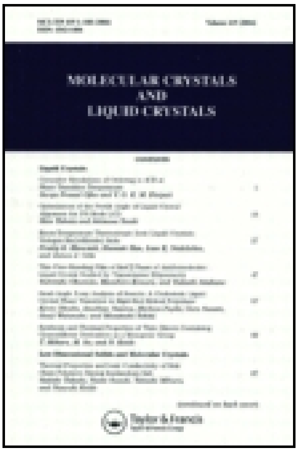

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Effect of Thin C_{60} Films Modification with Aminosubstituted Polycyclic Aromatic Hydrocarbons and Meso-tetraphenylporphine on Optical and Photoelectric Properties of Au/C_{60}/Si Photodiode Structures

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Effect of Thin C_{60} Films Modification with Aminosubstituted Polycyclic Aromatic Hydrocarbons and Meso-tetraphenylporphine on Optical and Photoelectric Properties of Au/C_{60}/Si Photodiode Structures

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*We present the results of comparative investigations of the effect of a direct solvent-free modification of C_{60} thin films with photosensitive molecules: aminosubstituted polycyclic aromatic hydrocarbons (1-aminopyrene, 1-pyrenemethylamine hydrochloride, 1,5-diaminonaphthalene) and meso-tetraphenylporphine on their optical properties, photoluminescence, and photoelectric characteristics of Au/C_{60}/Si photodiode structures ($\lambda = 400$–1100 nm). The optical properties (*n, k*) of the investigated C_{60} films are shown to differ slightly. The photoluminescence spectra measured at 2 K demonstrate a redistribution of the constituent bands intensities and their overall reduction for all C_{60} modifications. The greatest enhancement of the photocurrent and the photoconversion efficiency is observed for structures with C_{60} layers modified with meso-tetraphenylporphine.*

Keywords Fullerene; heterojunction; photodiode structure; photoelectric properties

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Introduction

The low-dimensional carbon materials (fullerenes, carbon nanotubes) are considered as important building blocks for the 'bottom-up' approach in nanotechnology and nanofabrication. In the case of fullerenes and their derivatives, the aspects of particular interest are supramolecular devices with applications in energy conversion, electronic and photonic devices, or nanosensorics [1,2]. The efficiency of solar cells, based on a heterojunction of C_{60} with organic or inorganic semiconductors, depends on both of their photoelectric properties and barrier and recombination characteristics of their interfaces. As opposed to the use of long-chain aliphatic diamines (or dithiols) capable of binding silver (or gold) nanoparticles [3,4], we applied, in this work, the direct solvent-free functionalization of fullerene C_{60} films with aminosubstituted polycyclic aromatic hydrocarbons to prepare chemically cross-linked C_{60} films. In a few works, the self-assembly of naturally occurred porphyrins was studied; however, most studies employ substituted porphines based on meso-tetraphenylporphine (also known as 21,23-dihydro-5,10,15,20-tetraphenylporphine or H_2TPP) without or with additional polar or hydrophobic groups in its phenyl rings [2,5,6]. The use of functional and oligomeric porphyrins allows for varying the nature of the intermolecular interaction between porphyrin units, their mutual orientation, and the periodicity of an array. An especially important circumstance is that the porphyrin self-assembly employs noncovalent interactions (hydrogen bonding, π-π stacking, solvophobic and surface effects, etc.) instead of the covalent bonding to a substrate: this approach has such advantages as the relatively easy synthesis and the purification of porphyrin structural units, spontaneous generation of the most thermodynamically stable structure, as well as a possibility of the self-repair. However, the optical and photoelectric properties of such structures are not sufficiently investigated.

In this work, we present the results of comparative investigations of the effect of a direct solvent-free functionalization of thin C_{60} films with H_2TPP and amino-substituted polycyclic aromatic hydrocarbons (1-aminopyrene – AP, 1-pyrenemethylamine hydrochloride – PMA, 1,5-diaminonaphthalene – DAN) on the optical and photoelectric properties of Au/C_{60}/Si structures.

Experimental Technique

Thin fullerene C_{60} films on a *n*-silicon substrate were obtained by the physical vapor deposition (C_{60}/Si) without heating the substrate [3]. The chemical modifications were carried out by gas-phase reactions of C_{60} films with 1-aminopyrene (AP), 1-pyrenemethylamine hydrochloride (PMA), diaminonaphthalene (DAN), or H2TPP. The reaction temperatures were of 220°C for aminosubstituted polycyclic aromatic hydrocarbons and 270°C for H_2TPP by 3 h in low vacuum. All the structures with modified C_{60} films had the own satellite structures with simultaneously deposited pristine C_{60} layers. For their optical characterization, the reflectance spectra were measured in the wavelength range $\lambda = 400$–$1100\,\text{nm}$ at a number of angles of incidence of *p*- and *s*-polarized light to determine the C_{60} layer thickness and the optical parameters (refractive index n and extinction coefficient k, $N = n\text{-}i \cdot k$) dispersion. The obtained results allowed us to calculate the absorption coefficient ($\alpha = 4\pi\text{k}/\lambda$) spectral dependences and the spectra of light transmittance in layered barrier structures metal (Au)/C_{60}/Si, photoelectric properties of which have been investigated.

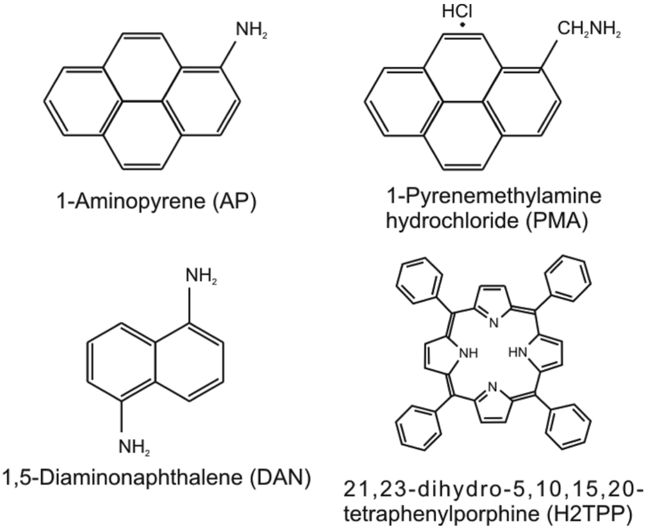


Figure 1. Chemical structures of used aminosubstituted polycyclic aromatic hydrocarbons and meso-tetraphenylporphine.

The photodiode structures were fabricated by the evaporation of a semitransparent Au layer on C_{60}/Si substrates through an opaque mask with an opening diameter of 1.3 mm and by the manufacturing of an In ohmic contact to the back side of the Si

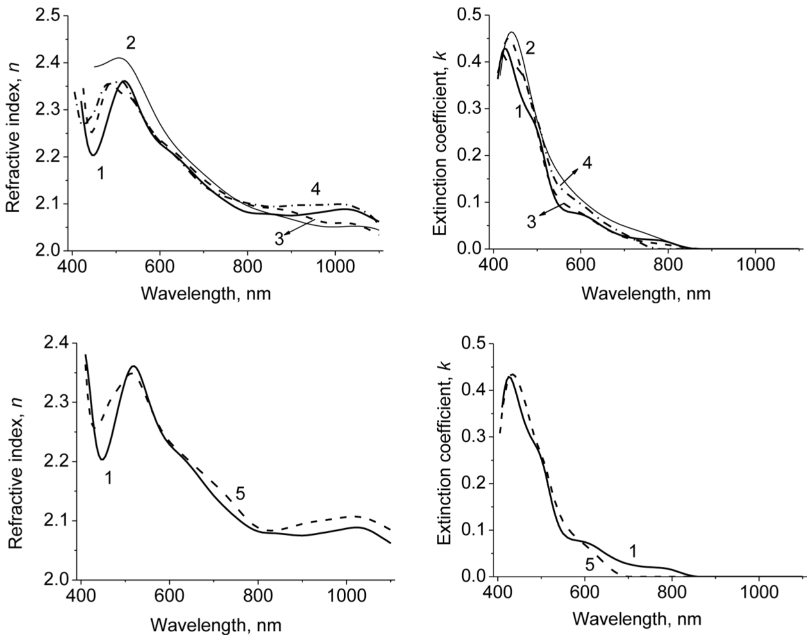


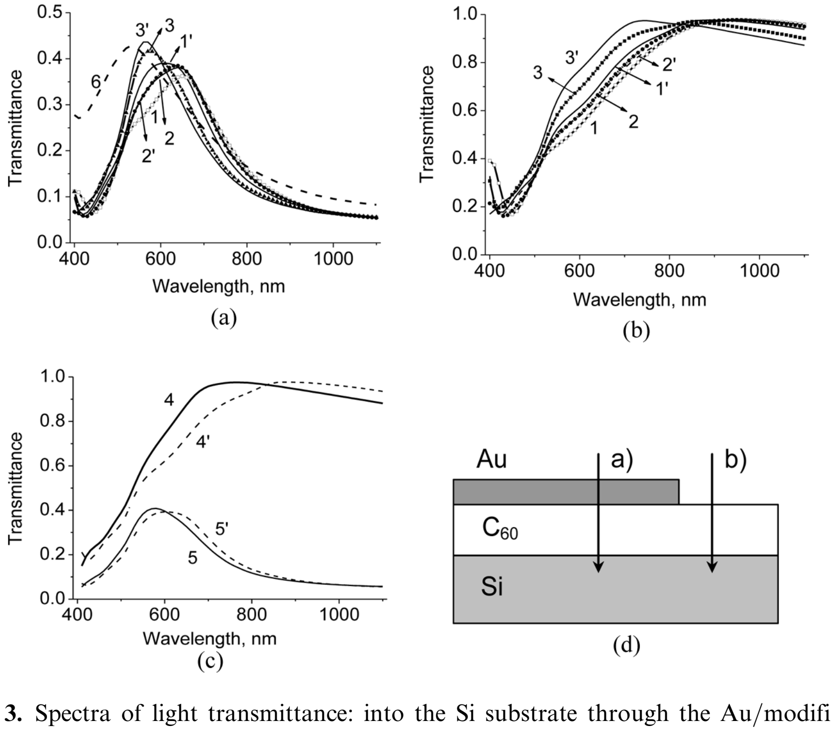
Figure 2. Optical parameters (*n, k*) dispersion of pristine C_{60} films (1) and C_{60} modified by aminosubstituted polycyclic aromatic hydrocarbons: AP (2), PMA (3), DAN (4), and meso-tetraphenylporphine H_2TPP (5) determined from the reflectance spectra (400–1100 nm) at a number of angles of incidence of *p*- and *s*-polarized light.

substrate. The spectra of their short circuit photocurrent were measured in the same spectral range as the optical characterization was made. The dark and light (at simulated AM0 illumination) current-voltage characteristics of these structures were measured as well. All the studies were carried out at room temperature in air. Low-temperature (2 K) photoluminescence (PL) spectra have been measured with a single-grating spectrometer MDR-3 with an infrared photomultiplier FEU-62 under the Ar ion laser (488 nm) excitation.

Results and Discussion

Figure 1 demonstrates the structure of organic molecules used for a modification of C_{60} films. We believe that the covalent attachment of aromatic amines (AP, PMA, DAN) applied here takes place across the 6,6 bonds of C_{60} pyracylene units similarly to studied previously aliphatic amines (1,2).

Meanwhile, the covalent addition of AP and PMA aromatic amines molecules to C_{60} cages occurs through one NH_2 termini, the attachment of diamine, DAN, lead to the formation of a cross-linked structure ensuring the system of conjugated links facilitating the carrier transport. The modification of a fullerene film applying meso-tetraphenylporphine is based on noncovalent π-π-interactions between the



(a)

(b)

(c)

(d)

Figure 3. Spectra of light transmittance: into the Si substrate through the Au/modified or pristine C_{60} layers (a), (c, 5, 5′) and through the modified or pristine C_{60} layers (b), (c, 4, 4′) for: C_{60}-AP (1), C_{60}-PMA (2), C_{60}-DAN (3), C_{60}-H_2TPP (4, 5), and for their satellite structures with pristine C_{60} (1′-5′). The transmittance of light through the Au layer (6). The thickness of modified (and pristine C_{60}) layers, nm: 116.6 (108.2) – 1 (1′), 113.3 (115.7) – 2 (2′), 96.1 (89.3) – 3 (3′), 90.0 (106.9) – 4, 5 (4′, 5′). Scheme of light transmittance in the investigated structures (d).

two components possessing highly delocalized π-electrons. However, due to the high photosensitivity of H_2TPP molecule, the enhancement of the Au/C_{60}-H_2TPP/Si structure should be expected. The spectra of optical parameters (*n* and *k*) determined in experiments and calculated in the framework of a one-layer model for pristine and modified C_{60} films on the silicon substrate are shown in Figure 2.

As is seen, the optical parameters (*n, k*) for these films differ slightly in the investigated spectral range. Apparently, this is a consequence of a small thickness of the modified C_{60} layer with respect to the full thickness of the C_{60} film, and, respectively, of a slight influence of the thin modified layer on optical parameters of the film in the framework of the one-layer model. Their differences manifest themselves more in the spectra of light transmittance into the Si base of photodiode structures, both through the Au/C_{60} (subdiode region of photocarrier generation) and C_{60}-layers (edge or lateral photogeneration) – Figure 3. These spectra were calculated with regard for the thicknesses of pristine and modified C_{60} layers defined by the optical characterization.

The photoluminescence spectra of the investigated structures are shown in Figure 4. In general, the photoluminescence spectra are similar to the known spectra of C_{60} fullerene films. The low-temperature PL spectra of all samples demonstrate a clearly defined structure. However, after the modification of C_{60} fullerene films, the changes in PL spectra have been observed.

The modifications lead to a redistribution of the intensity of the majority of constituent PL bands, to a slight broadening of bands, as well as to their overall

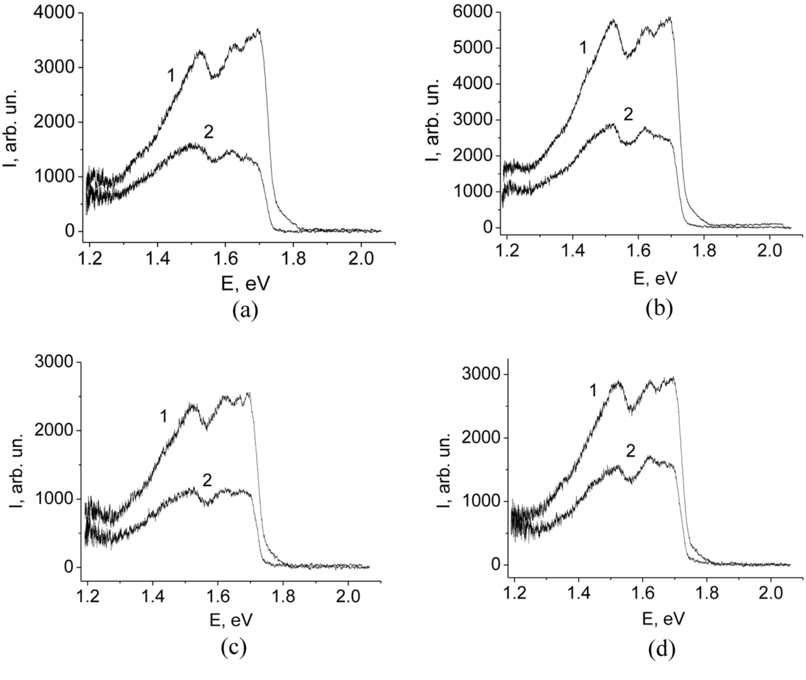


Figure 4. The photoluminescence spectra of C_{60}/Si structures (1) and structures with different chemical treatments of C_{60} (2) by: (a) 1-aminopyrene (AP), (b) 1-pyrenemethylamine hydrochloride (PMA), (c) 1,5-diaminonaphthalene (DAN) and (d) meso-tetraphenylporphine (H_2TPP); $T = 2\,K$, $\lambda_{exc} = 488\,nm$.

reduction. The PL band at 1.67–1.69 eV (Fig. 4) can be attributed to the radiative recombination of a Frenkel exciton delocalized over two adjacent molecules situated near some lattice disorder. There is one more peculiarity of the PL spectra of modified C_{60} fullerene films, namely the low-energy part of the spectra is growing slightly. Bands at lower energies (around 1.52 eV) are due to the emission from the so-called X traps [7] or defects presumably associated with the grain boundaries [8].

The more characteristic spectra of the short circuit photocurrent for the investigated structures are shown in Figure 5a,b as external quantum efficiencies normalized to the area of the diode. The photocurrent spectra of structures with all the C_{60} layers modified by aminosubstituted polycyclic aromatic hydrocarbons demonstrate the transformation which mainly correlates with a change of the light transmittance into Si, i.e., a decrease of the photocurrent at $\lambda = 500$–750 nm and an increase in the more long wavelength spectral range. Unlike them, the increase of the photocurrent for the Au/C_{60}-H_2TPP/Si structure as compared with that for Au/C_{60}/Si is observed all over the spectral range. These transformations of spectral photosensitivity are more obviously seen in the spectra of internal quantum efficiencies which are also normalized to diode areas (Figs. 5c, d). It is seen that an increase of the photocurrent for the Au/C_{60}-H_2TPP/Si structure occurs not only in the long wavelength spectral range, as for AP, PMA, and DAN modification of C_{60}, but also

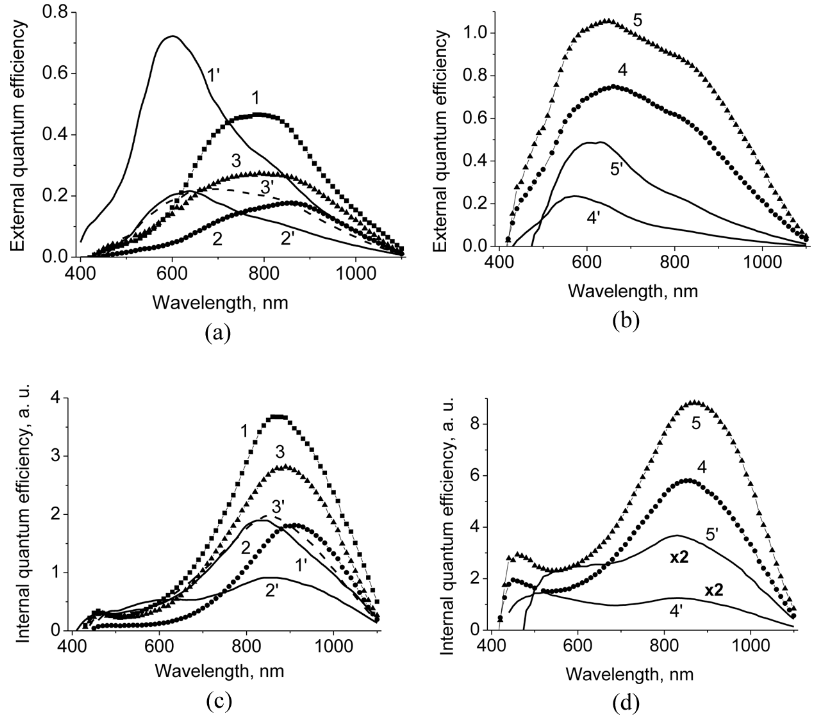
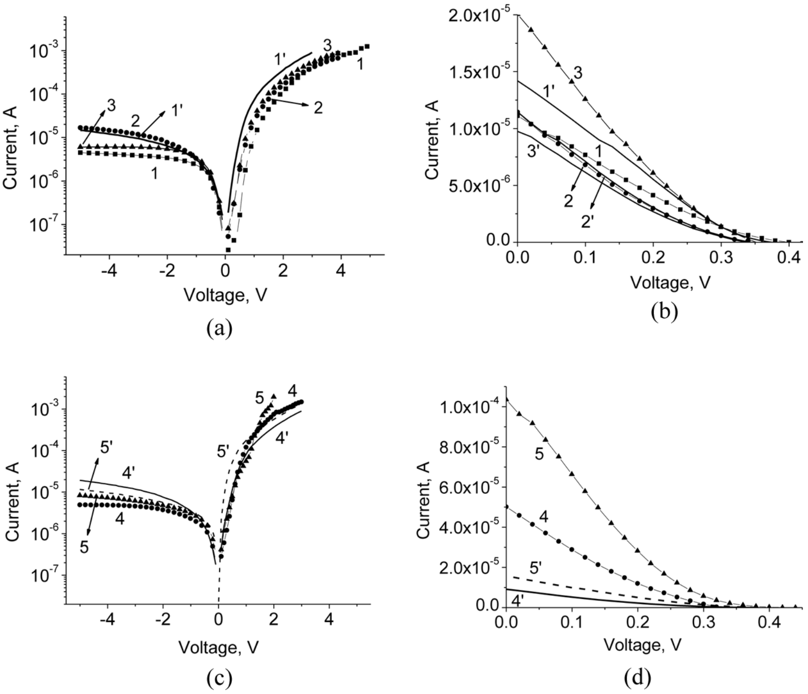


Figure 5. Spectra of external (a, b) and internal (c, d) quantum efficiency normalized to the area of the diode, for Au/C_{60}-AP/Si (1), Au/C_{60}-PMA/Si (2), Au/C_{60}-DAN/Si (3) and Au/C_{60}-H_2TPP/Si (4, 5), structures and their satellite Au/C_{60}/Si structures (1′-5′). The scale of curves 4′ and 5′ is increased × 2 times.



(a) (b) (c) (d)

Figure 6. Dark (a, c) and light (b, d) current-voltage characteristics for Au/C_{60}-AP/Si (1), Au/C_{60}-PMA/Si (2), Au/C_{60}-DAN/Si (3) and Au/C_{60}-H_2TPP/Si (4, 5), structures and their satellite Au/C_{60}/Si structures (1′-5′).

in the spectral range 400–550 nm. An example of the typical dark and light current voltage characteristics of the investigated photodiode structures is shown in Figure 6.

All the dark current-voltage dependences have barrier character (with the forward direction corresponding to $V > 0$ at the Au electrode) and slightly affected by a modification of the C_{60} layer. Some of the light current-voltage characteristics demonstrate an increase of the photocurrent for structures with the C_{60} layer modified by photosensitive AP, PMA and DAN molecules. But the more essential increase of the photocurrent without a decrease of the open circuit voltage and even an increase of the fill factor is observed for the Au/C_{60}-H_2TPP/Si structure. As a rule, an increase of the fill factor correlates with an enhancement of the short circuit photocurrent and results from a decrease of the series resistance of the structure. The change of the open circuit voltage due to modifications of the C_{60} film does not exceed its variation for diodes of the same structure. So, the modification of the C_{60} layer with meso-tetraphenylporphine enhances the efficiency of solar cells of such a type.

Conclusions

The optical properties of the investigated C_{60} films with a thickness of ~100 nm obtained by the sublimation of a C_{60} powder in vacuum on the unheated Si substrate are shown to differ slightly as a consequence of their gas phase modification with photosensitive molecules of AP, PMA, DAN, and H_2TPP. The peculiarities of the optical parameters (n and k) manifest themselves more in the spectra of light transmittance into the Si base of the $Au/C_{60}/n$-Si photodiode structure.

The changes in the photoluminescence spectra due to a modification of C_{60} films are observed. All the fullerene film modifications lead to a redistribution of the intensity of the constituent bands (low-energy part of the spectra is growing), as well as to their overall reduction.

The photocurrent spectra of structures with C_{60} layers modified by AP, PMA, and DAN molecules demonstrate the transformation which mainly correlates with a change of the light transmittance into Si, i.e., a decrease of the photocurrent at λ=500–750 nm and an increase in the more long wavelength spectral range. These transformations of the Au/C_{60}/n-Si structure photocurrent spectrum without an essential decrease of its value (unlike the diamine treatment effect [3]) should be considered and used at designing the photodetector and photovoltaic structures.

The external quantum efficiencies of Au/C_{60}-H_2TPP/n-Si photodiodes exceed those of $Au/C_{60}/n$-Si structures in all the spectral range; moreover the contribution of the lateral photogeneration to a photocurrent is essential there. The spectra of internal quantum efficiencies testify also to an increase of the photocurrent generated in the C_{60}-H_2TPP layer. So, the C_{60} nanolayer modified with C_{60}-H_2TPP may be the most perspective for applications in solar cells.

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