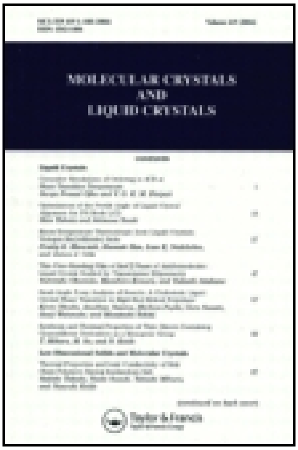

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The Surface Photoconductivity in Molecular Layers

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The Surface Photoconductivity in Molecular Layers

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The surface photoconductivity in vacuum evaporated tetracene and pentacene layers are reported. Particularly, the mechanism of free charge carrier production has been studied. It is concluded that the side of illumination and the structure of thin film can affect its photoconductivity properties.

Keywords: pentacene; surface photoconductivity; tetracene

INTRODUCTION

Utilizing molecular materials to perform electronics functions is at the present and in the nearest future a real challenge for scientific and engineering word [1]. The interest in these systems follows from their favourable physical and technological properties and very cheap manufacture.

Among electronics devices based on molecular materials much progress has been made on electrical properties of thin film transistors based on simple polyacene molecules [2]. Despite their promising futures, there are still many problems, which prevent their common usefulness in electronics. One of them is the existence of imperfections that affect negatively the device performance. Recently, it has been found that the performance of field-effect transistor based on thin organic film is affected by structural imperfections present near the substrate region, which constituted the device active region [3]. Furthermore, phenomena such as charge carrier generation and charge carrier transport require further investigations.

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The purpose of the present study is the analysis of surface photoconductivity in thin polycrystalline layers. Particularly the influence of the side of illumination and the thin film structure on photocurrent characteristics have been investigated.

EXPERIMENTAL

Tetracene and pentacene, (Aldrich, 98% pure), purified by repeated vacuum sublimation have been used for deposition. Thin films have been grown in high vacuum with deposition pressure of 10^{-3} Pa and deposition rate of about 2 Å/s at room temperature. The evaporation parameters were controlled by EDWARDS Auto 306 turbomolecular vacuum evaporation system.

The samples (Fig. 1) were fabricated by sequential vacuum evaporation of planar gold electrodes (20 nm thickness) and tetracene or pentacene layer ($d = 0.75$–$1.5\,\mu m$ thickness) onto glass plate ($150\,\mu m$ thickness).

A standard apparatus for photoconductivity measurements [e.g. 4] has been used to obtain experimental data. The experimental analysis was based on the measurements of photocurrent as a function of the wavelength, applied voltage and light intensity. Two different configurations of the sample illumination have been applied – from

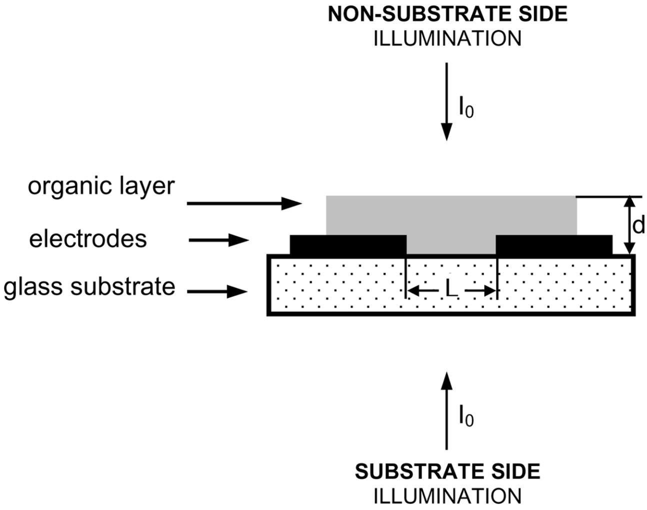

FIGURE 1 Schematic diagram of the sample with coplanar electrodes configuration. Different direction of the sample illumination from non-substrate and substrate sides are represented.

substrate side (S) and non-substrate side (NS). Depending on whether the illuminated side was substrate or non-substrate, the photocurrents were denoted I_S and I_{NS}, respectively.

EXPERIMENTAL RESULTS

Tetracene Layers

The spectral dependences of I_{NS} (A) and I_S (B) and the absorption spectrum of tetracene layer (C) are shown in Figure 2. It can be seen that in the whole wavelength region, the spectrum of $I_{NS}(\lambda)$ and $I_S(\lambda)$ is inversely proportional to the absorption coefficient (antibatic relationship). It is worth to point out that $I_{NS} > I_S$.

In Figure 3, the photocurrent as a function of the applied voltage measured at the excitation wavelengths 510 and 535 nm and light

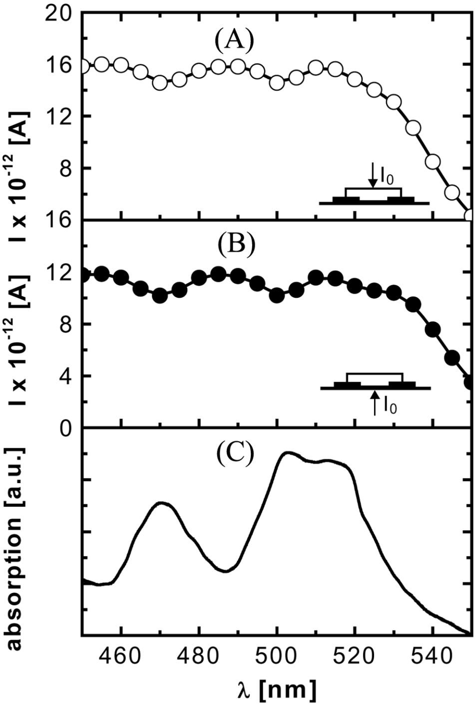

FIGURE 2 (A) Spectral dependence of I_{NS} (open circles) in tetracene layer (the sample is illuminated from non-substrate side); (B) Spectral dependence of I_S (solid circles) in tetracene layer (the sample is illuminated from substrate side); (C) The absorption spectrum of tetracene layer [20].

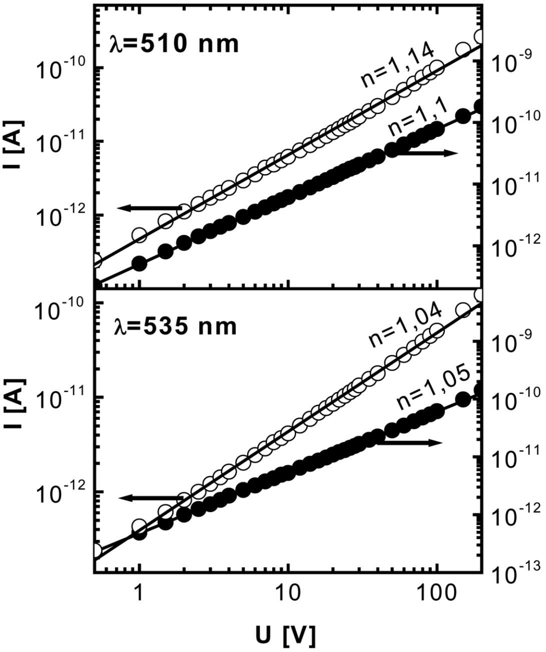

FIGURE 3 The photocurrent – applied voltage dependence measured under the sample illumination from non-substrate side (open circles) and substrate side (solid circles) for tetracene layers obtained at the excitation wavelengths of $\lambda = 510\,\text{nm}$ and $\lambda = 535\,\text{nm}$ and light intensity $I_0 = 10^{15}\,\text{ph/cm}^2\text{s}$.

intensity of 10^{15} photons/cm^{2}s are represented. The relationship between the photocurrent and the applied voltage can be approximated by the formula $I \propto U^n$, whilst the values of the power n estimated for I_S and I_{NS} are significantly bigger than 1. Furthermore the values of I_{NS} are close to those measured for I_S. The photocurrent vs. the light intensity characteristics obtained at the excitation wavelengths 510 and 535 nm have been measured and the relationship between the photocurrent and the light intensity may be expressed by a formula $I \propto I_0^n$ with $n < 1$.

From the antibatic wavelength dependence of I_{NS} and I_S it is concluded that the quenching of triplet excitons [5] is the main process responsible for the charge carrier production in tetracene layers. Nearly the same values of photocurrent measured under the sample illumination from NS and S side also support that statement. There are two processes, which could take part in the free charge carriers production, namely the interaction of excitons with trapped charge carriers [6] and the exciton – surface interaction [7]. Although, we assume that the interaction of triplet excitons with trapped charge carriers is a dominant mechanism of charge carrier production in tetracene layers. Moreover, the photoconductivity measurements suggest that taken to the examinations samples were single phased thin films with uniform trap distribution.

Pentacene Layers

In Figure 4, the spectral dependences of the photocurrent obtained under the sample illumination from non-substrate (A) and substrate sides (B) and the absorption spectrum of pentacene (C) are shown. It can be seen that spectrum of the photocurrent obtained for the sample illuminated from non-substrate side ($I_{NS}(\lambda)$) is inversely proportional

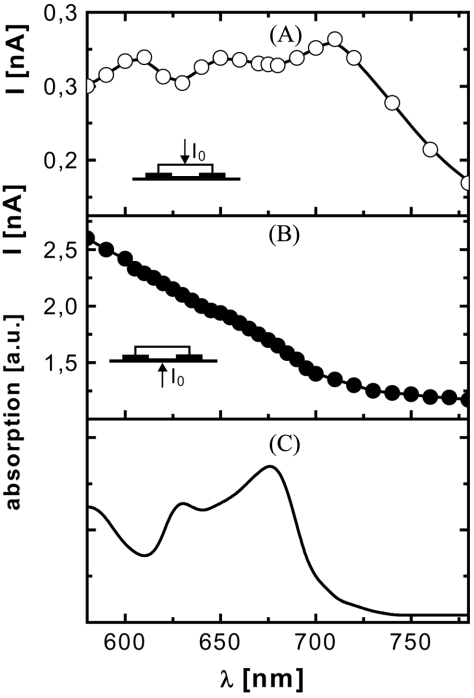

FIGURE 4 (A) Spectral dependence of I_{NS} (open circles) in pentacene layer (the sample is illuminated from non-substrate side); (B) Spectral dependence of I_S (solid circles) in pentacene layer (the sample is illuminated from substrate side); (C) The absorption spectrum of pentacene layer [21].

to the absorption coefficient (antibatic relationship). On the other hand, the wavelength dependence of photocurrent under the sample illumination from substrate side ($I_S(\lambda)$) does not correspond to the absorption spectrum and at short wavelengths the photocurrent increases rapidly with decreasing wavelength (Fig. 4. (B)). Furthermore, in the whole investigated region, $I_S \rangle I_{NS}$. In Figure 5, the photocurrent as a function of the applied voltage is presented for the values of light wavelength 580 and 710 nm and light intensity 10^{15} photons/cm^{2}s. According to the results represented in Figure 5. the relationship between the photocurrent and the applied voltage may be expressed by the formula $I \propto U^n$ with values of the power $n > 1$. The experimental results concerning the photocurrent vs. the light intensity obtained at the excitation wavelength of 580 and 710 nm show that for high values of light intensity ($I_0 > 10^{14}$ photons/cm^{2}s), the relationship between the photocurrent and the light intensity may be expressed by the formula $I \propto I_0^n$ with $n < 1$.

Since traps affect strongly the photogeneration properties [7] the pentacene film structure and its morphology should be taken into

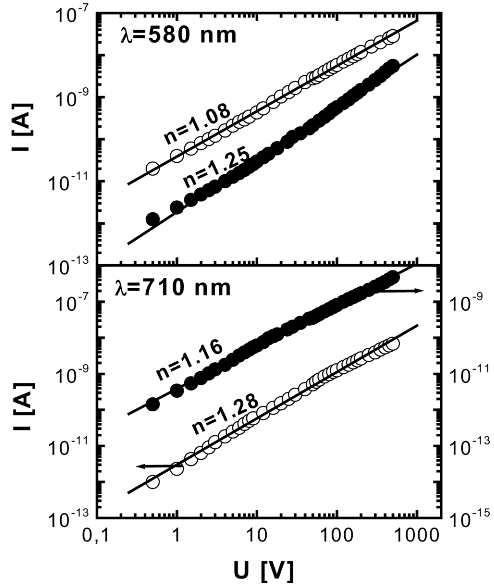

FIGURE 5 The photocurrent – applied voltage dependence measured under the sample illumination from non-substrate side (open circles) and substrate side (solid circles) for pentacene layers obtained at the excitation wavelengths of $\lambda = 580$ nm and $\lambda = 710$ nm and light intensity $I_0 = 10^{15}$ ph/cm^{2}s.

account to analyse experimental results. It has been shown that vacuum evaporated pentacene layers are polycrystalline and typically consist of two crystallographic phases [8]. These phases are generally referred to "thin film" and "bulk" phase. In literature, two polymorphs were reported to depend strongly on the nature of substrate, substrate temperature and the film thickness [9–11]. Thin film phase forms directly onto the substrate. Above a critical film thickness, which is dependent on substrate temperature the bulk phase is found with increasing fraction as a function of the film thickness [9]. According to the results of structural studies, the thin film phase has better charge transport properties then the bulk phase [12]. Moreover in ambient air the polar molecules could easy diffuse into the bulk phase and form extra traps [12–14]. All these facts show that the trap distribution in pentacene layer is non-uniform and reaches its maximum at the surface of the pentacene film. The trap distribution in pentacene layer can affect the charge carrier transport in the sample. We conclude that most of the charges transport occurs close to the substrate since the photocurrent is maximal when the sample is illuminated from NS and S side by wavelengths corresponding to deep and shallow light penetration, respectively.

According to chosen experimental conditions such as the electrode configuration, illumination spectral range and the direction of sample illumination and taking into account the results of structural analysis, we conclude that there are different mechanisms responsible for charge carrier production depending on the direction of sample illumination. Namely, the antibatic behaviour of I_{NS} photocurrent characteristic indicates its origin in the free charge carriers production due to the quenching of triplet excitons [15]. On the other hand, the lack of correlation between the photocurrent response $I_S(\lambda)$ obtained under the sample illumination from substrate side and the pentacene absorption spectra as well as the increase of photocurrent with decreasing wavelength show the intrinsic photogeneration seems to be the major process responsible for free charge carriers production near the substrate. These statements support also the fact that values of I_S are about one order bigger than those measured for I_{NS}. There is limited information about the basic physical properties for pentacene such as the HOMO (highest occupied molecular orbital) – LUMO (lowest unoccupied molecular orbital) gap and other optical characteristics [16]. The reported values of HOMO-LUMO gap for thin pentacene film ranges from $1.7 \sim 2.5\,\mathrm{eV}$ [16,17,18,19] depending on thin films of pentacene deposited on various substrates at various deposition temperatures. Since reorganization of molecular levels depends on structural disorder in the film, the value of HOMO-LUMO gap is expected to be smaller at the substrate and larger at the free surface [19].

CONCLUSIONS

To conclude the structure of vacuum evaporated tetracene and pentacene have a great impact on the surface photoconductivity. According to the experimental results different mechanism are responsible for charge carrier production in tetracene and pentacene layers. In tetracene layers with uniform structure and special trap distribution, the charge carrier production by excitons causes the increase in photoconductivity regardless the side of illumination. In pentacene layers, under the sample illumination from non-substrate side, the charge carriers production is mainly due to the quenching of triplet excitons via interaction with trapped charge carriers. However, the direct free charge carriers production by light excitation is dominant under the sample illumination from substrate side.

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