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Generation of Charge Carrier Pairs in Tetracene Layers

Malgorzata Obarowska, Ryszard Signerski, Jan Godlewski*

Department of Physics of Electronic Phenomena, Gdansk University of Technology,
Narutowicza 11/12, 80-952 Gdansk, Poland,
E-mail: mabo@mif.pg.gda/pl

Summary: The mechanism of negative and positive charge carrier generation by light absorption in tetracene layers has been studied. We conclude that there are different processes determining electron and hole production. Positive charge carriers are produced without recombination while the negative charge carrier generation depends strongly on the recombination process. The experimental data for charge carrier generation in tetracene layers are treated theoretically taking into account photogeneration, recombination of charge carriers, trapping and transport processes inside the sample.

Keywords: charge transport; photogeneration; recombination of the charge carriers; tetracene; thin films

Introduction

The charge carriers photogeneration process in polyacene crystals has been studied extensively in many papers, e.g.[1] Particular attention was focused on electron and hole photocurrent production and analysis of the role of trapping in that process was omitted. The study of tetracene has been focused on the analysis of the preliminary charge carrier generation e.g.[2], photoinjection mechanism e.g.[3], the charge-pair separation mechanism, e.g.[4], and description of charge carrier transport phenomena, e.g.[5]

The purpose of this paper is to analyse the electron and hole photogeneration process by studying the photocurrent in tetracene layers (in a sandwich-type arrangement with aluminum electrodes) obtained by ultraviolet light excitation. Particularly, we present experimental results concerning the photocurrent dependence on the wavelength, applied voltage and light intensity. The present study contains theoretical interpretation of the experimental data.

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Experimental

All measurements were carried out on vacuum-evaporated tetracene layers in a sandwich-type arrangement with Al electrodes. First, tetracene powder was purified by sublimation in a high vacuum. A sample was fabricated by sequential vacuum evaporation of the Al electrode (bottom) - tetracene layer and aluminum as the top electrode onto glass plate. The thickness of the tetracene layer was 1 ± 0.1 μm and the substrate temperature was 300 K. All measurements were performed using an experimental set-up consisting of a monochromator, a xenon lamp producing light from the ultraviolet to visible region and the measurement chamber, where the sample was placed. A picoammeter with internal voltage source was used to measure the current. The entrance slit of the monochromator was adjusted to give the same quantum light intensity at different wavelengths. The thin-layer sample was illuminated through the top Al electrode. Depending on whether the illuminated side had a negative or positive potential, the photocurrents were denoted j^- and j^+, respectively.

Results and discussion

The experimental analysis were based on the measurements of photocurrent as a function of the wavelength, light intensity and applied voltage. The absorption spectrum (A) and the spectral dependences of positive (B) and negative (C) photocurrents are shown in Figure 1. It can be seen that the wavelength dependence of j^+ follows the absorption coefficient (symbatic relationship), in contrast to j^- (antibatic relationship). According to the experimental results presented in Figure 2 (A), the relationship between photocurrent density and the light intensity may be expressed by the formula $j \propto I_0^n$. However, the values of the power of n estimated for j^+ are close to unity whilst are significantly smaller for j^- (Fig. 2 (B)). In Figure 3, the hole and electron photocurrent density as a function of the applied voltage are presented for the values of light wavelength 280, 300, 330 nm and light intensity $I_0 \approx 10^{13}$ photon/cm^{2}s. It is evident that j^- increases more rapidly with the applied voltage than for the hole current j^+.

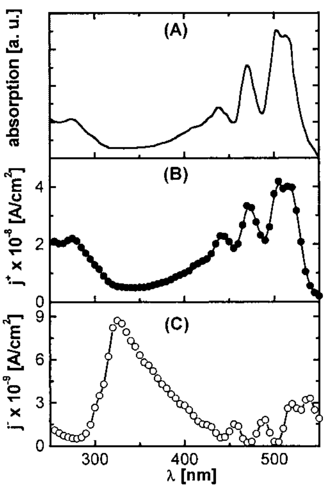

Figure 1 (A) The absorption spectrum of a polycrystalline tetracene film [2]; (B) Spectral dependence of j^+ photocurrent in tetracene layer (positive electrode illuminated); (C) Spectral dependence of j^- photocurrent in tetracene layer (negative electrode illuminated). $I_0 \approx 10^{13}$ photon/cm^{2}s.

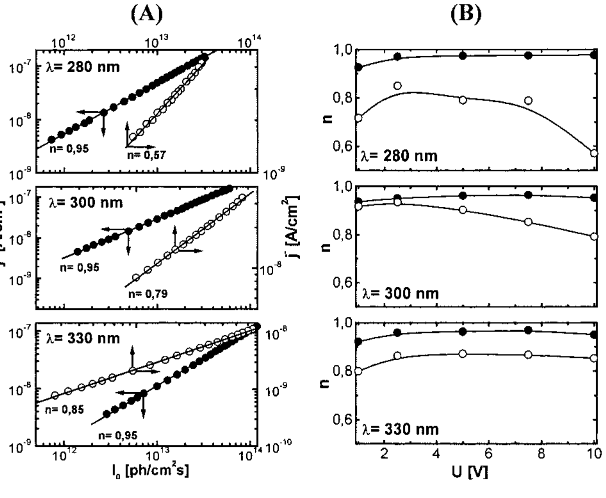

Figure 2. (A) The positive (solid circles) and negative (open circles) photocurrent densities as a function of light intensity (I_0) for tetracene layers at an applied voltage of U = 10 V. (B) The values of the power n as a function of applied voltage.

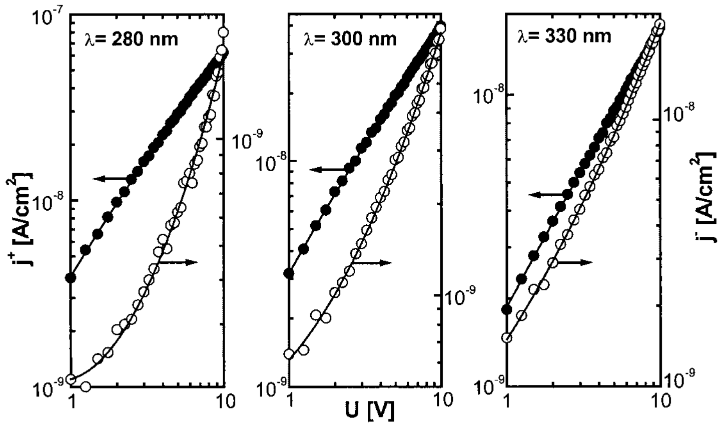

Figure 3. The positive (j^+) (solid circles) and negative (j^-) (open circles) photocurrent densities as a function of applied voltage for a tetracene layer at room temperature and light intensity $I_0 \approx 10^{13}$ photon/cm^{2}s.

On the basis of the above results, it is concluded that the symbatic wavelength dependence of j^+ (Figure 1A) is the result of photogeneration without charge carrier recombination. However, the antibatic wavelength dependence of j^- (Fig. 1 (C)) can be explained as the result of a strong charge carrier recombination at the surface of the electrode. It is interpreted that the negative photocurrent is a result of exciton injection from the bottom electrode (not illuminated) in the long wavelength region ($\lambda > 400$ nm). However, in the short wavelength region ($\lambda < 400$ nm), this process can be hidden as, under the same values of the absorption coefficient, the values of j^- obtained at $\lambda = 330$ nm significantly differ from those obtained for $\lambda = 540$ nm. The negative photocurrent density is generally much smaller than the positive except at 330 nm where the values of density for both currents are similar. This supports the conclusion that the charge carrier generation occurs in the bulk. A theoretical explanation of the obtained results is presented in the next section.

Theoretical model

To describe the voltage and light intensity evolution of the photocurrent, we consider the continuity and the Poisson equations for steady-state condition [6]:

$$\frac{\partial p(x,t)}{\partial t}=G(F,I,x)-\alpha\, n_t(x)p(x)-\frac{1}{e}\frac{\mathrm{d}j^{+}(x)}{\mathrm{d}x}=0 \tag{1}$$

$$\frac{\partial n(x,t)}{\partial t}=G(F,I,x)-\alpha\, p_t(x)n(x)+\frac{1}{e}\frac{\mathrm{d}j^{-}(x)}{\mathrm{d}x}=0 \tag{2}$$

$$j^{+}(x)=p(x)e\mu_{\mathrm{p}}F(x) \tag{3}$$

$$j^{-}(x)=n(x)e\mu_{\mathrm{n}}F(x) \tag{4}$$

$$j=j^{+}+j^{-} \tag{5}$$

$$\frac{\mathrm{d}F(x)}{\mathrm{d}x}=\frac{e}{\varepsilon\varepsilon_0}\left[p_t(x)-n_t(x)\right] \tag{6}$$

$$G(F,x,I)=\Omega(F)I_0\,\kappa\exp(-\kappa x) \tag{7}$$

Here *n(x)* and *p(x)* are concentrations of free electrons and holes, respectively, as a function of distance from the electrode *x*; $n_t(x)$, $p_t(x)$ are concentrations of trapped electrons and holes; *G(F, x, I)* is the generation term of charge carriers, which can be a function of the electric field (*F*) and light intensity (*I*); κ is the absorption coefficient; Ω(*F*) is the charge carrier dissociation efficiency; *e* is elementary charge, α is bimolecular recombination rate of charge carriers; $j^{-}(x)$ and $j^{+}(x)$ are electron and hole photocurrent densities, respectively; μ_n and μ_p are electron and hole mobilities; ε_0 and ε are the electric permittivities of vacuum and tetracene crystal. In the above equations we assume that the role of the charge carrier diffusion motion is negligible compared with the drift motion.

The exact solution of the set of equations (1-7) is impossible. To find photocurrent dependences on the light intensity and applied voltage, further analysis is made with the following assumptions:

(i) The recombination between trapped electrons and free holes is not very likely in spite of the recombination between trapped holes and free electrons. In accord with our previous discussion, we assume the recombination process between trapped holes and free electrons as a predominant process in tetracene layers. Hence, we can neglect the second term on the right-hand side of Eq. (1). However, the analogous term in Eq. (2) should be taken into account.

(ii) The trap distribution is exponential, which means that the relation between the concentration of trapped and free holes can be represented by the following formula [7]:

$$p_t(x) = \frac{p(x)}{N_{\mathrm{eff}}} \frac{\pi H}{\ell \sin(\pi/\ell)} \left[\frac{A \kappa I_0}{\nu} \exp(-\kappa x) \right]^{(1/\ell)-1} . \qquad (8)$$

In the above equation, N_{eff} is the effective density of states, H is the concentration of traps, A is the quantity transforming the light flux into free carriers, ν is the thermal collision factor, and ℓ is the characteristic trap parameter. The equation can be utilized under the assumption that the optical detrapping is the predominant process.

(iii) There are no space charge carriers. According to the assumption, the relationship between the electric field and applied voltage can be presented as $F = U/d$, where d is the thickness of the tetracene layer.

Based on Eqs. (1) and (7), the following expression can be obtained for j^+:

$$j^+ = e\Omega(F) I_0 [1 - \exp(-\kappa d)]. \qquad (9)$$

It is noteworthy that the relation between the positive photocurrent and the applied voltage is rather complicated and but can be determined in terms of $\Omega(F)$, which can be described in the framework of the Onsager model.

An analogous relationship for the negative photocurrent may be obtained from the set of equations (1-8) taking into account the above assumptions:

$$j^- = \frac{C}{B d^2} U^2 I_0^{\left(1-\frac{1}{\ell}\right)} \left\{ 1 - \exp\left[\frac{B}{\kappa d^2} \frac{I_0^{\left(\frac{1}{\ell}\right)}}{U^2} \left(\exp(-\kappa d) - 1\right) \right] \right\} , \qquad (10)$$

where

$$C = e\Omega(F)\kappa , \qquad B = \frac{\alpha \pi H \Omega(F)}{\mu_p \mu_n N_{\mathrm{eff}} \ell \sin(\pi/\ell)} \left(\frac{A\kappa}{\nu} \right)^{\left(\frac{1}{\ell}-1\right)} . \qquad (11)$$

From the above equations it follows that the spectral dependence of j^+ is symbatic for $\kappa d < 1$, but the spectral dependence of j^- is antibatic. The relationship between the positive photocurrent density and the applied voltage is determined by the Onsager model. The negative photocurrent density changes more rapidly with voltage than j^+. Both j^+ and j^- photocurrents are functions of the light intensity in the form $j \propto I_0^n$. However, from Eqs. (9) and (10) it follows that the value of the power n for j^+ is equal 1 and for j^-, $n = 1 - (1/\ell)$.

Conclusions

The mechanism of the negative and positive current generation in tetracene layers by light absorption in the ultraviolet region has been studied. From the experimental results it follows that the relation between the current generated by light excitation with a wavelength close to 280 nm and the light intensity is of the type $j \propto I_0^n$ (Fig. 2). For high electric fields the values of coefficient n obtained for the positive current are close to 1 and for the negative current are much smaller and close to 1/2. This remains in a good agreement with predictions of theoretical model (Eqs. 9 and 10) under assumptions that the negative (electron) current is determined by the near-surface recombination and the positive (hole) current avoids that process. The existence of the efficient recombination process between trapped holes and free electrons can be also confirmed by the current dependence on the applied voltage. According to experimental results (Fig. 3), the values of the positive current density are greater than those obtained for the negative current. On the basis of the main experimental results, we can conclude that the positive charge carriers are created directly after light illumination; however, the number of electrons (created inside the sample) depends on the photogeneration yield and the recombination between free electrons and trapped holes.

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