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Influence of different types of solvents on morphology, optical and conductive properties of PCBM films

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Abstract: **The article deals with the influence of various types of solvents on the spectral characteristics and conductive properties of films [6,6] -methyl phenyl-C61-butyric acid, precipitated from solutions. It is clearly shown that the effect of the nature of the solvent affects the morphology of the film surface. Analysis of the spectra of the optical range showed the presence of a maximum of the absorption coefficient in the frequency range of 340-490 nm. The calculation of the optical band gap clearly demonstrates the possibility of modernizing the atomic structure of films by using various types of solvents. A study of the current-voltage characteristics showed the presence of a photocurrent in carbon films deposited with dichloromethane, toluene, and chloroform.**

Keywords: PCBM, thin films, optical band gap, current-voltage characteristics, photoelectric effect

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Contents

1. INTRODUCTION

Over the past decade, the interest of researchers in organic photovoltaics has increased [1-3]. This is due to the relative low cost of manufacturing combined with the ease of production of the final product, which is an indisputable advantage over more expensive and difficult-to-manufacture analogues [4,5]. For example, the use of roll-to-roll technology makes it possible to produce microcircuits by directly "printing" electronic circuits at a high speed [6]. Due to its excellent electron-acceptor properties, fullerene has established itself as a promising component in organic electronics [7]. In particular, fullerene C_{60} is a fairly good n-type semiconductor, which demonstrates a high electron mobility 11 $cm^2V^{-1}s^{-1}$; therefore, it is widely used in the creation of OFET (Organic field-effect transistor) [8]. The use of fullerene as a transfer layer for electrons makes it possible to improve the electrical characteristics of organic light-emitting diodes (OLEDs) [9].

Along with fullerene C_{60}, its derivatives, for example, [6,6]phenyl-C_{61}-butyric acid methyl ester (PCBM), have also become very popular.

Currently, PCBM is widely used in pharmaceuticals and organic photovoltaic systems [10-11]. More recently, the energy conversion efficiency for solar cells using PCBM and polymer materials has reached 7-8% [12-15]. Nevertheless, despite the extensive list of works devoted to the creation of devices using PCBM, the question of choosing the optimal solvent for obtaining thin-film structures with the maximum photocurrent remains relevant. Considering all of the above, it was these prerequisites that prompted this study, in which we considered how the use of various types of solvents affects the electrophysical and electrodynamic properties of carbon thin-film structures deposited by the method of watering from solution onto dielectric substrates [16].

2. SYNTHESIS AND DEPOSITION OF CARBON FILMS, EXPERIMENTAL TECHNIQUE

PCBM was synthesis was carried out according to a modified method proposed by F. Wudl [17]. This method is based on the process of 1,3-dipolar addition of methyl ester of δ-phenylbutyric acid to the fullerene core. The main benefit of the final product is the increase in PCE (power conversion efficiency) up to 5.3%.

The formation of films from the initial PCBM powder material was carried out by pouring from a solution onto substrates. Non-aromatic solvents were used: dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), carbon tetrachloride (CCl_4) and aromatic: toluene ($C_6H_5CH_3$), benzene (C_6H_6). The concentration of the starting substance in the solution was 0.5 mg/ml. After thorough mixing and holding (at least 48 h at room temperature), the resulting suspensions were applied to dielectric and conductive substrates, with a volume of 1 ml of the latter. Cover glasses with geometric parameters of 18×18 mm were used as dielectric substrates. To measure the conducting characteristics, indium tin oxide (ITO) with a resistivity of 16-18 Ω/sq was used as a contact group, as well as thin aluminum films obtained by vacuum deposition

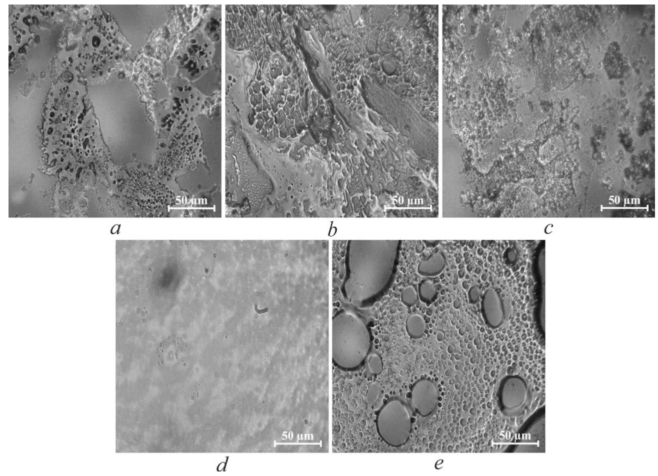

Fig. 1. *Surface morphology of PCBM films depending on the type of solvent: a - dichloromethane; b - chloroform; c - carbon tetrachloride; d - toluene; e - benzene.*

on sitall, having high uniformity, low roughness with resistivity 20 Ω/sq.

The analysis of the surface relief and volumetric irregularities was carried out by means of transmission and reflection microscopy based on a LOMO Mii-4M microinterferometer using additional illumination with a semiconductor laser and an extended optical path on a camera with a 1/2FF 10MP matrix (**Fig. 1**). To determine the electrodynamic characteristics, a GBC Cintra-4040 spectrophotometer was used to study the interaction of electromagnetic radiation in the optical range and obtain the transmission, absorption (**Fig. 2**) and reflection coefficients. A distinctive feature of this device is the presence of a double monochromator in the Czerny-Turner configuration. Tungsten and deuterium lamps were used as radiation sources. Due to this, the range of incident radiation was from 250 to 850 nm. During the experiment, a

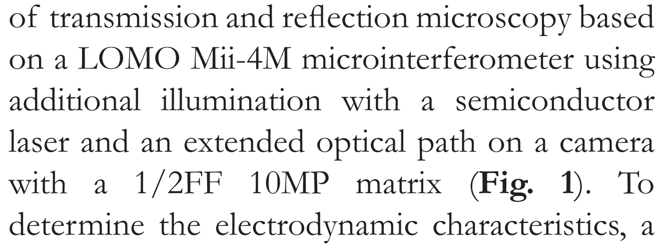

Fig. 2. *Absorption spectra of the optical range (a) and the optical band gap (b) of films depending on the solvent: 1) dichloromethane, 2) chloroform, 3) tetrachloromethane, 4) toluene, 5) benzene.*

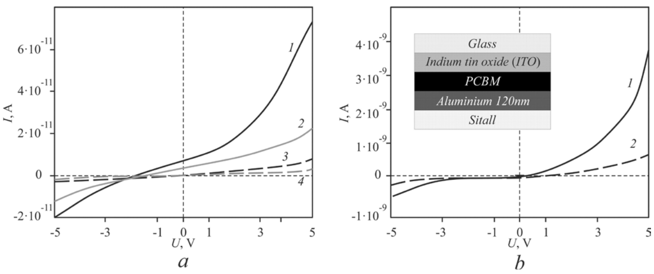

Fig. 3. *(a) Current-voltage characteristics of PCBM, where: 1 - light PCBM in toluene; 2 - light PCBM in dichloromethane; 3 - dark PCBM in toluene; 4 - PCBM in dichloromethane. (b) Current-voltage characteristics of PCBM in chloroform, where: 1 - light; 2 - dark.*

clean substrate was used as a normalization basis. The study of current-voltage characteristics **(Fig. 3**) was carried out using a keysight B1500A semiconductor analyzer. To analyze the photoactivity of the studied carbon films, an LED matrix was used as an illumination source, with a flux density of about 300 W/m_2 and an incoming power of 60 mW. All measurements were carried out at least ten times at room temperature not exceeding 30°C using a shielding chamber and subsequent averaging of the results obtained.

As a result of surface analysis, it was found that the use of various types of solvents significantly affects the final surface morphology of PCBM films. For example, films deposited with dichloromethane (CH_2Cl_2) are characterized by an "island-like" structure (Fig. 1*a*). Moreover, its thickness varies in the range from 8 to 25 μm. A more uniform surface is observed for films deposited with chloroform ($CHCl_3$). It is worth noting the formation of "cells" with a diameter of 10-15 μm on the surface of the film. The thickness of the film itself is 4-5 μm (Fig. 1*b*). PCBM films synthesized with tetrachloromethane (CCl_4) also showed the presence of an "island-like" structure, 5-10 μm thick (Fig. 1*c*). The highest homogeneity of the PCBM film was achieved using toluene ($C_6H_5CH_3$) as a solvent (Fig. 1*d*). The thickness of such films is about 500-600 nm. The use of benzene (C_6H_6) made it possible to obtain a relatively uniform film with a thickness of about 5-6 μm (Fig. 1*e*).

Thus, the nature of the solvent effect on the final homogeneity and morphology of the carbon film is clearly shown.

3. OPTICAL PERFORMANCE

Due to the variety of the surface morphology of the films and the characteristic feature of each type of samples, it is necessary to evaluate the optical properties, in particular, the absorption spectra (Fig. 2*a*). Analysis of the optical characteristics showed that the highest absorption coefficient is possessed by PCBM films obtained with the use of toluene. Absorption maximum ~ 0.9 a.u. falls on the wavelength range of 340-490 nm and is accompanied by a further decline to the near infrared spectral range. The next largest film in terms of absorbing properties is benzene, with a maximum absorption coefficient of ~ 0.6 a.u. The use of tetrachloromethane made it possible to obtain an absorption maximum of ~ 0.5 a.u. The remaining two types of images differ insignificantly from each other, with the absorption coefficient at the peak: for chloroform ~ 0.4 a.u., for dichloromethane ~ 0.3 a.u.

Considering the similarity of the frequency dependences of the optical range and the insignificant difference in the structures of the obtained films, one should assume the presence of an optical gap in the experimental samples Assuming that the main transitions between the valence and conduction bands are indirect allowed transitions, depending on the absorption coefficient on the incident photon energy, according to the Tauz formula, let us take a power exponent m equal to two [18,19]:

$$\alpha \sim \frac{1}{h\nu}(\mathrm{h}\nu - E_g)^m,$$

where α is the absorption coefficient; hν is the energy of the optical quantum; E_g is the band gap of the material. In this case, the optical band gap: PCBM in dichloromethane – 2.75 eV; PCBM in chloroform – 2.26 eV; PCBM in tetrachloromethane – 2.14 eV; PCBM in toluene

– 1.95 eV; PCBM in benzene – 1.84 eV (Fig. 2*b*). The results obtained clearly demonstrate the possibility of modernizing the atomic structure of carbon films by using various types of solvents.

4. CURRENT-VOLTAGE CHARACTERISTICS

To research the electrical parameters, PCBM carbon films were formed in the form of a "sandwich" structure: Al-PCBM-ITO. The geometric parameters of both layers (Al and ITO) were 10×10 mm (inset in Fig. 3*b*). The use of thin-film aluminum and tin indium oxide as a contact group is due to the fact that the electron work function of ITO is comparable to that of polymers, which provides ohmic contact with the organic layer, while Al forms a rectifying barrier due to a lower work function [20].

The primary study of the charge kinetics was carried out by analyzing the current-voltage characteristics (I-V characteristics) in the range from –5 to 5 V. For PCBM deposited with toluene, the current-voltage characteristic is nonlinear and asymmetric at forward currents of 8 pA and reverse currents of 2.6 pA (Fig. 3*a*). Using dichloromethane, the currents flowing in the film were 1.3 pA for the forward leg and 0.7 pA for the reverse leg (Fig. 3*a*). For the samples: $CHCl_3$, CCl_4, C_6H_6, the limiting values of the currents in the forward branch were 3.5 nA, 5 pA, 4.8 pA, respectively, the reverse currents were 0.4 nA, 9 pA, 7 pA.

It is worth noting the presence of light sensitivity in three of the five types of images, when the latter is irradiated with an electromagnetic wave of the optical range (Fig. 3*a,b*). The greatest increase in the charge kinetics upon irradiation was recorded in films deposited with toluene (an increase of 8.8 times) and dichloromethane (an increase of 8.5 times). The smallest increase was recorded for PCBM in chloroform (5.8 times increase). Comparison of the I–V characteristic with the surface morphology makes it possible to conclude that a galvanic bond is formed between individual centers of agglomerators growth that form the basis of carbon films.

5. CONCLUSION

Thus, the paper considers the electrical properties of PCBM-based carbon films deposited using 5 types of solvents. The main feature is the presence of light sensitivity in three of the five types of samples. For samples precipitated using toluene, the increase in kinetics was ~ 8.8 times, for dichloromethane ~ 8.5 times, for chloroform – 5.8 times. It is also worth noting that the mobility of charge carriers is not determined over the entire surface of the "film" structure, but is formed by separate sections and agglomerations, which are successive connected chains.

Analysis of the surface morphology clearly showed that when using toluene, the result is the most uniform film surface. The analysis of the optical characteristics showed that the maximum of the absorption spectrum for all types of carbon films is observed in the wavelength range of 340-490 nm. The highest absorption (~ 0.9 a.u.) is possessed by the PCBM film deposited with toluene. The smallest absorption coefficient was recorded for the film in dichloromethane (~ 0.3 a.u.). The calculation results of the optical band gap clearly demonstrate the possibility of modernizing the atomic structure of carbon films by using various types of solvents.

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