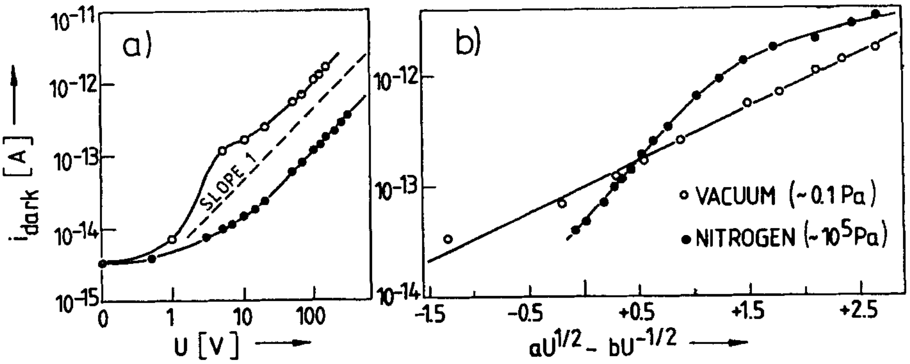

FIGURE 3 Voltage behaviour of the dark current. Sample: the same as in Figs.1 and 2. The STLIC parameters $a = 0.22\ V^{-1/2}$ and $b = 13.0\ V^{1/2}$ in vacuum, and $a = 0.15\ V^{-1/2}$ and $b = 12.6\ V^{1/2}$ in nitrogen.

The intensity dependence of the photocurrent fits a $i_{ph} \sim I_0^m$ relationship with $0.5 < m < 1$. From Figure 4 it is seen that m increases in low-vacuum ($\cong$ 0.1 Pa) conditions in all of the three regions distinguished. This would confirm an increasing

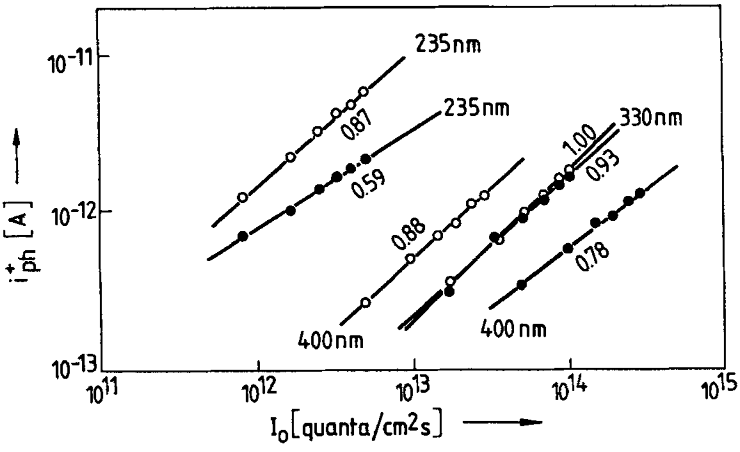

FIGURE 4 Light intensity dependence of the photocurrent at different wavelengths and ambient conditions:open circles-vacuum (≅0.1Pa), full circles-nitrogen (≅10^5Pa); the slopes of the straight line log-log plots are given along the lines.

role of the surface-injected charge contribution to the current. The bulk generation mechanism becomes more pronounced in the nitrogen ambient (especially in Region I, where photoionization is an efficient process of charge generation; ionization potential of phenothiazine is 5.15 eV[8]). However, m = 0.78 at λ = 400 nm, suggests a remarkable contribution of the bulk-generated carriers. This could be a generation of carrier pairs involving impurity molecules or host CT excitons as suggested previously to explain a large photocurrent peak at λ = 410 nm in single phenothiazine crystal.[5] However, the photoenhancement mechanism cannot be excluded as the origin of the photocurrent features in this spectral region (Region III). Some further studies as a function of sample thickness are necessary to infer about this issue. Fairly good linearity $i_{ph}(I_0)$ at λ = 330 nm strongly supports the explanation based on molecular exciton injection of the carriers (holes or electrons) from the near-electrode region into the bulk.

CONCLUDING REMARKS

We have analyzed measurements of steady-state photocurrent produced in the system Al/Phenothiazine/Al sandwich cells in terms of extrinsic (surface) and intrinsic (bulk) charge carrier generation. Over the quantal energy range (2.5-6.2) eV, voltage and light intensity dependences of the photocurrent are seen to change shape from almost purely intrinsic (4.1-6.2) eV, through combined intrinsic-extrinsic (2.5-3.4) eV to mainly extrinsic (3.4-4.1) eV, explaining the complex behaviour of the action spectrum. Both holes and electrons contribute to the photoconductivity. The surface-injected currents are due to intrinsic ionization within the near-electrode layer (≅ 1 μm for Regions I and II, and < 10 μm for Region III) and subsequent charge injection into the bulk. Though the mechanism of carrier production cannot be established conclusively from the present data, it is presumably due to autoionization of different molecular and CT states, dependent on the spectral region.

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