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PHOTOPHYSICAL PROPERTIES OF POLY (3–HEXYLTHIOPHENE) ON THE ISLET SILVER FILMS

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Influence of surface plasmon resonance of the islet silver films on the transformation of light energy in polymer films of poly (3–hexylthiophene) has been studied. It is established that the increase in the intensity of absorption and fluorescence of films of the polymer P3HT about four times on the surface of the islet silver films. The observed dependence was associated with the change in the rate of electronic transitions in macromolecules of the polymer under the action of the local electromagnetic fields near the surface of silver nanoparticles. Study of the effect of plasmonic silver nanoparticles on the photovoltaic parameters of organic solar cells based on bulk hetero junction was performed. The increase of the photovoltaic parameters of the cell by 1.6 times during the registration volt-ampere characteristic of solar cells on the effect of the plasmon resonance was recorded.

Keywords: silver, plasmon resonance, fluorescence, poly (3-hexylthiophene), films, current-voltage characteristics.

Introduction

In recent years, the growing interest in nanocomposite materials based on organic semiconducting polymers and metal nanoparticles (NPs) has been noted. The interest in these materials is associated with their unique optical properties due to the phenomenon of surface plasmon resonance (SPR), which is manifested in the intense absorption bands in the visible region of the spectrum [1-4]. The study of such nanocomposites is important because most problems in understanding the mechanisms and the possibility of using the SPR process in the development of new materials for efficient optoelectronic and photovoltaic devices.

One of the most promising semiconducting polymers for organic solar cells (OSCs) with bulk heterojunction is poly [3 - hexylthiophene]. This is due to the fact that P3HT has a high hole mobility (≈ 0.1 cm^{2}V^{-1}c^{-1}), good chemical stability and low band gap (1.9 – 2.0) eV. The maximum value of the efficiency factor for the active layer in a bulk heterojunction based on Poly(3-hexylthiophene-2.5-diyl: [6.6]:Phenyl C61 butyric acid methyl ester (P3HT: PCBM) were (4 – 5) % [5-9]. The results of the OSCs were achieved by optimizing the ratio of mixture components, thickness, and morphology [10]. Because almost every photon absorbed in the active layer of P3HT: PCBM gives a couple of charges on the electrodes, and the resulting values of efficiency for these materials are almost marginal [11]. Currently, the new semiconducting polymers are synthesized or excitation of plasmons on the surface of metallic NPs is used to improve the efficiency of OSCs. Thus, plasmonic silver NPs in different layers of OSCs based on bulk heterojunction systems P3HT: PCBM in [12] work was used. It is shown that the best value of the OSCs efficiency was obtained using the silver NPs in direct contact with the active layer. Thus, it is very important to investigate hybrid solar cells based on plasmonic metallic NPs in connection with improving the efficiency of OSCs with bulk heterojunction.

The greatest interest is the study of optical properties of polymer P3HT near the surface of plasmonic metallic NPs. The inclusion of plasmonic metallic NPs into the active environment may lead to significant changes in the effective properties of the latter due to the fact that the polarization NPs in the field of an electromagnetic wave changes the characteristics of this field in the environment [13, 14]. Moreover, the intensity of these resonances can be effectively adjusted by

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changing the topological and morphological parameters of the metallic NPs. In particular, enhancement of absorption spectra and fluorescence of single polymer molecule P3HT due to generation outage in cubic silver NPs was demonstrated in [15] work. It is shown that the enhancement of P3HT fluorescence depends on the overlap between the emission frequency of the fluorophore and SPR.

The solution to this problem can be achieved with the islet films of NPs of metals. This is because, the methods of vacuum deposition contribute to the production of films with thickness from fractions of a nanometer to hundreds of nanometers, with a low content of impurities, in contrast to methods of electrochemical or plasma chemical deposition. Choosing the right deposition parameters, you can easily and with high precision to control the frequency of plasmon resonance, the film thickness and its microstructure.

Thus, the interest in this subject due to the need to clarify fundamental aspects of the interaction of radiation with matter and application tasks, as the possibility of controlling the properties of the active layers is still a major issue in organic photovoltaics. The results of the study of the plasmonic effect influence of the islet silver films on spectral-luminescent and photovoltaic properties of P3HT polymer films are presented in this paper.

1. Experimental technique

The islet silver films were obtained by thermal spraying $AgNO_3$ on a substrate in a vacuum with residual pressure $P = 5 \cdot 10^{-4}$ millimeter of mercury. Before spraying of the samples, the surface of the substrate was subjected to thorough processing. Thermal modification of the films was carried out in temperature-controlled muffle furnace in air for 10 minutes at temperatures $T = 60^0$C, 180^0C, 240 ^{0}C. The size and shape of the islet films of silver NPs were determined using scanning electron microscope (SEM) TESCAN Mira 3.

P3HT polymer film on the surface of the islet silver films were obtained by spin–coating. Registration of absorption spectra of investigated samples was carried out on spectrophotometer Cary 300 UV-Vis. The necessary film of silver NPs was used in the measurement of the dependence of the absorption spectra of the films P3HT in the presence of the silver NPs as a sample for comparison. Kinetics of fluorescence decay P3HT films was measured by a pulsed spectro fluorimeter with pico-second extension and check in the mode of time-correlated photon counting (Becker & Hikl, Germany).

The glass substrate with a conductive ITO layer was used to build organic solar cells (Indium tin oxide, 8 Ohm/cm2, Sigma-Aldrich). PEDOT: PSS (Poly (3.4-ethylene dioxythiophene) / poly(styrenesulfonate) 1.1 % in H_2O, $PC_{61}BM$ ([6.6]-Phenyl C61 butyric acid methyl ester, 99.5%) and P3HT (Poly(3-hexylthiophene-2.5-diyl, 99.995 %) were purchased in Sigma-Aldrich. P3HT:PCBM was dissolved in C6H5Cl for 24 hours at a temperature of 500 C with vigorous stirring, at a speed of 5000 rpm. The concentration of the active layer of P3HT: PCBM for solar cells amounted to 1.0:1.0. All work was performed in a sealed glove box with an inert atmosphere of Ar (99.998 %) with automatic removal system of H_2O and O_2 with an accuracy of 1 ppm. The current-voltage characteristics of the battery were measured under irradiation by light with a spectrum close to AM1.5 (100 mW/cm^2) using a solar simulator Photo Emission Tech Inc. Solar Cell IV Measurement.

2. Discussion of results

Annealed islet silver films on a solid substrate, which were performed with a scanning electron microscope, are shown in figure 1. As shown by data obtained because of thermal annealing, there is a gap of continuous film and self-organization of islets, which reduces the size of the silver islets increases and their number. The observed change of surface morphology of the film due to the fact that the temperature significantly affects the crystallization of the silver films, as it results in a more agglomerated structure of the silver films on the surface of solid substrate. The size of island ranges from 40 up to 90 nm.

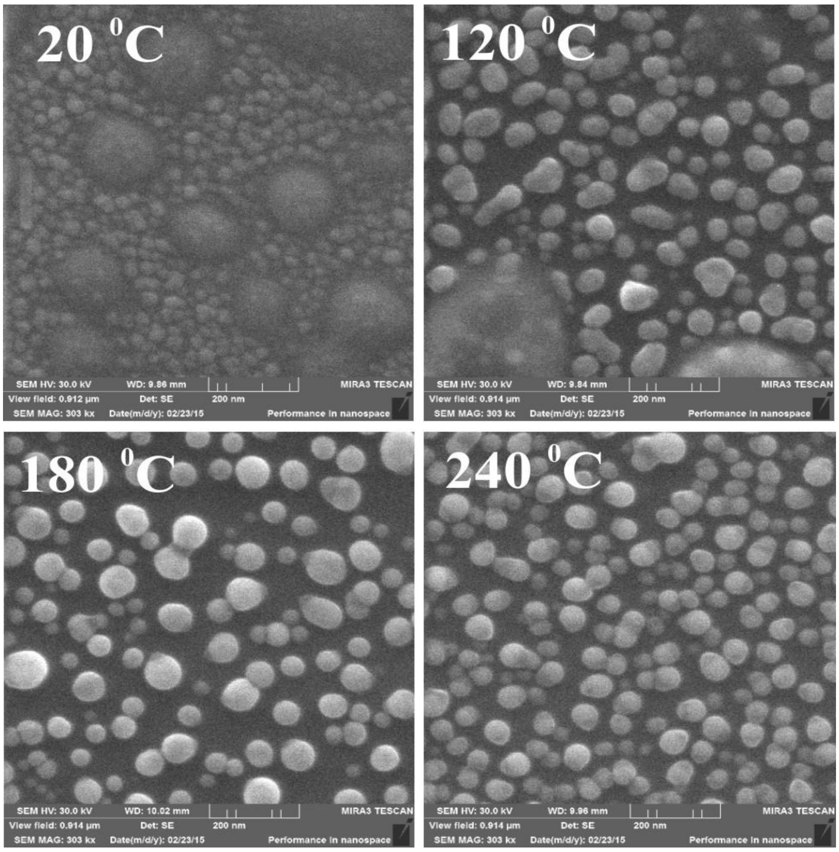

Fig.1. SEM image of the islet silver films on a solid substrate which were obtained with different annealing temperatures.

The plasmon absorption spectra of silver films obtained by vacuum spraying and subsequent annealing at different temperatures were shown in figure 2.

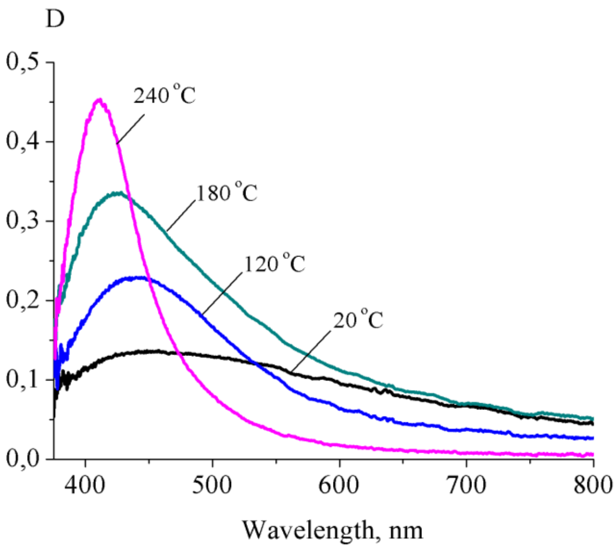

Fig.2. The plasmon absorption spectra of silver films prepared by spraying of metals in vacuum and subsequent annealing

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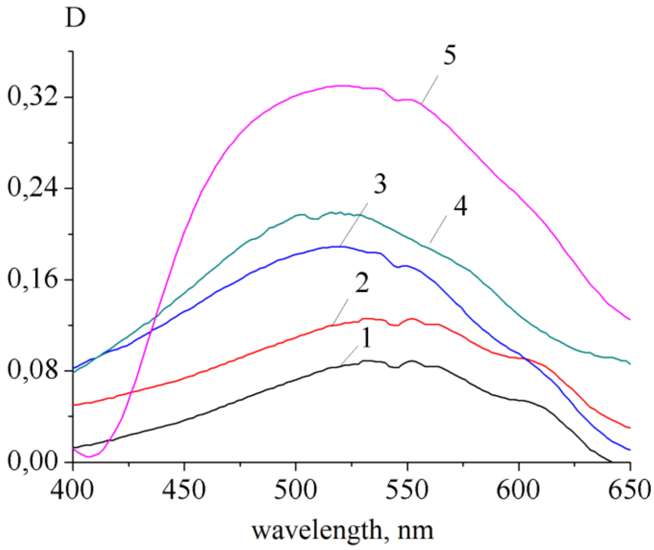
Plasmonic silver films obtained directly after spraying are characterized by the presence of broad bands with a maximum λ_{max}= 457 nm and the half-width of $\Delta\lambda^{abs}_{1/2}$ = 309 nm. At the annealing temperature of 240 C, the band maximum of the plasmon resonance experiences a short-wave shift to λ_{max}= 411 nm and a significant narrowing of half-width $\Delta\lambda^{abs}_{1/2}$ = 68 nm compared to the strip plasmon resonance of the unannealed film. The observed short-wave shift of the plasmon resonance band is interpreted by the result of the restriction of the free path length with a diameter of spherical particles, which leads to a reduction of the band maximum of the plasmon resonance, while for particles of larger size, the maximum is shifted towards larger wavelengths and is expanding due to the excitation of higher order modes [16, 17]. The position and shape changes of plasmon absorption bands of silver films with changing annealing temperature correlate well with changes in surface morphology of these films.

Absorption spectra of films of polymer P3HT on the surface of the islet silver films obtained at different annealing temperatures are shown in Figure 3. As can be seen from the figure, the absorption band of the polymer P3HT in the absence of silver films has a maximum at a wavelength of λ_{max}=530 nm and the half-width of $\Delta\lambda^{abs}_{1/2}$ = 152 nm. The overlap of polymer molecules P3HT on the islet silver film leads to an increase in optical density of the molecular layer in ~ 4 times. The shift of the maximum absorption band to shorter wavelengths of 15 nm is also observed. This increase in the optical density of the absorption spectrum of P3HT interacts with the electromagnetic field effect of the silver NPs. Excitation of multiple plasmon in the particle provokes an effective scattering of light and the formation of enhanced electromagnetic fields near the surface of the NPs. Ambient light can be re-absorbed by the photoactive component P3HT, thereby significantly increasing the amount of absorbed light by the system as a whole [3].



1 – without NPs; 2 – 20 ^{0}C; 3 – 120 ^{0}C; 4 – 180 ^{0}C; 5 – 240 ^{0}C.

Fig.3. Absorption spectra of polymer films P3HT on the surface of the islet silver films

Fluorescence spectra of films of polymer P3HT on the surface of the islet silver films are shown in Figure 4. Photo excitation of the polymer films was carried out P3HT on the length of the wave is equal to 520 nm. From the data obtained it is seen that the fluorescence spectra of the polymer P3HT have maxima at a wavelength equal to 572, 642 and 708 nm with the half width of the strip $\Delta\lambda^{fl}_{1/2}$ =122 nm. The increase of luminescence intensity at the wavelength of 572 nm is approximately ~ 4 times and a decrease in the half width of the spectrum are observed when measuring the fluorescence spectra of the polymer P3HT on the surface of the islet silver films.

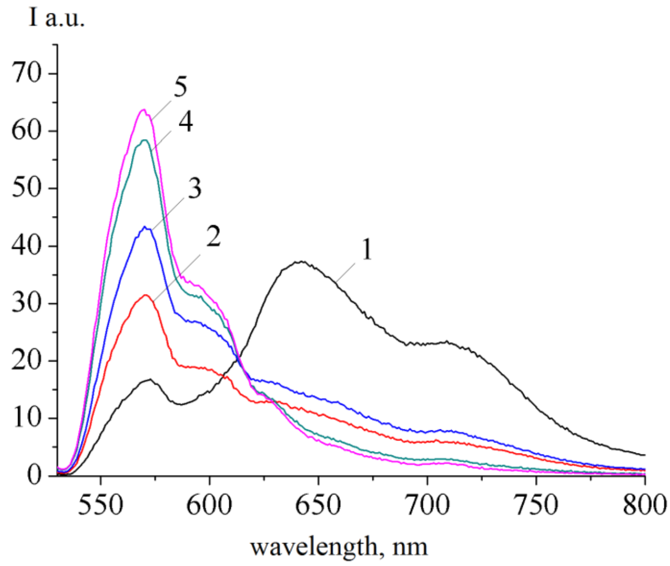


Fig.4. Fluorescence spectra of the films P3HT on the surface of the islet silver films obtained at different annealing temperatures: 1 – without NPs; 2 – 20 ^{0}C; 3 – 120 ^{0}C; 4 – 180 ^{0}C; 5 – 240 ^{0}C.

Kinetics of fluorescence decay P3HT films on the surface of the islet silver films is shown in figure 5. The fluorescence excitation of the sample was performed using a semiconductor laser with wavelength generation of λ_{gen} = 488 nm with a pulse duration of τ = 40 ns. The lifetime of the P3HT excited state, calculated from the decay curve of the fluorescence at the wavelength of 572 nm was τ_{fl}=0.33 ps. The duration of luminescence of the polymer decreased on the islet silver films (table 1).

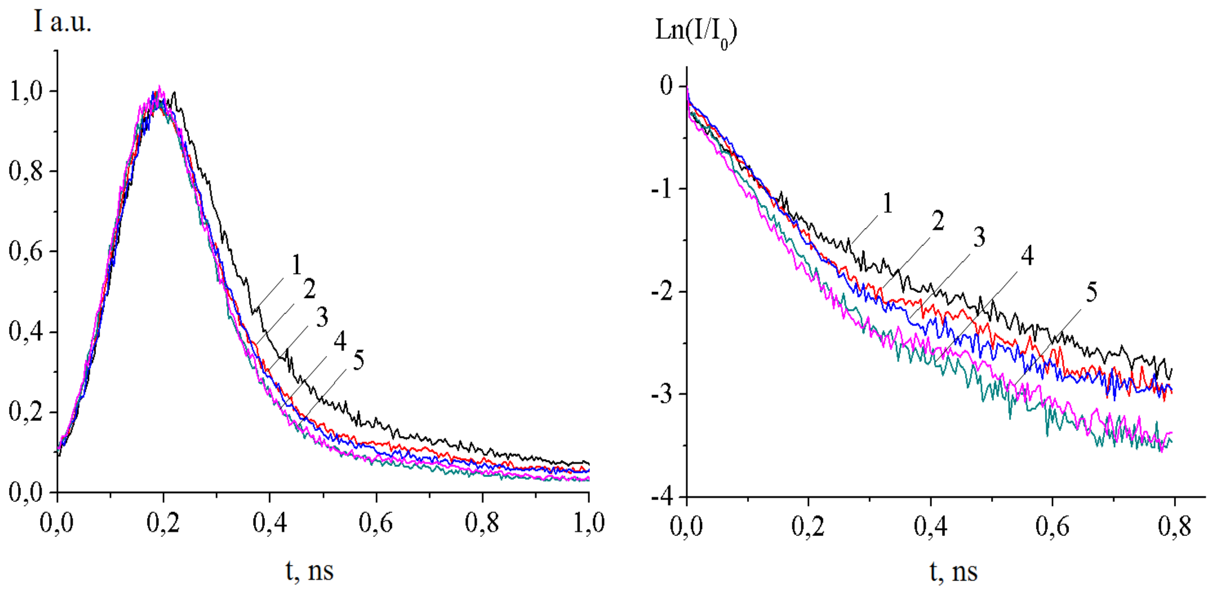


Fig.5. The kinetics of fluorescence decay P3HT films on the surface of the islet silver films: 1 – without NPs; 2 – 20 ^{0}C; 3 – 120 ^{0}C; 4 – 180 ^{0}C; 5 – 240 ^{0}C.

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Table 1. The values of fluorescence lifetime calculated from the kinetics decay of the glow polymer P3HT

	T, ^{0}C	τ, ns
1	without NPs	0.33
2	20	0.3
3	120	0.28
4	180	0.26
5	240	0.24

Solar cells, the design of which is presented in figure 6 were collected to investigate the influence of plasmonic effect on OSCs photovoltaic properties.

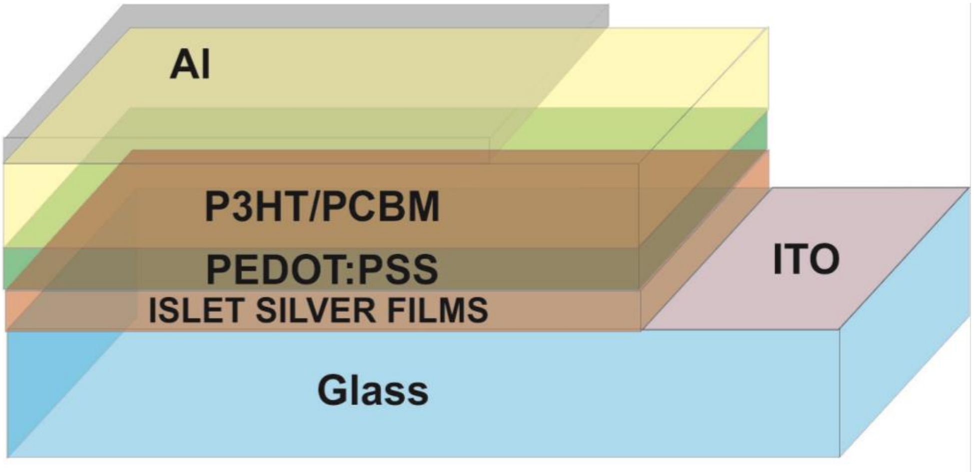

Fig.6. Design of organic solar cell with bulk heterojunction

OSCs current-voltage characteristics with islet silver films are shown in Figure 7. Comparing the curves, we can see that adding to the design of the NPs cell of the islet silver films increases the current density of 2.4 and the efficiency of the cell of 1.6 times.

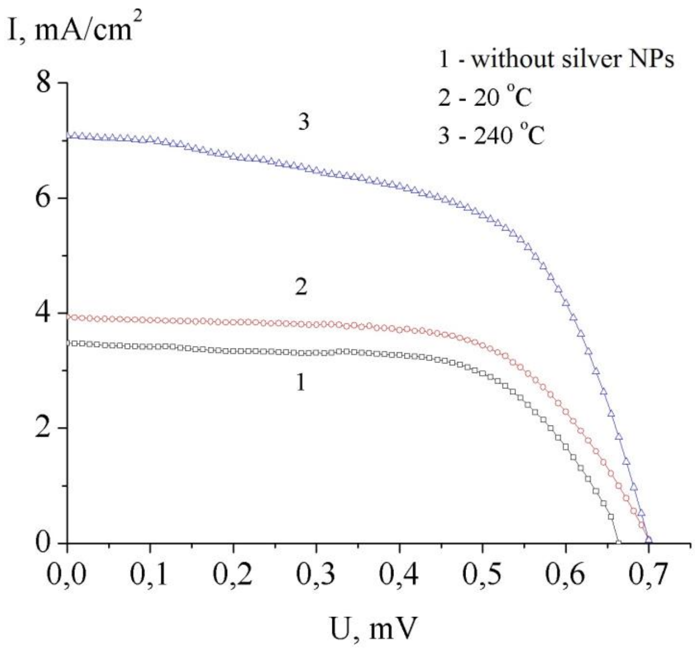

Fig.7. Current-voltage characteristics of organic solar cells with the islet silver films

The open-circuit voltage practically does not change. The effect of efficiency increasing of the cells is associated with the increase in the intensity of light absorption by the molecule photoactive layers caught in the locally enhanced near field of metal NPs, which leads to more generation of free charge carriers. The main results of the measurements are shown in table 2.

Table 2. Parameters of organic solar cells with silver NPs

Sample	U_{xx}, mV	I_{kz}, mA/cm^2	R_s, ohm	R_p, ohm	*FF*	η, %
Without NPs	0.66	3.47	80	5400	0.61	1.47
20 ^{0}C	0.69	3.93	72	4300	0.62	1.7
240 ^{0}C	0.7	7.08	70	1500	0.56	2.4

In addition, tabular data, we see that the magnitude of the serial R_s are also reduced with the increase of annealing temperature the islet films and shunt resistors R_p. As you know, R_S consists of in-series resistance of contact layers, and R_P reflects the possible channels of current leak, in the ideal case it would be $R_s \to 0, R_p \to \infty$.

Conclusion

Thus, it is established that the increase of the absorption intensity and fluorescence of P3HT associated with the change in the rate of electronic transitions in polymer macromolecules the under the action of the local electromagnetic fields near the surface of the silver NPs. The effect of efficiency increasing of OSCs is associated with the increase in the intensity of light absorption in the P3HT photoactive layer.

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