

Researches of topography and optical properties of the thin films NiPc/PTCDA donor acceptor couple

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Properties

ABSTRACT

Purpose: The aim of this work consists of researches of surface topography and optical properties of organic thin films of NiPc : PTCDA blends deposited by thermal evaporation from one source. Thin films of organic materials are provided as donor/acceptor couple in heterojunction solar cells.

Design/methodology/approach: Films consisting of NiPc and PTCDA mixture were deposited by thermal evaporation from one source. By using blends with different PTCDA to NiPc ratios and steering the temperature of the sources and hence deposition rate different properties of layers are obtained.

Findings: Both the chemical composition and technological parameters of deposition process has appeared to influence on optical properties and surface morphology of thin films. These parameters were found to influence surface morphology and UV-Vis absorption spectra.

Research limitations/implications: The paper shows the methodology of deposition NiPc/PTCDA donor/acceptor blends and the influence of evaporation parameters on properties of thin films. That can be used for the research of the planar heterojunction solar cells based on NiPc/PTCDA heterojunction donor-acceptor couple active layers.

Practical implications: Results of researches suggest that blends of NiPc and PTCDA can be useful materials in organic photovoltaic device. However right deposition parameters and the blends proportions determine the properties of NiPc/PTCDA donor/acceptor thin films.

Originality/value: The goal of this paper is to define the surface topography and optical properties of thin films NiPc/PTCDA blends prepared with different proportions of components and parameters of evaporation process.

Keywords: Organic thin films; Thermal evaporation; Donor acceptor couple; Phthalocyanine; PTCDA; UV-Vis spectroscopy; AFM microscopy

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1. Introduction

Semiconducting organic compounds offer the possibility of simpler production of optoelectronic devices and photovoltaic cells in comparison with devices based on inorganic semiconductors [1,2].

Using the organic materials as group of industrial materials can strongly reduce the costs associated with the production of photovoltaic components and reduce the global consumption of silicon [3].

Adapting the organic materials for electronics, optoelectronics and photovoltaics makes possibility to use their property in conjunction with electrical conductivity and semiconductor properties [1-4].

Organic materials render possible to produce low weight and flexible electronic devices (light sources, low-cost integrated circuit boards, flexible solar cells) [6,7].

The main advantages of organic solar cells are [8-10]:

- the possibility of a simple production using economical technology, e.g. spin-coating (wet production) or evaporation technologies (dry production);
- material savings: relatively small required thickness of the organic material (100 nm);
- simplicities of processing in order to obtain the required energy gap between conduction and valence bands, charge carriers transport, as well as the solubility and other structural properties;
- wide range of possible chemical structures of organic materials which can be mixed.

The researches have been focused primarily on improving the efficiency above 15%. The second most important aim of researches is reducing the cost of photovoltaic devices and hence "solar" electricity [6,9].

One of the main problems in the technology of organic solar cells is developing the technology of preparing the layered structures containing the p-n junction [8].

Therefore, the search for optimal solutions includes not only the development of a material with suitable properties but also the technology selection process [1-9].

In case of inorganic p-n junction the contact of p- and n-type semiconductors results in charges flows, so that electric field is created. This electric field and large dielectric constants of these materials make exciton dissociation very easy and quick [10-12].

In case of organic materials the energy gained by the transition of electron from the electron donor material to the electron acceptor one must be sufficient to overcome the exciton binding energy in the donor polymer [8].

Nowadays appropriate charge separation was carried out in different configurations of cells [8,13-15]:

- bilayer cell structure consisting of n-type and p-type semiconductors ("sandwich" structure);
- bulk heterojunction cell structure consisting the mixture of the p-type and n-type semiconductors (Fig. 1);
- tandem cells consisting of combination of n-type and p-type semiconductors.

In organic bilayer cells generated excitons must reach the donor/acceptor interface where charge separation is done [15].

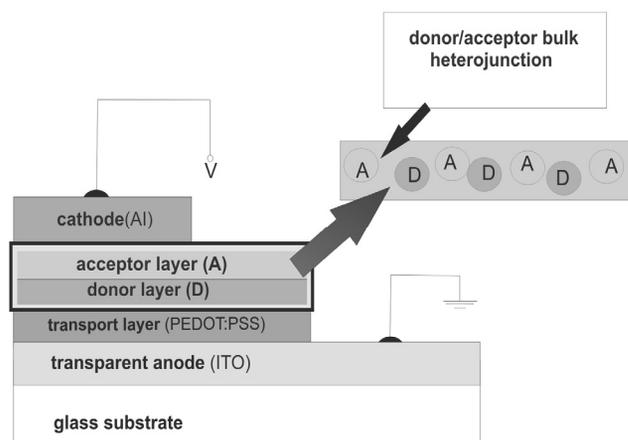


Fig. 1. Scheme of bilayer and bulk heterojunction solar cells structures [13-15]

One limitation is that in case of organic semiconductors the diffusion length range of the exciton is only 10 nm, so that the thickness of active layers in bilayer systems must be less than 20 nm. Higher thickness of organic films lead to charge recombination and lost of effect. However, active layer thickness of 20 nm has very low energy conversion efficiency due to the limited number of absorbed photons in such a small volume [16].

In case of bulk heterojunction, one can it as composed of two interpenetrating networks of electron donor and acceptor materials. Inside the blend films, particles of electron donor and electron acceptor are spaced apart by less than 10 nm in the entire volume, which makes donor/acceptor interface surface greater than this is the case for bi-layer contact surface between two semiconductors. Additionally, the active layer may have a much greater thickness than 20 nm, even up to 100 nm, and higher efficiency [14-16].

Organic materials compared with inorganic counterparts exhibit a much lower carrier mobility, but higher absorption coefficients allow them to absorb a sufficient amount of light for the cells to work effectively even when their thickness is of ~ 100 nm [14-16].

One of the most promising structures of organic cells use of insoluble organic semiconductor materials with low molecular weight, molecular structure of which is unattainable for polymer materials [14].

The possibility of achieving very high degree of chemical purity of the vacuum sublimation is the great advantage of the use of molecular organic semiconductors [1-14].

In particular, the metal phthalocyanine are often used as light absorbing material in photovoltaic devices due to their high absorption coefficient 10^5 cm^{-1} in a wide spectrum of solar radiation, as well as their high photochemical stability and their charge transport properties [14,18].

Phthalocyanine as an electron donor in photovoltaic devices are blended with the materials of high electron affinity serving as electron acceptors, such as C60 fullerene or perylene derivatives [19,20].

2. Experiment

2.1. Material and methodology

To study organic materials 3,4,9,10-Perylene tetracarboxylic dianhydride (PTCDA) and nickel phthalocyanine (NiPc) were chosen. PTCDA acts as an acceptor and NiPc acts as electron donor in in all the produced layers of such blends.

These materials meet the following criteria:

- possibility of using the vacuum evaporation process;
- availability in the international market;
- similar range of evaporating temperature.

Preliminary tests were made for each deposition rate of organic materials to determine suitable parameters of vacuum evaporation process and optimal temperature range of evaporation.

Organic thin films were deposited on glass boron-silicate (BK7) substrates. Substrates were prepared for evaporation process according by standard procedure which contains:

- rinsing in distilled water or deionized water;
- washing in an organic solvent in an ultrasonic washer;
- washing in acetone or methanole;
- drying in centrifuge.

Mixtures of perylene derivative and nickel phthalocyanine (PTCDA/NiPc) were prepared by mechanical mixing.

Evaporation process has been performed after obtaining the relevant homogeneity of the mixture.

For deposition thin films thermal vacuum evaporation from one sources was chosen.

Figure 2 show the scheme of the vacuum evaporation equipment.

The parameter changed during the researches was crucible temperature, which affects the changes of evaporation rate. In our study nine experiments were performed.

Summary of process parameters are presented in Table 1.

The growth rate of the deposited layers was determined by using a quartz crystal monitor.

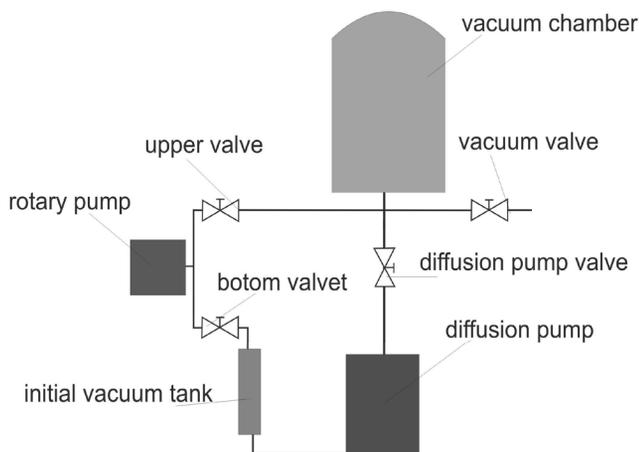


Fig. 2. Scheme of the vacuum evaporation equipment

Table 1.

Parameters of evaporation process

Layer number	PTCDA/NiPc mass ratio, %	Temperature of crucible, °C	Deposition rate, nm/sek
1	75/25	300	0.1
2	75/25	350	0.2
3	75/25	400	0.3
4	50/50	300	0.1
5	50/50	350	0.2
6	50/50	400	0.3
7	25/75	300	0.1
8	25/75	350	0.2
9	25/75	400	0.3

3. Results

UV-Vis absorption spectra taken on the as-deposited films are shown in Figures 3-11. The spectra cover energy interval spreading from 1.5 to 4 eV (wave-length range 420-820 nm).

UV-Vis spectra of samples deposited from the mixtures containing 75% wt. PTCDA and 25% wt. NiPc (layers 1, 2, 3) reveal strong peaks at about 2.3 and 2.6 eV. These values of strong absorption are characteristic for PTCDA (Fig. 12). One can see also for all samples peaks characteristic for nickelphthalocyanine (Fig. 13) are noticeable. It indicates the presence of phthalocyanine in samples however, in small amounts. In this case evaporation temperature and hence deposition rate have no apparent effect on the shape of the spectrum.

UV-Vis spectra of samples deposited from the mixtures containing 50% wt. PTCDA and 50% wt. NiPc (layers 4, 5, 6) also reveal high peaks in values characteristic for PTCDA. However peaks characteristic of nickelphthalocyanine are explicitly visible. The peaks characteristic of phthalocyanine are the strongest in the sample deposited with the highest evaporation temperature (layer 6). In this case increasing the evaporation temperature affects the strengthening peaks related to the phthalocyanine and to intensity reduction of the peaks characteristic of the perylene derivative.

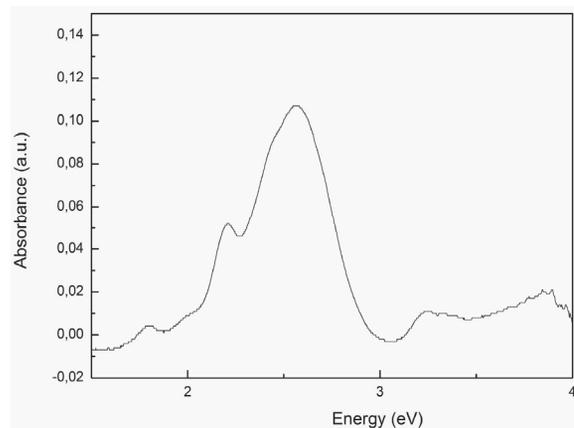


Fig. 3. Spectra of UV-Vis absorption thin film of layer 1 (evaporated at temperature 300°C from mixture of 75% wt. PTCDA and 25% wt. NiPc)

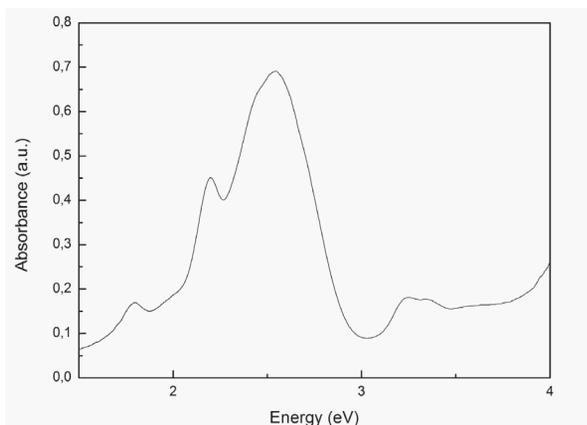


Fig. 4. Spectra of UV-Vis absorption of thin films of layer 2 (evaporated at temperature 350°C from mixture of 75% wt. PTCDA and 25% wt. NiPc)

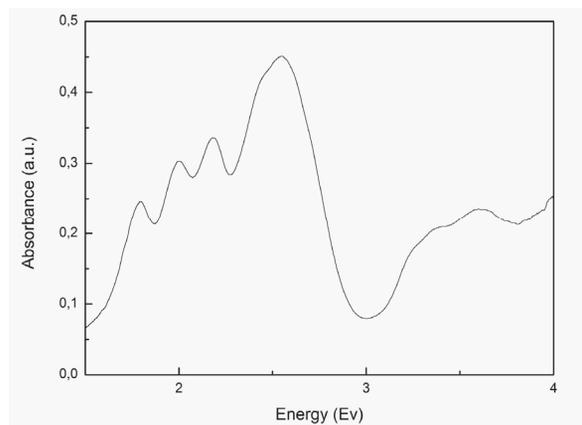


Fig. 7. Spectra of UV-Vis absorption of thin films of sample 5 (deposited at temperature 350°C from mixture of 50% wt. PTCDA and 50% wt. NiPc)

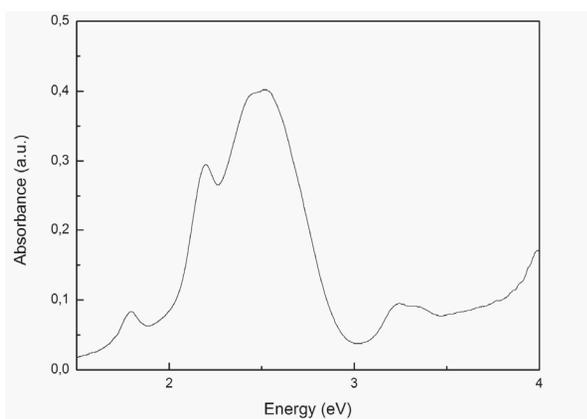


Fig. 5. Spectra of UV-Vis absorption of thin films of layer 3 (evaporated at temperature 400°C from mixture of 75% wt. PTCDA and 25% wt. NiPc)

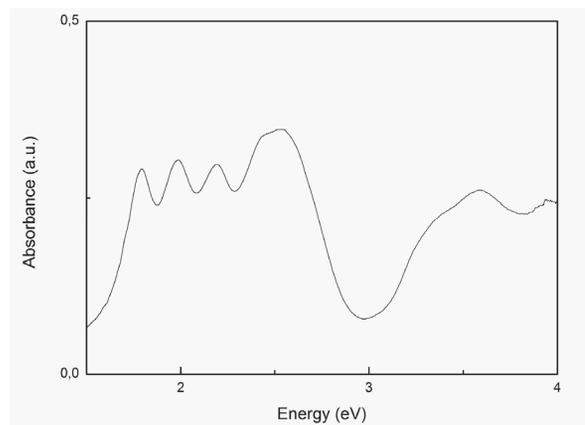


Fig. 8. Spectra of UV-Vis absorption of thin films of layer 6 (evaporated at temperature 400°C from mixture of 50% wt. PTCDA and 50% wt. NiPc)

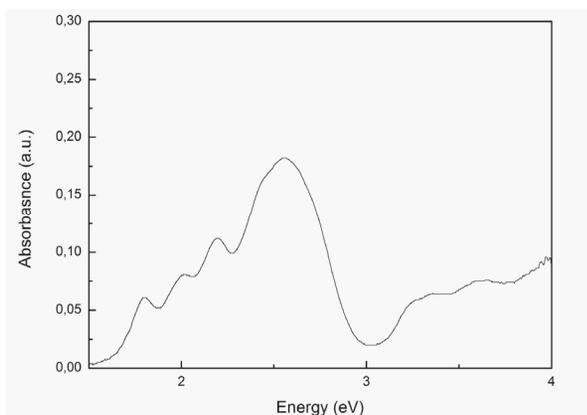


Fig. 6. Spectra of UV-Vis absorption of thin films of layer 4 (evaporated at temperature 300°C from mixture of 50% wt. PTCDA and 50% wt. NiPc)

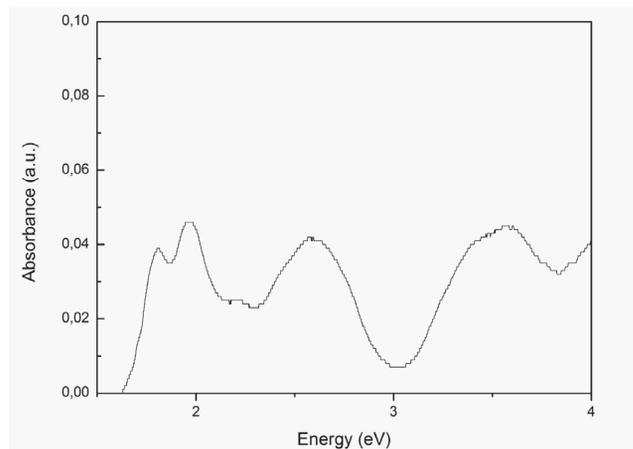


Fig. 9. Spectra of UV-Vis absorption of thin films of layer 7 (evaporated at temperature 300°C from mixture of 25% wt. PTCDA and 75% wt. NiPc)

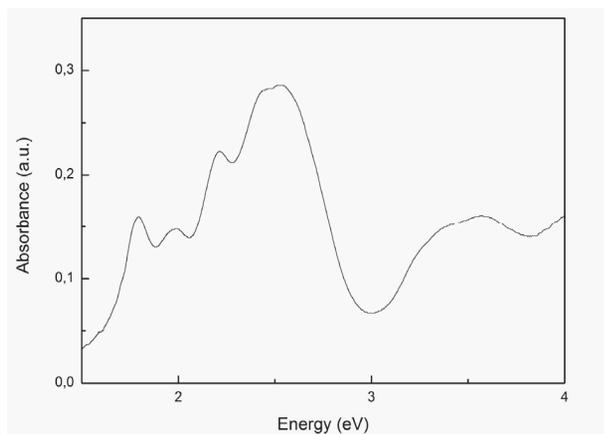


Fig. 10. Spectra of UV-Vis absorption of thin films of layer 8 (evaporated at temperature 350°C from mixture of 25% wt. PTCDA and 75% wt. NiPc)

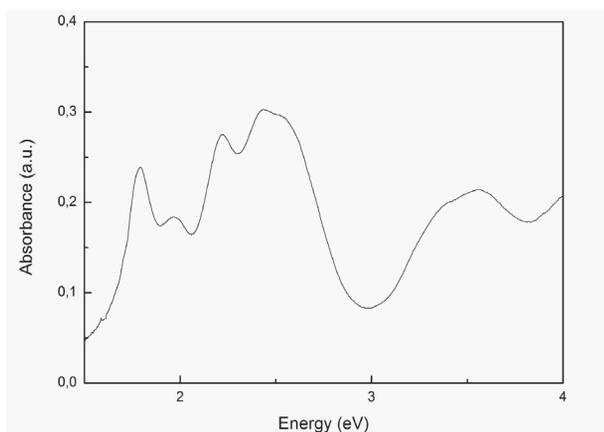


Fig. 11. Spectra of UV-Vis absorption of thin films of layer 9 (evaporated at temperature 400°C from mixture of 25% wt. PTCDA and 75% wt. NiPc)

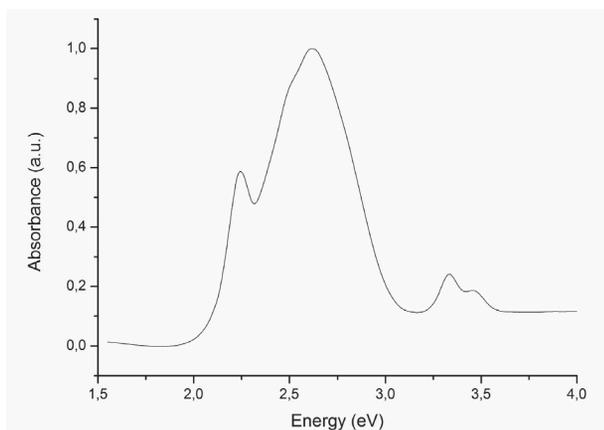


Fig. 12. Spectra of UV-Vis absorption of thin films of PTCDA

In case of UV-Vis spectra of samples deposited from the mixture containing 25% wt. PTCDA and 75% NiPc wt. (layers 7, 8, 9) reveals peaks characteristic of nickelphthalocyanine but peaks characteristic of PTCDA are still visible.

The peaks characteristic of phthalocyanine are strongest in sample deposited with the lowest evaporation temperature (layer 7). However in the other samples peaks typical for phthalocyanine are also strong, which suggest the high content of phthalocyanine in the films.

The morphology of thin films were studied with the use of Atomic Force Microscopy (AFM).

AFM is a basic tool for research of surface topography of organic thin layers. Due to the very low hardness of deposited films, to image layer surface noncontact mode of AFM was used.

Topographic images of thin films surfaces are shown in Figs. 14-22.

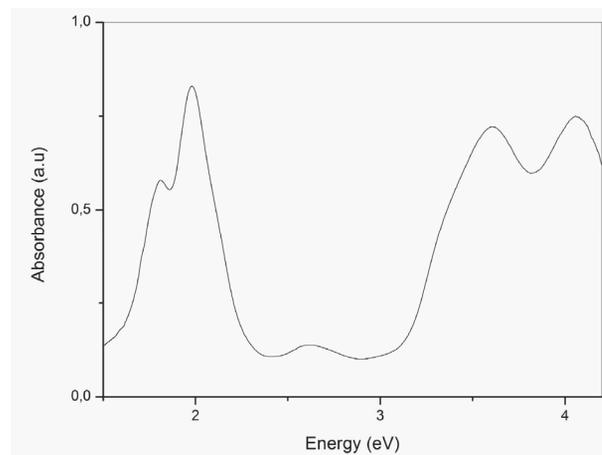


Fig. 13. Spectra of UV-Vis absorption of thin films of NiPc

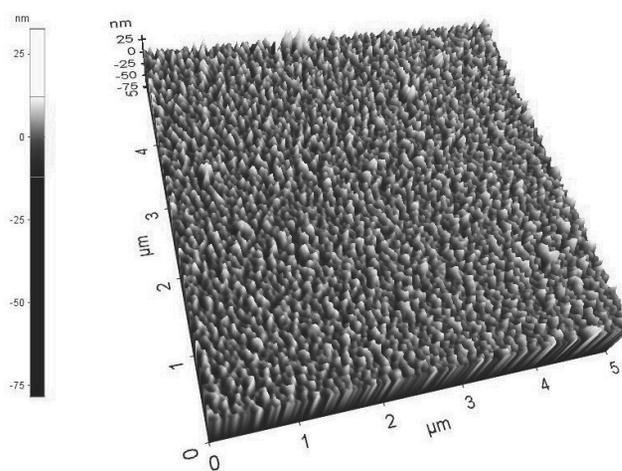


Fig. 14. Topographical image of a surface of layer 1 (evaporated at temperature 300°C from mixture of 75% wt. PTCDA and 25% wt. NiPc)

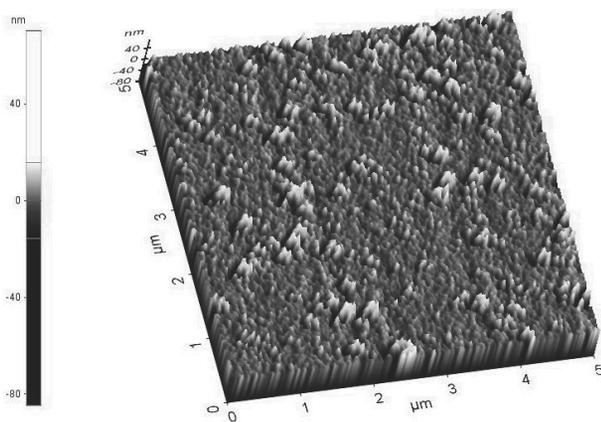


Fig. 15. Topographical image of a surface of layer 2 (evaporated at temperature 350°C from mixture of 75% wt. PTCDA and 25% wt. NiPc)

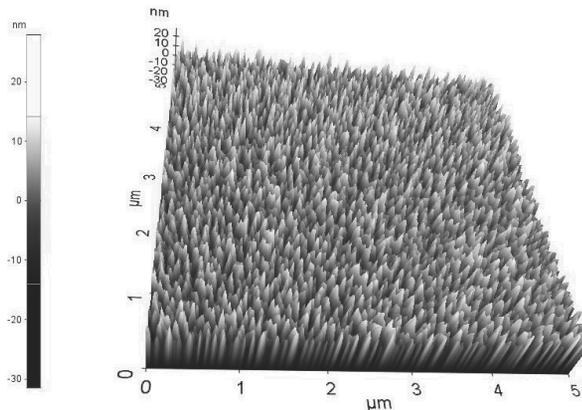


Fig. 16. Topographical image of a surface of layer 3 (evaporated at temperature 400°C from mixture of 75% wt. PTCDA and 25% wt. NiPc)

Layers deposited from mixture containing of 25% wt. NiPc and 75% wt. PTCDA (layers 1,2,3) characterized granular structure, indicating the columnar growth. Additionally, the temperature of the crucible and, in result, layer growth rate clearly affects its surface topography.

Granules in sample 2 are more thicker, which may suggest the merging neighboring granules during the deposition process.

Additionally, films evaporated at the lowest temperature (300°C) is characterized by a homogeneous surface with a few inequality. Layer evaporated at higher temperature (layer 2) has unevenness on the surface. Layer prepared at from the highest temperature (layer 3) similarly like layer 1 reveal granular structure and the granules have comparable thickness. However layer 3 has most heterogeneous surface and the highest surface roughness.

In the case of mixture containing 50% wt. NiPc and 50% wt. PTCDA (layers 4, 5, 6) granules size for the layers 4 and 5 are very similar, in contrast to films prepared at 300°C and 350°C temperatures for mixture of 75% wt. PTCDA and 25% wt. NiPc.

Temperature of the crucible and in result layer growth rate affects surface topography. Thin film evaporated with the lowest temperature (layer 4) and higher temperature (layer 5) has a few unevenness on the surface but in this case differences between topography are barely visible.

Layer made from the highest temperature (layer 6) has heterogeneous surface, the high surface roughness and a number of inequalities. Surface inhomogeneities of the last layer in this case are stronger than in case of layer deposited from mixture of 75% wt. PTCDA and 25% wt. NiPc (layers 1,2,3).

Likewise in previous cases layers deposited from mixture of 50% wt. NiPc and 50% wt. PTCDA (layers 4,5,6) presented a granular structure. It can be assumed that their growth is columnar.

Films deposited from mixture containing 75% wt. and NiPc 25% wt. PTCDA (layers 7,8,9) presented a granular structure, but only for the layer deposited with lowest deposition rate. Thin film evaporated with the higher temperature (350°C and 400°C) has more compact structure which suggest strong granule merging. Layer 8 has few unevenness on the surface. In case of layer 9 it can be noticed that layer made from the highest temperature has porous surface.

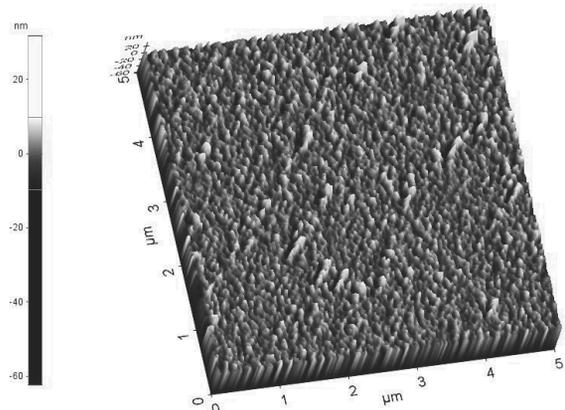


Fig. 17. Topographical image of a surface of layer 4 (evaporated at temperature 300°C from mixture of 50% wt. PTCDA and 50% wt. NiPc)

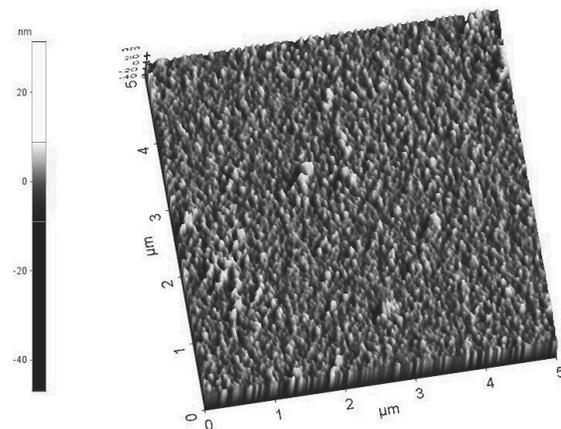


Fig. 18. Topographical image of a surface of layer 5 (evaporated at temperature 350°C from mixture of 50% wt. PTCDA and 50% wt. NiPc)

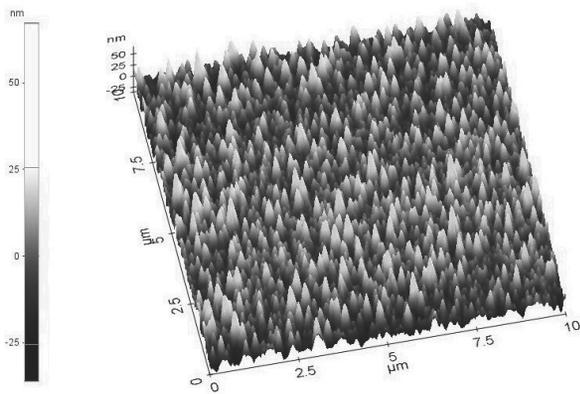


Fig. 19. Topographical image of a surface of layer 6 (evaporated at temperature 400°C from mixture of 50% wt. PTCDA and 50% wt. NiPc)

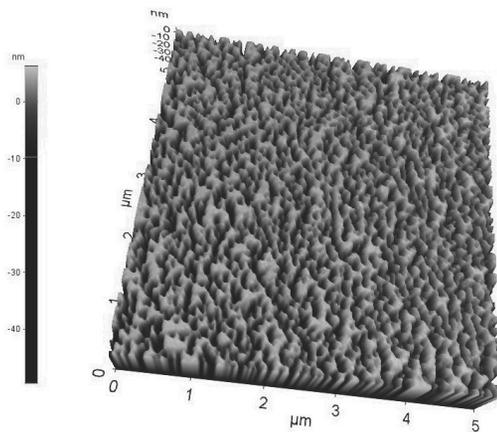


Fig. 22. Topographical image of a surface of layer 9 (evaporated at temperature 400°C from mixture of 75% wt. PTCDA and 25% wt. NiPc)

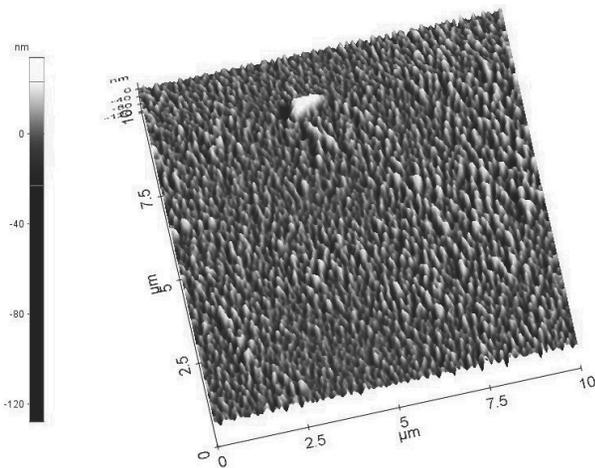


Fig. 20. Topographical image of a surface of layer 7 (evaporated at temperature 300°C from mixture of 75% wt. PTCDA and 25% wt. NiPc)

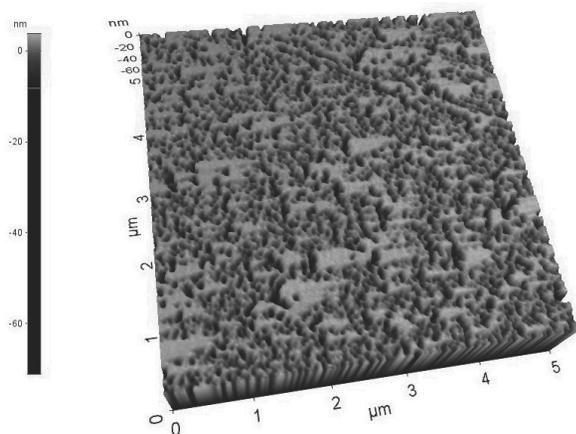


Fig. 21. Topographical image of a surface of layer 8 (evaporated at temperature 350°C from mixture of 75% wt. PTCDA and 25% wt. NiPc)

4. Conclusions

The absorption spectrum of PTCDA reveal energy interval with very high absorbance while NiPc spectrum reveals in the same range very low absorption. Then, one can expect that light absorption band in PTCDA:NiPc solid solution will be larger than in each of them. One can see that absorption distribution in case of the as-deposited thin films depends on compositions of starting material and the source temperature. It can be seen that the absorbance strength of each component depends on its contents in the solid alloy and is proportional to its contents.

Additionally morphology of the as-deposited films depends on source temperature. Source temperature define evaporation rate, and in all of as-deposited films the surface of films deposited in the highest source temperature are characterized by the unequal surfaces. Results obtained for as-deposited films may also suggest that surface topography depends of composition of used mixture.

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References

- [1] H. Hoppe, N.S. Sariciftci, Organic solar cells: An overview, *Journal of Materials Researches* 19/7 (2004) 1924-1945.
- [2] J. Żmija, M.J. Małachowski, J. Zieliński, M. Waclawek, K. Ścieżka, Organic materials for electronics, *Metrology* 11/1-2 (2006) 69-81 (in Polish).
- [3] B. Hajduk, Researches of morphology and physical properties of thin films poliazometin, PhD Thesis, Gliwice 2012.

- [4] J. Wieszka, L.A. Dobrzański, P. Jarka, J. Jurusik, B. Hajduk, M. Bruma, J. Konieczny, D. Mańkowski, Studying of spin-coated oxad-Si properties, *Journal of Achievements in Materials and Manufacturing Engineering* 37/2 (2009) 505-511.
- [5] M.A. Green, Photovoltaic principles, *Physica E* 14 (2002) 11-7.
- [6] R. Koeppel, P.A. Troshin, A. Fuchsbaauer, R.N. Lyubovskaya, N.S. Sariciftci, Photoluminescence Studies on the Supramolecular Interactions Between a Pyrrolidinofullerene and Zinc-Phthalocyanine Used in Organic Solar Cells, *Fullerenes, Nanotubes, and Carbon Nanostructures* 14 (2006) 441-446.
- [7] M. Palewicz, A. Iwan, Poliazometine: properties and applications in photovoltaics, *Institute of electrical works*, 243, 2009
- [8] H. Derouiche, J.C. Berne'de, J.L'Hyver, Optimization of the properties of bulk heterojunctions obtained by coevaporation of Zn-phthalocyanine/perylene, *Dyes and Pigments* 63 (2004) 277-289.
- [9] M. Egginger, R. Koeppel, F. Meghdadi, P.A. Troshin, R.N. Lyubovskaya, D. Meissner, N.S. Sariciftci, Comparative studies on solar cell structures using zinc phthalocyanine and fullerenes, *Organic Optoelectronics and Photonics, Proceedings of the SPIE*, 6192, 2006.
- [10] L.A. Dobrzański, M. Musztyfaga, A. Drygała, P. Panek, Investigation of the screen printed contacts of silicon solar cells using Transmission Line Model, *Journal of Achievements in Materials and Manufacturing Engineering* 41 (2010) 57-65.
- [11] A. Drygała, L.A. Dobrzański, Materials for solar cells - state of the art and perspectives, *Materials for solar cells - state of the art and perspectives, Proceedings of the 12th International Scientific Conference "Achievements in Mechanical and Materials Engineering" AMME'2003, Gliwice-Zakopane, 2003*, 2-6.
- [12] LA Dobrzański, M Musztyfaga, A Drygała, P Panek, Electrical and optical properties of photovoltaic cells produced by screen printing method, *Electronics - Structures, Technologies, Applications* 5 (2010) 63-65 (in Polish).
- [13] H. Hoppe, N.S. Sariciftci, Morphology of polymer/fullerene bulk heterojunction solar cells, *Journal of Materials Chemistry* 16/45 (2006) 45-61.
- [14] D. K. Susarova, P.A. Troshin, D. Höglinger, R. Koeppel, S.D. Babenko, R.N. Lyubovskaya, V.F. Razumov, N.S. Sariciftci, Donor-acceptor complex formation in evaporated small molecular organic photovoltaic cell, *Solar Energy Materials & Solar Cells* 94 (2010) 803-811.
- [15] A. Tada, Y. Geng, Q. Wei, K. Hashimoto, K. Tajima, Tailoring organic heterojunction interfaces in bilayer polymer photovoltaic devices, *Nature Materials* 10 (2011) 450-455.
- [16] A. Pivrikas, M. Ullah, C. Simbrunner, H. Sitter, H. Neugebauer, N.S. Sariciftci, Comparative study of bulk and interface transport in disordered fullerene films, *Physical Status Solidi B* 248/11 (2011) 2656-2659.
- [17] D.K. Susarova, E.A. Khakina, P.A. Troshin, A.E. Goryachev, N.S. Sariciftci, V.F. Razumov, D.A.M. Egbe, Photovoltaic performance of PPE-PPV copolymers: effect of the fullerene component, *Journal of Dynamic Materials Chemistry* 21 (2011) 2356-2361.
- [18] D.A. Evans, H.J. Steiner, A.R. Vearey-Roberts, V. Dhanak, G. Cabailh, S. O'Brien, I.T. McGovern, W. Braun, T.U. Kampen, S. Park, D.R.T. Zahn, Perylenes and phthalocyanines on GaAs(0 0 1) surfaces, *Applied Surface Science* 212-213 (2003) 417-422.
- [19] R. Aïch, B. Ratier, F. Tran-van, F. Goubard, C. Chevrot, Small molecule organic solar cells based on phthalocyanine/perylene-carbazole donor-acceptor couple, *Thin Solid Films* 516 (2008) 7171-7175.
- [20] R. Ye, M. Baba, K. Suzuki, K. Mori, Structure and morphology of CuPc and F16CuPc p-n heterojunction, *Applied Surface Science* 254 (2008) 7885-7888.