A study of the effect of fullere ne concentration in active layers on the spectral characteristics of organic photosensitive structures based on the ZnPc:C60 system

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Abstract. The paper considers the effect of fullere ne concentration in active layers on the spectral characteristics of organic photosensitive structures based on the ZnPc:C60 system. The studied samples were created using the vacuum thermal evaporation method. Absorption, transmission, and photosensitivity spectra were studied for the created samples.

1. Introduction
People have faced the problem of finding alternative sources of energy due to a reduction in traditional fuel supplies, such as oil, gas, and coal. The most important role is now assigned to solar energy, since the power of solar energy that reaches Earth far exceeds the needs of humanity. Solar energy is converted into electricity by solar panels. Modern solar cells are based on inorganic semiconductor materials, primarily crystalline and amorphous silicon.

Organic solar cells have been actively studied all over the world. These cells can reduce the cost of converting solar energy into electrical energy. The low cost of organic batteries is associated with the simple manufacturing technology and the low cost of their production. Organic semiconductors are usually soluble in organic solvents. This property makes it possible to produce liquid “ink” and print them onto flexible polymer substrates [1].

Flexibility is an important advantage of organic solar cells. All classical electronics is based on the use of rigid and at the same time fragile structures, which is determined by the physical properties of inorganic materials. Organic semiconductors allow making flexible and plastic films, which is the most important advantage of this class of materials. Such batteries can be integrated into clothing, coat materials, food packaging, etc. [2].

2. Experiments, measurements and results
The paper considers the effect of the fullerene concentration of the deposited organic materials film on the photosensitivity of structures. Glass coated with FTO (Fluorine-doped Tin Oxide) was used as a substrate. The FTO layer acted as an optically transparent contact. Layers of ZnPc(Zinc phthalocyanine):C60(Fullerene)/C60/Al were sequentially deposited onto the FTO surface using the vacuum thermal evaporation method [3]. Figure 1 shows the structure of the layers, and figure 2 illustrates the energy level diagram. Layers of organic materials and aluminum contacts were applied at a residual gas pressure of 2·10⁻⁵ Torr. The substrate was heated to 60°C during the deposition of organic layers, and when the metal contact was applied, the substrate temperature was maintained at 70°C. This was done to improve the adhesion of the material to the substrate.
Evaporation of a substance occurs when it is being heated. In this research, the evaporated substance was heated by the flow of current through the boat, which was preloaded with organic material or metal of the required mass. The thickness of the deposited film is directly proportional to the mass of the evaporated substance and inversely proportional to the distance between the substrate and the boat. In this experiment, the height from the substrate to the evaporated substance remained unchanged at 15 cm.

![Figure 1. Structure of the studied samples.](image1)

![Figure 2. Diagram of energy levels of the studied samples.](image2)

A series of photosensitive structures with different thicknesses of the active layers was manufactured. Sample 4 was also created with an additional transport layer BPhen (Bathophenanthroline). It is used to create an additional energy barrier for holes, to suppress the recombination and improve the charge carrier collection [4]. Below is the thickness of the active layers ZnPc:C_{60}/C_{60}:

- sample 1: h1 = 396 nm (ZnPc(15 mg):C_{60}(15 mg)/C_{60}(25 mg)),
- sample 2: h2 = 470 nm (ZnPc(15 mg):C_{60}(20 mg)/C_{60}(30 mg)),
- sample 3: h3 = 338 nm (ZnPc(15 mg):C_{60}(10 mg)/C_{60}(20 mg)),
- sample 4: h4 = 349 nm (ZnPc(15 mg):C_{60}(10 mg)/C_{60}(20 mg)/BPhen(7 mg)).

The absorption and transmission spectra of ZnPc:C_{60}/C_{60} layers, which were measured with a USB4000 fast-scanning spectrometer, were studied by using an incandescent lamp.
Figure 3 shows the absorption spectra of the samples under study. The spectra have 2 areas of high absorption. The first region is in the wavelength range of 400–550 nm and corresponds to the absorption in the fullerene layer. It can be seen that a decrease in the fullerene concentration decreases the absorption in this region (sample 3). The second region with high reshaping is at wavelengths of 550–730 nm. It is caused by absorption in the layer of zinc phthalocyanine. The increase in absorption for the fourth sample is due to the influence of the processes occurring in the additional layer of BPhen. The second peak at wavelengths of 550–730 nm arises due to the absorption of zinc by phthalocyanine.

In order to improve the characteristics of photosensitive structures, it is necessary to select the optimal compositions of the active layers, which provide high absorption, efficient generation, separation and transport of charge carriers. An important feature of organic materials is that the excitons, which are mainly formed in them under the influence of light, are difficult to separate. The exciton can dissociate at the ZnPc/C₆₀ heterojunction. The characteristic distance that an exciton travels during a zinc phthalocyanine lifetime is approximately 10 nm [5]. Consequently, only photons absorbed near the heterojunction region can provide a contribution to the photocurrent. To increase the probability of separation of a photoexcited exciton, solar cells with a bulk heterojunction are created.

In such solar cells, fullerene is not only applied as a separate layer, but also distributed inside the phthalocyanine layer. This allows you to increase the area of the heterojunction and reduce the distance that the exciton needs to travel before separation. This makes it possible to significantly increase the number of separated charge carriers. Further, this charge is transported to the corresponding electrodes.

To assess the effect of changes in the mass of the sprayed material on the thickness of the structures created, the created samples were studied by scanning electron microscopy (figure 4). The measurements were carried out on a Tescan MIRA3 LMU high resolution scanning electron microscope. It is shown that a change in the mass of the applied fullerene from 30 to 50 mg increases the thickness of the structure from 338 nm to 470 nm. Studies have shown acceptable quality of the created structures.
The photosensitivity spectra (figures 5, 6, 7) were studied by using a diffraction grating monochromator with a Keithley 6483 picoammeter. The incandescent lamp was used as an emitting source.

Figure 4. The thickness of the sample 3 that was examined with an electron microscope.

Figure 5. The photosensitivity spectra of the studied structures in relative units.
A comparison of the shape of the photosensitivity spectra for the studied samples shows the following (figure 5). The spectrum primarily contained the long-wavelength component corresponding to the
absorption in zinc phthalocyanine. This may indicate a difficulty in the transport of photogenerated excitons in the fullerene layer. A decrease in the fullerene concentration leads to a shift of the spectrum to the shortwave side, which is due to the greater manifestation of effects associated with absorption in phthalocyanine. This is confirmed by a brighter manifestation of a maximum in sample 3 at a wavelength of 620 nm, also observed in the absorption spectrum for phthalocyanine. The introduction of BPhen, an additional hole-blocking layer, into the structure makes it possible to expand the range of sensitivity by improving the collectability of charge carriers that occur in all layers of the structure.

The deterioration of the transport properties of the structure with increasing fullerene concentration is confirmed by comparing the photoresponse for samples 1–3. It can be seen that sample 3 demonstrated the best parameters (figure 6), which had the lowest fullerene concentration. Adding a blocking BPhen layer made it possible to improve the sensitivity parameters of the structure (figure 7). This is ensured not only by improving the collection of holes, but also, possibly, by increasing the probability of separating photo-generated excitons in the upper part of the structure. This is confirmed by the broadening of the sensitivity spectrum. The BPhen layer is tunnel-transparent for electrons.

3. Conclusion

Thus, the paper considers the effect of fullerene concentration in the ZnPc:C₆₀/C₆₀ layers on the optical characteristics of the FTO/ZnPc:C₆₀/C₆₀/Al photosensitive structures grown by vacuum thermal deposition on a glass substrate.

The absorption spectra were investigated for the created samples and individual layers. Two regions of strong absorption of radiation were found, corresponding to the absorption in fullerene and phthalocyanine. In the photosensitivity spectra, the signal is observed only in the long-wavelength part, which may indicate a difficulty in transporting photogenerated excitons in the fullerene layer. The deterioration of the transport properties of the structure with increasing fullerene concentration is confirmed by comparing the magnitude of the photoresponse for the created samples. It was revealed that the signal decreases with an increase in the fullerene concentration in the composition of the active layer.

It was also shown in the work that the introduction of an additional BPhen hole-blocking layer into the structure of organic solar cells allows us to expand the range of sensitivity and significantly increase the photosensitivity. This occurs due to a decrease in recombination and an improvement in the collection of charge carriers that are generated in the structure, and, possibly, due to an increase in the probability of separating photogenerated excitons in the upper part of the structure.

References

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