

Formation of Polymer Films in Organic Photovoltaic Systems

M.N. Orlova¹, L.I. Kolesnikova², I.V. Schemerov¹, S.I. Didenko¹

¹ National University of Science and Technology "MISiS", 4, Leninsky Pr., 119049 Moscow, Russia

² The Institute of Energy Problems of Chemical Physics named by V.L. Talrose of Russian Academy of Sciences, 38, Leninsky Pr., 119344 Moscow, Russia

(Received 19 May 2014; revised manuscript received 01 July 2014; published online 15 July 2014)

The influence of elementary processes on the effectiveness of an organic semiconductor based photovoltaic cell designed for energy conversion is highly dependent on the active polymer layer structure. The most urgent task is, therefore, to develop experimental methods for forming films of organic semiconducting polymers with various structures from thin (monolayer films) a few nanometers thick to multilayer ones up to a few micrometers thick.

Research has indicated that the layer morphology of the films obtained (up to 350 nm thick) gives reason to postulate film structure and composition being dependent on the value of relative fluorescence variation under the influence of a superimposed magnetic field. Moreover, the transmittance and absorption spectra of polymer films which in many ways define the architecture of a photovoltaic cell are highly dependent on the concentration of solutions in the 300-325 nm wavelength range.

Keywords: Photovoltaic cell, Organic semiconductors, Polymer, Magnetic effect.

PACS numbers: 85.60.Bt, 85.40.Ls, 85.60. – q,
84.60.Jt

1. INTRODUCTION

Research in organic semiconductors has recently become quite essential for both organic chemistry and for scientific fields up till now fairly remote from organic chemistry such as physics, energy development and a number of related disciplines. There can be a number of reasons behind this interest, the most significant of which being unique physical and chemical properties of films that contain a great variety of organic compounds on the one hand, and a very wide range of possibilities of contemporary polymer chemistry for creating new substances with pre-defined properties at a significantly lower cost as compared to inorganic semiconductors both in production and in practical application.

One of the most interesting lines of this research is creating and studying the abilities of photovoltaic cells to convert solar power into electric energy. Numerous studies [1-4] in this field have indicated not only prospective viability of this direction in terms of alternative energy, but also suggested considerable difficulties in understanding primary elementary processes of organic converters. Such as virtually complete inapplicability of classical band theory to polymer photovoltaic cells which is closely related to numerous intermediate particles participating in the processes of forming of, and transporting, free carriers. A number of other difficulties have also appeared which could be overcome – in order to produce fairly effective photoconverters – only through applying fundamental knowledge of elementary processes occurring in organic photovoltaic systems. These include the most basic interactions in which the particles under consideration might participate such as ionization, recombination, charge exchange, excitation etc.

The way such elementary processes influence the efficiency of a photovoltaic cell designed for energy conversion depends significantly upon active polymer layer structure.

So the most actual task is to develop experimental methods for forming films of organic semiconducting polymers with different structures from thin (monolayer films) a few nanometers thick to multilayer films a few micrometers thick.

One of the principal groups of such processes are formation, transportation and interaction of the Frenkel excitons in an organic semiconductor. These interactions can be of varying character which has not yet been thoroughly investigated. Very little is known about the speed of diffusion and factors that determine the process.

All of that is to be a subject of detailed research to figure out the optimum characteristics of polymer molecule structure, supramolecular structure of polymers as well as the solar cell architecture. Superimposing an external magnetic field and studying its influence on photoconductivity and fluorescence of the active polymer layer is one of the ways to investigate such interactions, and it provides a possibility to estimate the contribution of each specific group of elementary processes.

2. DESCRIPTION OF OBJECT AND INVESTIGATION TECHNIQUES

One of the principal and general requirements to solar cell samples under research is reproducibility of the characteristics to be measured. In this respect, organic semiconductors differ greatly from inorganic substances due to their chemical activity.

Solar cell characteristics depend not only upon the choice of material used to produce the working layer, but also upon the cell structure itself. The choice of a solar cell structure is a complicated issue. Due to exciton dissociation prior to its decay being a significant problem it is essential to make excitons diffuse quickly into donor-acceptor heterojunction which is the only place for the dissociation to be effective in a pure material. Thickness of an organic layer must be comparable

to the diffusion length of the carriers. Reducing organic layer thickness, however, leads to a reduction in the optical absorption constant.

The principal target parameters that characterize a solar cell are its photovoltage and fluorescence when exposed to electromagnetic solar spectrum radiation – derivatives of a whole number of elementary processes occurring in a cell and determining the complex mechanism of its functions [5].

The specific task to be solved in this work is to develop a methodology of applying a semiconductor polymer onto the substrate to produce a solar cell. To this end, the centrifuge method has been selected. This method is well-known as “spin coating” and it allows to define the thickness and to control the film’s homogeneity along the entire working area of a sample. This method implies a dose of a polymer solution being applied to the substrate, whereupon the substrate is rotated at constant angular velocity ω .

From the physical point of view the application of a polymer solution onto the substrates using the centrifuge method can be characterized in terms of two simultaneously occurring processes: removal of the solvent from the building polymer film and shifting of the polymer-atmosphere interface.

During centrifugation the film is being flattened over a period of several minutes. The time of spreading for the solution is proportional to the rotation frequency ω and can be estimated through interference colors on the plate after centrifugation. The flattened film then dries as a result of solvent evaporation. During centrifugation, after the original solution height has been decreased by 1 / 3 the evaporation terminates and the hard component concentration reaches its ultimate value when the substance transfer ceases completely due to high viscosity. At this point about 30 % of the solvent has left the film, and the evaporation during centrifugation reaches a transitional stage, after which the film begins to slowly dry. The drying itself occurs in a special drying cabinet at a temperature of 70 °C.

It should be noted, however, that the outcome of the film formation depends greatly upon the nature of the polymer, many of which are characterized by, among other things, high levels of potential oxidation. To avoid the influence of oxidation reactions an inert atmosphere, in which a solar cell were to be formed, would be required. In a form most conducive to physical investigations the sample would be a quartz or glass 10 × 20 cm rectangle 1 mm thick with an optically transparent conductive layer made of a mixture of indium and tin oxides, this mixture being applied in advance. The photovoltaic cell is being formed by coating the substrate with the active layer and with the second electrode.

The polymer under testing is a mixture of two isomeric – cis-transoid and trans-cisoid – forms, shown on Fig. 1.

As the Figure indicates, the polymer chain structure of both forms contains phenyl groups which prevent the molecule from irregular twisting. The polymer is characterized by a significant number of conjugated bonds conducive to movements of carriers.

Conjugated polymers are characterized by a unified collective system of electrons appearing as a result of overlapping p-electron clouds delocalized along the conjugated chain. Such polymers should thus, in general,

provide favorable conditions for movements of carriers. Photoelectric properties of such a polymer are related to optical absorption at junctions. Conjugated bonds in polymer molecules lead to a shift of the absorption band towards the long-wave region.

To study the magnetic effect the original magnetic field modulation is a linear modulation. This is necessary to be able to understand which magnetic field values lead to fluorescence and photovoltage variations. Magnetic field variation by rectangular pulses was chosen as the method as it provides maximum sensitivity.

Effect of a magnetic field on photovoltaic characteristics of organic semiconductors

The Wigner rule prohibits intercombination transitions between triplet and singlet particle states. In molecules with an even number of electrons and antiparallel spin orientation the multiplicity of the corresponding electron state is equal to one as

$$M = 2|S| + 1, \quad (1)$$

where S is the spin quantum number total.

Multiplicity states of $M = 1$ are called singlet states. If the spins of two electrons are parallel in a specific electron state of a molecule and the multiplicity of such states is three, these are called triplet states. If, however, a strong magnetic field is to be superimposed the inhibition could be overruled which is supposed to entail a photoconductivity or fluorescence intensity variation. Which offers an opportunity to determine the role singlet and triplet states play in the conversion process [6].

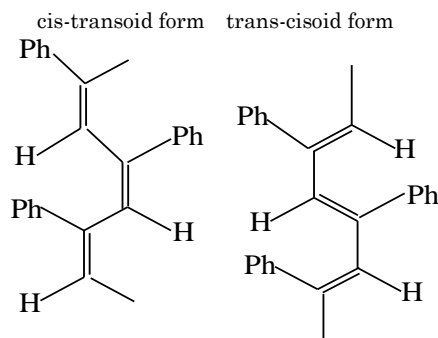


Fig. 1 – Structural formulae of principal isomers of the polymer applied

3. EXPERIMENTAL RESULTS

Results of research conducted by means of a force microscope at × 100 and × 400 magnification have indicated that the optimum solvent concentration would be 0.05 g/ml. The number of local nonsolutes, roughnesses and imperfections at such concentration would be much less than at a concentration of 0.1 g/ml – both in the centre of the film and at the edges (see Fig. 1 and 2).

Transmittance spectra obtained by means of a spectrophotometer are shown on Fig. 3 and 4.

Investigating the magnetic effect on oxidized films has indicated that, despite great losses in spectral characteristics, the film has retained the capacity to fluoresce although the value of relative fluorescent signal variation has dropped by around 10 %.

Provisional investigation of such magnetic effects has shown that layer morphology of the obtained films (up to

350 nm thick) gives reason to suggest a correlation between the structure and the composition of the films on the one hand and, on the other hand, the value of fluorescent signal relative variation after a magnetic field has been superimposed. Moreover, the transmittance spectra of polymer films which in many ways define the architecture of a photovoltaic cell are highly dependent on the concentration of solutions in the (300-325 nm) wavelength range.

4. CONCLUSIONS

The research in the properties of samples has indicated a large magnetic effect value of 15 % to 30 % depending on the type of film. Atomic force and digital microscopy made it possible to select the type of solvent and the optimum concentration for producing homogeneous films ($\sim 0,05$ g/ml) as well as the thickness

(~ 350 nm) to study the spectral characteristics. The investigation of oxidized layers has shown that the polymer structure retains the capacity to fluoresce even after interaction with oxygen. The value of the effect drops by no +more than 10 % even at significant variations in spectral characteristics. Studying the magnetic effect for samples with various structures allowed us to discover a relation between an increase in the magnetic effect and the morphology of the layers obtained.

ACKNOWLEDGMENTS

The work was carried out with financial support from the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of MISIS.

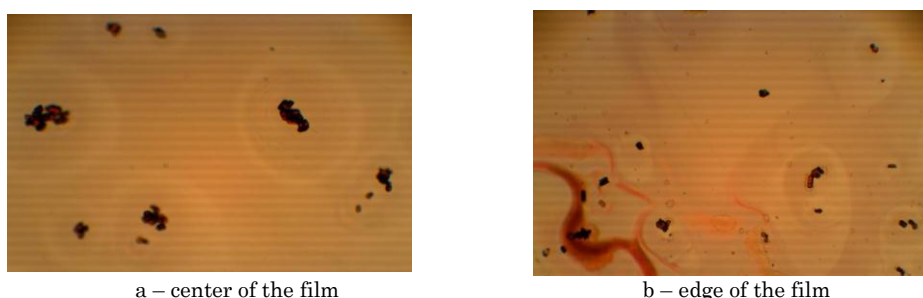


Fig. 1 – Polymer amorphous film, $C = 0.1$ g/cm³, non-dissolved particles, magnification $\times 400$ and $\times 100$ respectively

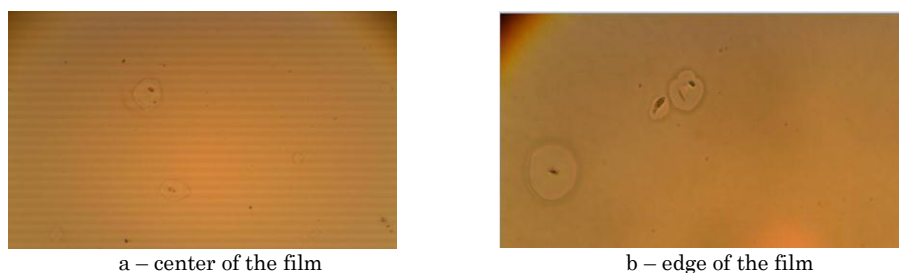


Fig. 2 – Polymer amorphous film, $C = 0.05$ g/cm³, area of uniformity, magnification $\times 400$ and $\times 100$ respectively

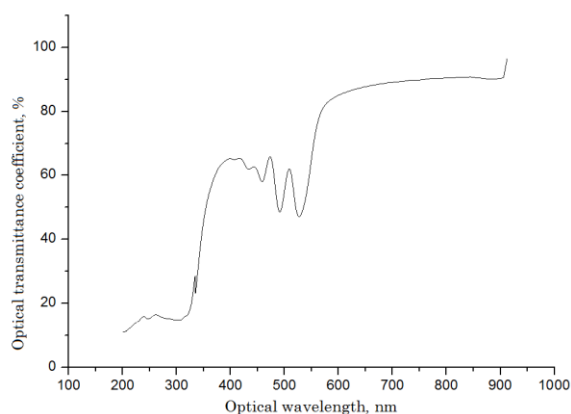


Fig. 3 – Transmittance spectrum. Sample thickness 300 nm ($C = 0.1$ mg/cm³)

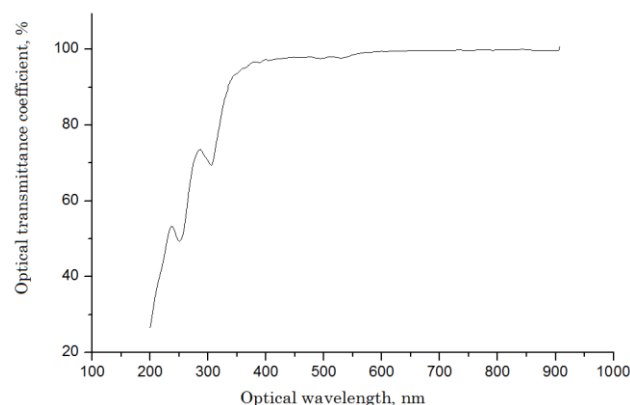


Fig. 4 – Transmittance spectrum for the 350 nm ($C = 0.05$ mg/cm³) sample

REFERENCES

1. R. Po, M. Maggini, N. Camaioni, *J. Phys. Chem. C* **114**, 695 (2010).
2. Yu. Parapikes, A.I. Kokorin, *Russ. Chem. Mag.* **52** No 6, 107 (2008).
3. C.J. Brabec, *Sol. Energ. Mater. Sol. C* **83**, 273 (2004).
4. L. Peter, *Acc. Chem. Res.* **42** No11, 1839 (2009).
5. A.S. Korolchenko, S.A. Legotin, V.N. Murashev, M.N. Orlova, *Metallurgist* **54** No 5-6, 328 (2010).
6. 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).