

Film Growth Based on an Organic Basis for Photovoltaic *p*-Cells

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The main measured parameters characterizing the solar cell are its photocurrent and fluorescence under the influence of electromagnetic radiation of the solar spectrum – derivatives of a number of elementary processes in the cell and determining the complex mechanism of its functioning.

The main issue is to determine the allowable concentration of the polymer and the acceptor, allowing to obtain a film having a desired density and at the same time, the thickness, the optimum from the point of view of the diffusion length and the probability of dissociation of the intermediate particles with the formation of free charge carriers. From a comparison of the synthesized samples micrographs it can be concluded that the polymer concentration of 12.5 g/l gives a sufficiently dense and relatively uniform film without substantial amounts of undissolved polymer.

Keywords: Solar cells, Polymer photovoltaic cells.

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1. INTRODUCTION

Interest in renewable energy, in particular, to the conversion of solar energy is continuously increasing, particularly the direct use of solar radiation [1] To produce electrical energy. To do this, based on both organic and inorganic materials [2] created photovoltaic cells. At present time, the most common solar cells based on inorganic semiconductor materials such as silicon, gallium arsenide, and others. [3] Commonly different methods for increasing characteristics are used- include simulation [4, 5].

Organic polymeric materials based on organic compounds such as carbon-polymer nanocomposites, which molecules are chains of a large or a relatively small number of units of identical components have unique properties, in particular they can form thin flexible films.

One significant advantage of solar cells based on polymer compounds is their price, as they can in principle be much cheaper to manufacture than the same battery based on silicon. For mass consumption is price and exceptional mechanical properties of polymers are crucial. However, they have significant drawbacks, yet do not allow organic solar cells to be fully competitive in comparison with inorganic. Today, one of the main drawbacks is the low efficiency of these cells (4-5 %). Also it is worth remembering that by using semiconductor polymers it should be prevented oxidation or other reactions degrade in air, since such processes alter the physicochemical properties of the active layer. Therefore, to improve the performance of solar cells based on organic compounds requires a detailed understanding of the elementary processes that occur within the solar cell.

Analyzing the growing interest to photovoltaic products for the aerospace, telecommunications and portable power sources, as well as practical applications of organic semiconductors for commercial use of

heterostructure photovoltaic cells (solar cells) a relevant research of the most effective technologies becomes for the use of organic semiconductors for a new generation of light-transforming devices and create a solution to the problem of high-quality solar cells based on organic semiconductors. In scientific terms, this applies to the resolution of questions of improving the optical absorption of light in the active layers of the module, the improvement of the quality of the active layers in heterocascade themselves and heterojunctions, leading to increased efficiency and new technologies to reduce the cost of production. One of the main and general requirements for research samples of solar cells is the reproducibility of the measured characteristics. In this regard, organic semiconductors differ from inorganic substances due to its chemical activity [6]. Specific task, which is solved in this paper is to develop a methodology applying a semiconducting polymer onto a substrate to create solar cells. The main measured parameters characterizing the solar cell is its photocurrent and fluorescence under the influence of electromagnetic radiation of the solar spectrum - derivatives of a number of elementary processes in the cell and determining the complex mechanism of its working.

At the initial stage it was decided to develop a system which allows to produce polymer films of a given thickness. The method of spin coating has been chosen, this method is well known under the English title "spin coating", which allows to set and control the thickness uniformity of the film across the entire operating region of the sample. One should also consider the properties of organic semiconductors, [7], many of which exhibit in solution, for example, enhanced ability to oxidation and other chemical characteristics. In the most convenient form for physical research sample is a crystal or glass rectangle measuring 10 × 25 mm or 10 × 20 mm and a thickness of 1 mm pre-coated with an optically transparent conductive layer of a mixture of indium and tin

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oxides. Photovoltaic cells are formed on a substrate by applying the active layer and the second electrode. Cutting substrates with required size of round billets requires not only the creation of special equipment, but also the adoption of special measures to prevent disruption of the structure of the film when cutting. In order to avoid the influence of oxidation reactions it is required an inert atmosphere in which to set up a solar cell. Note that in the manufacture of solar cells, as substrates to be used quartz plate coated with ITO (Indium Tin Oxide), which are transparent to light, have a sufficiently smooth surface to reduce scattering of light and do not require mechanical pretreatment. The main features of the hydrodynamics of a physical model for the process of applying a film of the solution on the substrate by spin coating rectangular form are considered in [8]. Dose applied onto the substrate polymer solution, and then the substrate was rotated at a constant angular velocity ω . Under the action of centrifugal forces resulting solution was spread on a substrate to form radially extending flow. In this case, the flow front is thickened circular roller due to the action of surface tension. Roller as its radial expansion is fueled from the "outer layer" extending out of the solution. Under the outer layer means a layer moving at a greater velocity than the boundary layer. The thickness of the liquid film formed by the rear roller expanding, commensurate thickness of the boundary layer and can be determined by the expression:

$$\delta = 2,78 \sqrt{\frac{\nu}{\omega}} \quad (1)$$

where δ – liquid film thickness; ν – dilute solution viscosity; ω – angular velocity.

When reach the edges of the outer layer of the substrate is reset with her, but at the edges of the substrate is maintained edge roller.

Thicken areas in the different quarters of the rectangular substrate is determined by the direction of rotation (clockwise or counterclockwise) and the orientation of the vectors of the Coriolis force (see Fig. 1).

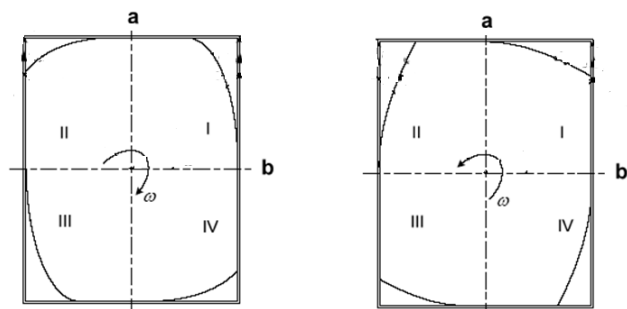


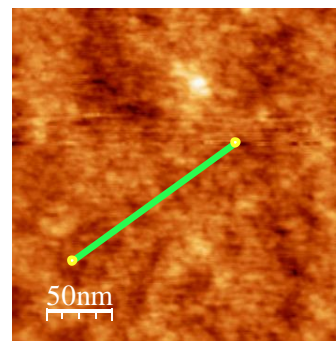
Fig. 1 – Placing thicken areas in the corners of the substrate depending on the direction of its rotation

By rotating the substrate clockwise thickened region is formed on the sides of the substrate with the size b in the I and III quarters and at the sides with a size a and in II and IV according to Fig. 1a. By rotating the substrate counterclockwise it is observed mirroring pattern thicken areas as shown in Fig. 1b. From a physical point of view, the process of applying the polymer solution on

the substrate by spin coating can be characterized by two processes run in parallel, namely the removal of the solvent from the film forming polymer and the movement of the interface "polymer-gas environment". By spin coating film aligns for a few seconds [3]. Time spreading solution inversely proportional to the frequency ω of rotation and can be estimated from interference colors on the plate centrifuged. Then lined film dries by evaporation of the solvent. During spin coating, after the initial height of the solution is reduced by one third, the evaporation is stopped and the concentration of solid component reaches its final value when the transfer of the substance ceases entirely due to the high viscosity. At this stage the film loses about 30 % of the solvent and evaporation of spin coating time reaches the transition phase, and then slowly drying film by diffusion of the solvent. Determination of film thickness in the areas of film (edge-center-edge) was carried out as follows: first cantilever "pressed into" the surface of the polymer film with a constant force, that is carried out scratch, then performs a scan of the surface area with the resulting scratch (mechanical defect) and using height difference "film-glass" the unknown quantity is calculated.

2. RESULTS AND DISCUSSION

The main issue is to determine the allowable concentration of the polymer and the acceptor, allowing to obtain a film having a desired density and at the same time, the thickness, which is optimum from the point of view of the diffusion length and the probability of dissociation of the intermediate particles with the formation of free charge carriers. Solutions samples were prepared for synthesis in the two dimensional ratios: 2 ml solvent and 50 mg of the polymer (concentration 25 g/l) and 4 ml of solvent and 50 mg (concentration 12.5 g/l) of the polymer. After preparation, the solution was subjected to ultrasonic treatment for the (10-15) min. The topography of the sample in its various parts showed very low roughness (0.6 nm) and a relatively small amount of undissolved particles and small size (height \approx 30 nm). Thus, given that the surface roughness is in the range of 10 Å, and the size of the undissolved particles is of the order of tens of nanometers, it can be concluded that it was possible to obtain a film with practically limit smoothness (for the method see. Fig. 2 and 3) and were defined optimum layer formation conditions: the type of solvent, concentration, spin speed [9].



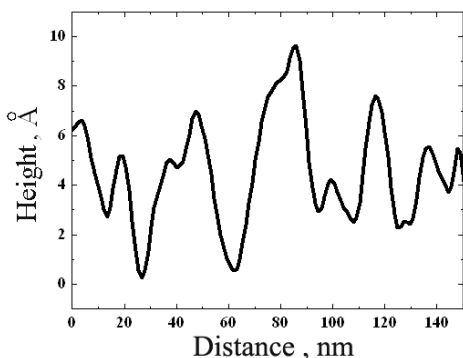


Fig. 2 – Topographical image of the surface of the film (250 × 250 nm²) and corresponding surface profile

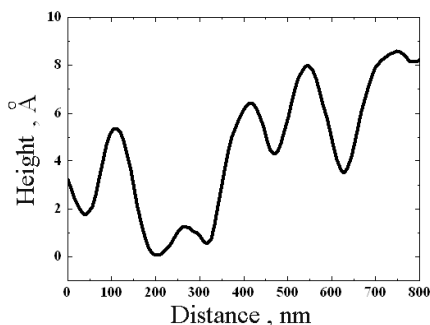
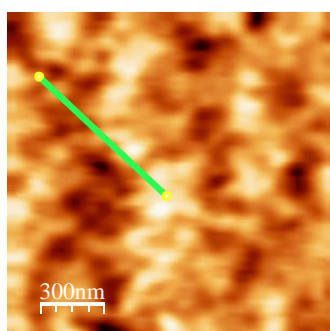


Fig. 3 – The topographical image of the surface center of the film (1500 × 1500 nm²) and the corresponding surface profile

The last stage of the manufacture of photovoltaic cells is that for the research capability of the cell resulting in the air or when the long-term storage, it is necessary to enclose it in a protective coverage.

In Fig. 4 it is shown a photomicrograph of a film of a solution containing 25 g/l.



Fig. 4 – Micrograph of a film from a solution with a concentration of 25 g/l (magnification × 400)

The photomicrograph clearly shows that the polymer forms a film in the form of microcrystals. This fact leads to the development of the acceptor interface with

the polymer, which is significantly (by orders of magnitude) increases, the conductivity of the mixed film. Virtually the same surface structure, (see Fig. 5), is obtained by applying the polymer on the surface of the film after it is dried at 80 °C.

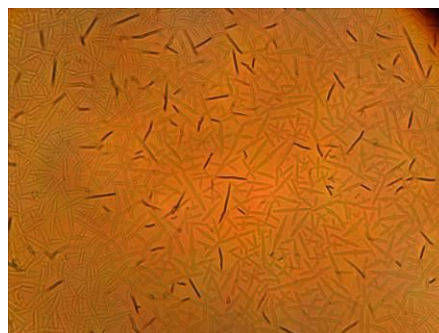


Fig. 5 – Micrograph of a film of a solution containing 12.5 g/l (magnification × 400) after drying at 80 °C

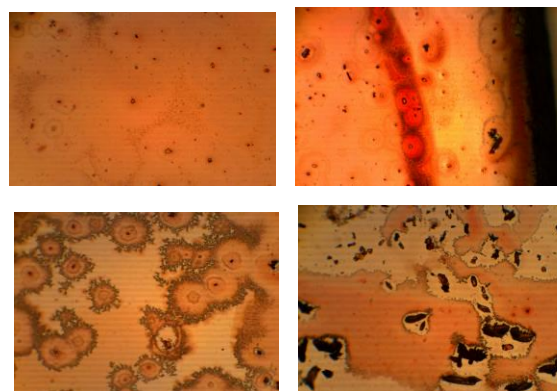


Fig. 6 – The amorphous film of the polymer, 25 g/l, undissolved particles × 400 (left column – sample center) and × 100 (right column – sample edge)

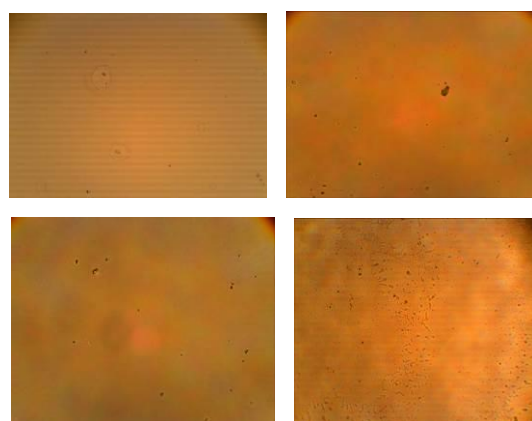


Fig. 7 – The polymer amorphous film, 12.5 g/l, a uniform region, × 400 (left column – sample center) and × 100 (right column – sample edge)

The results of studies on force microscope (shown microphotographs of films prepared from solutions of 25 g/l and 12.5 g/l in toluene) with magnification × 400 and × 100 showed that the optimal concentration is 12.5 g/l. When applying the film the number of local spin coating undissolved roughness and irregularities at such a concentration will be much less than with a con-

centration of 25 g/l as in the center of the film as at the edges (see Fig. 6 and 7). In pictures designs created, you can see the undissolved particles that had fallen into a new phase.

A comparison of these micrographs it can concluded that the polymer concentration of 12.5 g/l gives a sufficiently dense and relatively uniform film without substantial amounts of undissolved polymer

3. SUMMARY

For implementation further experimentation it is necessary to develop sufficiently reliable and reproducible method of forming photovoltaic cells based on polymers with additives of various acceptors, allowing to form single-layer film having a thickness of about 100 nm, as well as multilayer films, which may be necessary to increase the absorption of light by the polymer.

Using saturated solutions containing 25 grams per liter of the solvent gives rises to films not sufficiently dissolved polymer particles with size of a few microns, despite the ultrasonic influence on solution. Ability to effectively filter of these particles and their effect on the photovoltaic properties of the polymer are subject to further investigation, as saturated solutions with a concentration of 25 g/l give the greatest density of the thin film.

Desideration of saturated solution to be twice the

concentration of 12.5 g/l significantly reduces the size and concentration of insoluble particles in a synthetic film. Photovoltaic properties of these films are also subject to further investigation.

Growing of multilayer – from two-layer to six-layer – films is a more difficult task than getting a single-layer films, due to the possible dissolution of the upper layer of the pre-deposited film newly applied layer of liquid for subsequent spin coating. Comparison of the measured absorbance single or multilayer films showed a marked increase in the absorption of light in the most important area: 300-400 nm. Accurate measurement of the absorption increase with increasing film thickness can be carried out, if it need be, with the use of a monochromator and a calibrated UV detector.

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REFERENCES

1. S.A. Legotin, V.N. Murashev, F.M. Baryshnikov, A.A. Krasnov, O.I. Rabinovich, *Proceedings of the International Scientific and Technical Conference them. Leonardo da Vinci*, **1** 135 (2013).
2. A.S. Korolchenko, S.A. Legotin, S.I. Didenko, S.P. Kobeleva, M.N. Orlova, V.N. Murashev, *Russ. Microelectron.* **40** No 8, 620 (2011).
3. O.I. Rabinovich, S. Didenko, *Proceedings of the International Scientific and Technical Conference them. Leonardo da Vinci*, **1** 173 (2013).
4. O.I. Rabinovich, *Light Eng.* **21** No 2, 78 (2013).
5. O.I. Rabinovich, S.A. Legotin, S.I. Didenko, *J. Nano-Electron. Phys.* **6** No 3, 03021 (2014).
6. R. Po, M. Maggini, N. Camaioni, *J. Phys. Chem. C* **114** No 2, 695 (2010).
7. C.J. Brabec, *Sol. Energ. Mater. Sol. C.* **83**, 273 (2004).
8. M.Z. Hein, *Development and investigation of photoresist films at nonround substrates, PhD work* (M.: 2008).
9. M.N. Orlova, L.I. Kolesnikova, I.V. Schemerov, S.I. Didenko, *J. Nano-Electron. Phys.* **6** No 3, 03009 (2014).