



# Study of thin films for application in photovoltaic cells

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## ABSTRACT

**Purpose:** of this paper: The major aim of this paper was describing technical conditions of thermal evaporation method of organic thin film used as active layers for photovoltaic cells.

**Design/methodology/approach:** The organic thin films have been obtained by thermal evaporation process from two sources. The two sources technique alleged to using the mixtures of two kinds of materials on deposited substrate and created the bulk p-n junction. By steering the source temperature the deposited rate of substrates has been changed which has led to changes in the share component in the layer.

**Findings:** The obtained results describe the influence of evaporation process from two sources on optical properties and surface morphology of thin films which consist molecular materials - perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) and metal phthalocyanines (NiPc, TiOPc) blends.

**Research limitations/implications:** The morphology and optical properties of thin films made of organic materials MePc:PTCDA were described. This paper include also influence of physical vapor deposition process conditions on properties of thin films.

**Practical implications:** The obtained results allowed to create the bulk p-n junction. The MePc:PTCDA thin films can be used in photovoltaic applications.

**Originality/value:** The value of this paper is defining the optimal parameters of thermal evaporation from two sources for preparing MePc:PTCDA thin film with the best properties for photovoltaic applications. This paper describes the use of molecular materials for PVD technology. Results of these researches allowed to develop the technology of bulk heterojunction of molecular materials.

**Keywords:** MePc:PTCDA; Thin films morphology; AFM microscopy; PVD; Absorbance

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## PROPERTIES

### 1. Introduction

High interest in the use of organic materials is observed in recent years in electronics, particularly in optoelectronics and

photovoltaics [1]. At the moment, the solar cells technology is dominated by solar cells based on the inorganic materials, mainly crystalline and amorphous silicon, and to a lesser extent on gallium arsenide GaAs or copper indium selenide CuInSe [2]. However, it can be assumed that the proportion of cell based on

molecular organic materials and polymer is steadily increasing along with better knowledge and understanding of the chemical and electronic structure of these materials [2-6]. Organic semiconducting materials make possibility to easy and cheap production of optoelectronic devices and photovoltaic cells compared with devices built on inorganic semiconductors [7]. Flexible light sources and high surface displays, low-cost integrated circuit boards, flexible solar cells may be obtained through the use of organic compounds [8-11].

For many years intensively developed research on organic photovoltaic focused primarily on improving the efficiency, which is currently at a level not exceeding 10%, and reduce the cost of electricity production. One of the primary problems in the technology of organic solar cells is to develop a technology of layers comprising a p-n junction [8-12].

Therefore, the search for optimal solutions includes not only the development of a material having suitable properties, but also the selection of process conditions in the manufacturing process of the organic thin layers [13-14].

## 2. Materials and experiment conditions

In researches the organic materials have been used: perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) which acts as electron acceptor in all of deposited layers and nickel phthalocyanine (NiPc) which acts as an electron donor (Table 1).

The structural formulas of the molecules of used materials are shown in Figs. 1-2. Materials were subjected to a vacuum evaporation from two sources. Terms of thin film deposition of NiPc: PTCDA blends was modified by changing the source temperature of the layers component: PTCDA or NiPc. Detailed conditions of deposition processes are given in Table 1. Evaporation processes were also performed to NiPc:PTCDA thin films on substrates heated to 100°C while maintaining the remaining process parameters.

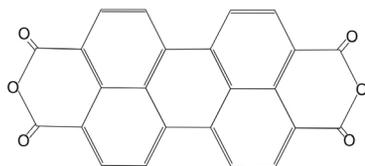


Fig. 1. The structural formula of the molecule PTCDA

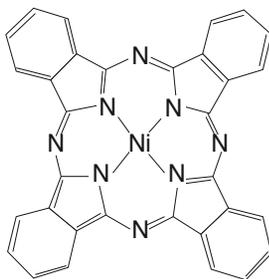


Fig. 2. The structural formula of the nickel phthalocyanine molecule

The measurement of the absorption spectra was performed using a single beam, UV-Vis spectrophotometer 4000 + HR Ocean Optics what enable to register, the entire range of visible light and near ultraviolet (in the wavelength range 200-1000 nm).

Table 1.  
Parameters of evaporation process from two sources

No.	Temperature of source containing PTCDA, °C	Temperature of source containing NiPc, °C
1	300	300
2	300	350
3	300	400
4	350	300
5	350	350
6	350	400
7	400	300
8	400	350
9	400	400

The thin layers of NiPc: PTCDA blends deposited on a (BK7) glass substrate have been investigated in the wavelength range 270-820 nm. An UV-Vis spectrophotometer was used, capable of measuring the intensity of the absorption spectra and determination of the components of the blends NiPc:PTCDA by identifying the position of the absorption maxima. The contribution of each component of NiPc:PTCDA blends was estimated based on a comparison of the obtained absorption spectra with the spectra generated by summing the absorption spectra of components. The NiPc spectra are characterized by a minimal absorption in the range in which the PTCDA absorption has maximal value. As the intensity of the absorption reflects the interest component in the layer, so the spectrum of the mixture NiPc:PTCDA was calculated from the formula (1) and (2):

$$I_{NiPc:PTCDA} = a \cdot I_{NiPc} + b \cdot I_{PTCDA} \quad (1)$$

where:

a - content of PTCDA,

b - content of NiPc,

$I_{NiPc}$  - the absorbance value of NiPc,

$I_{PTCDA}$  - the absorbance value of PTCDA;

Estimates of nutrient content in the blend was based on the values of the coefficients a and b, which resulted in the absorption spectrum of the sum of the components, similar to the obtained spectrum.

## 3. Results

The Figs. 3-5 present absorbance measurements of the NiPc:PTCDA layers comparing with the spectra obtained by submitting NiPc and PTCDA spectra. Absorbance measurements of NiPc:PTCDA layers on the substrate at a temperature of 100°C comparing with spectra obtained by submitting NiPc and PTCDA spectra are shown in Figs. 6-8.

Figs. 9-17 show the images of surface topography of NiPc:PTCDA layers deposited on the substrate at room temperature. Images of surface topography of NiPc:PTCDA layers deposited on the substrate at temperature of 100°C are presented in Figs. 18-26.

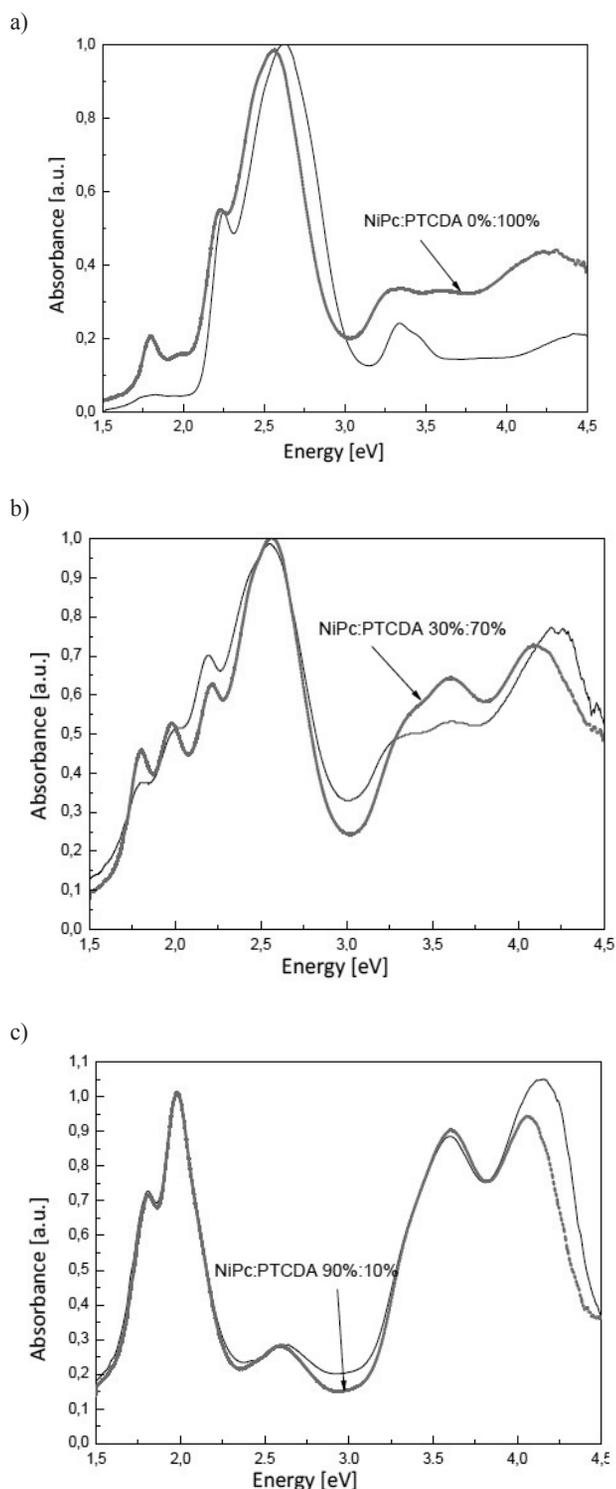


Fig. 3. Absorption spectrum of the organic thin film formed on the substrate at room temperature from two sources at a temperature of: a) 300°C for PTCDA, and 300°C for NiPc, b) 300°C for PTCDA and 350°C for NiPc, c) 300°C for PTCDA and 400°C for NiPc, obtained using a UV-Vis spectrophotometer

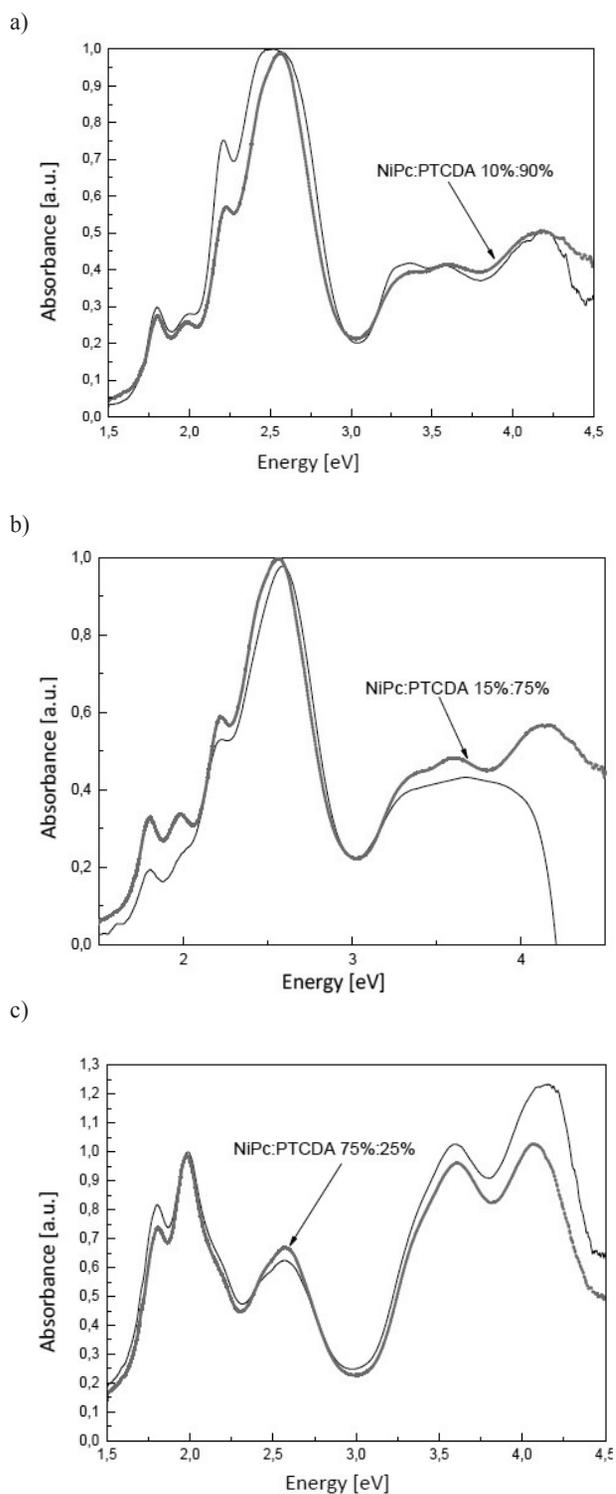


Fig. 4. Absorption spectrum of the organic thin film formed on the substrate at room temperature from two sources at a temperature of: a) 350°C for PTCDA, and 300°C for NiPc, b) 350°C for PTCDA and 350°C for NiPc, c) 350°C for PTCDA and 400°C for NiPc, obtained using a UV-Vis spectrophotometer

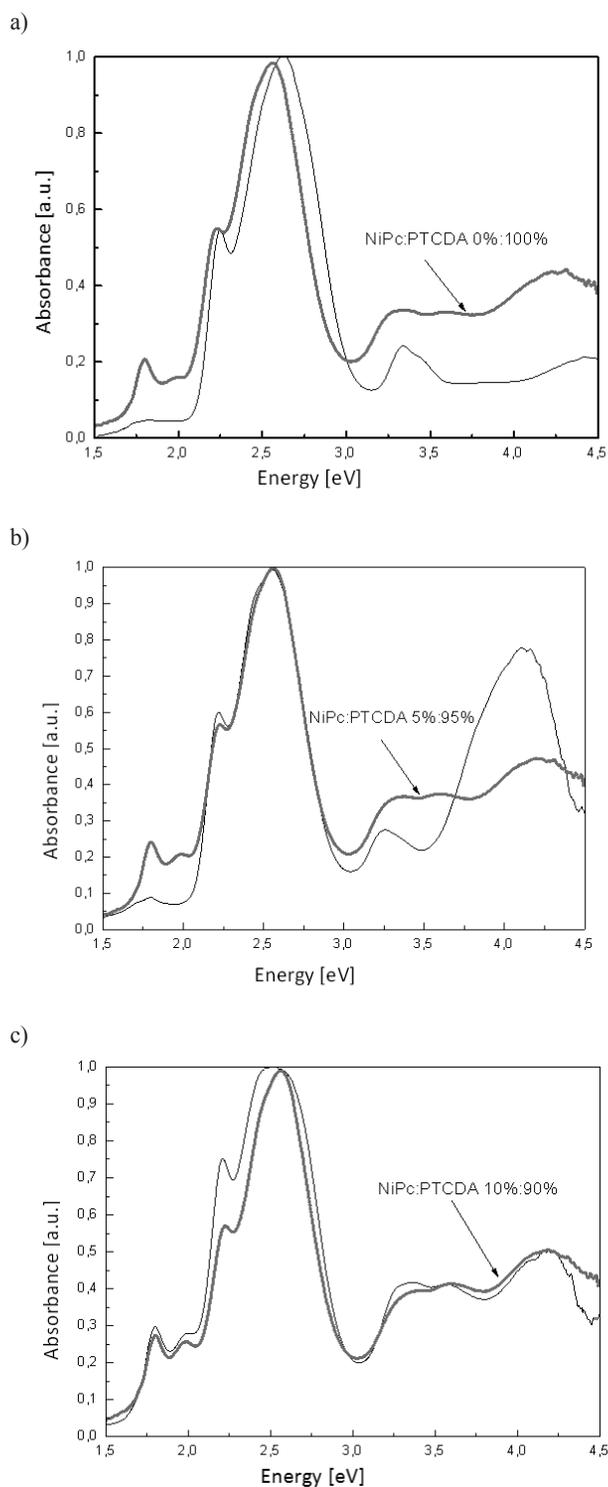


Fig. 5. Absorption spectrum of the organic thin film formed on the substrate at room temperature from two sources at a temperature of: a) 400°C for PTCDA, and 300°C for NiPc, b) 400°C for PTCDA and 350°C for NiPc, c) 400°C for PTCDA and 400°C for NiPc, obtained using a UV-Vis spectrophotometer

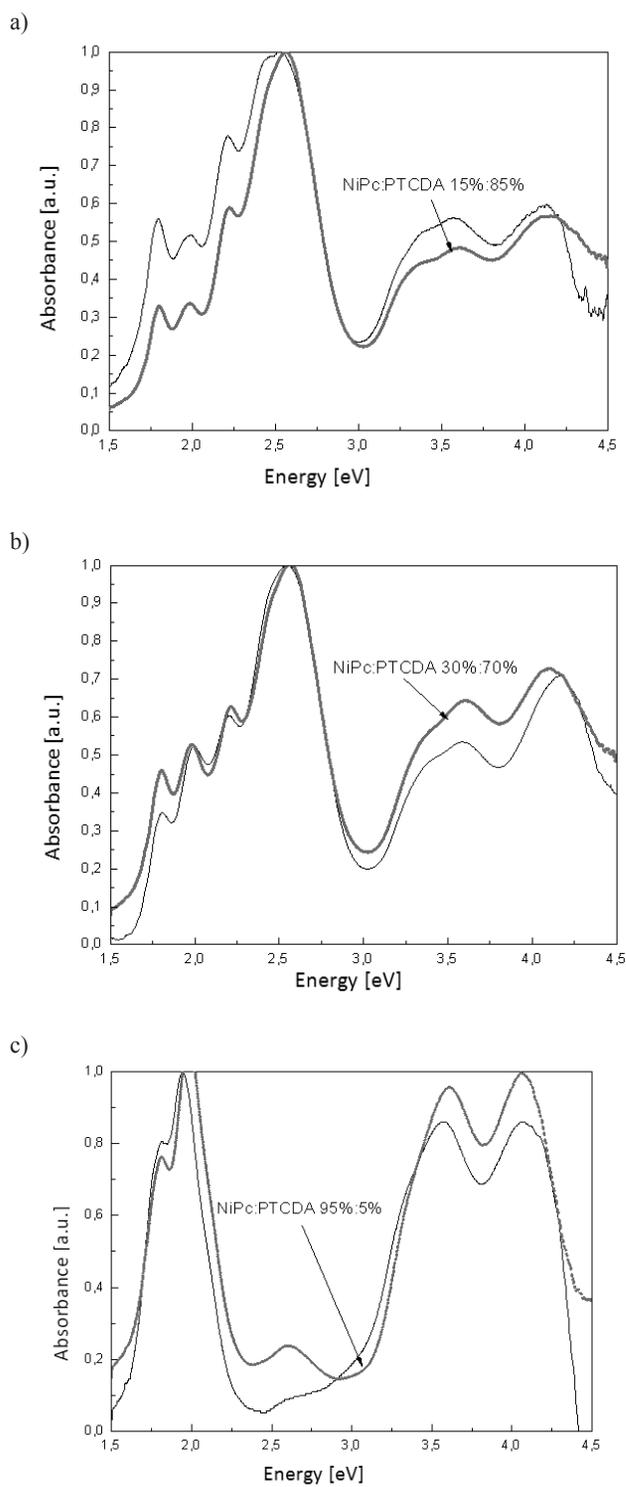


Fig. 6. Absorption spectrum of the organic thin film formed on the substrate at temperature of 100°C from two sources at a temperature of: a) 300°C for PTCDA, and 300°C for NiPc, b) 300°C for PTCDA and 350°C for NiPc, c) 300°C for PTCDA and 400°C for NiPc, obtained using a UV-Vis spectrophotometer

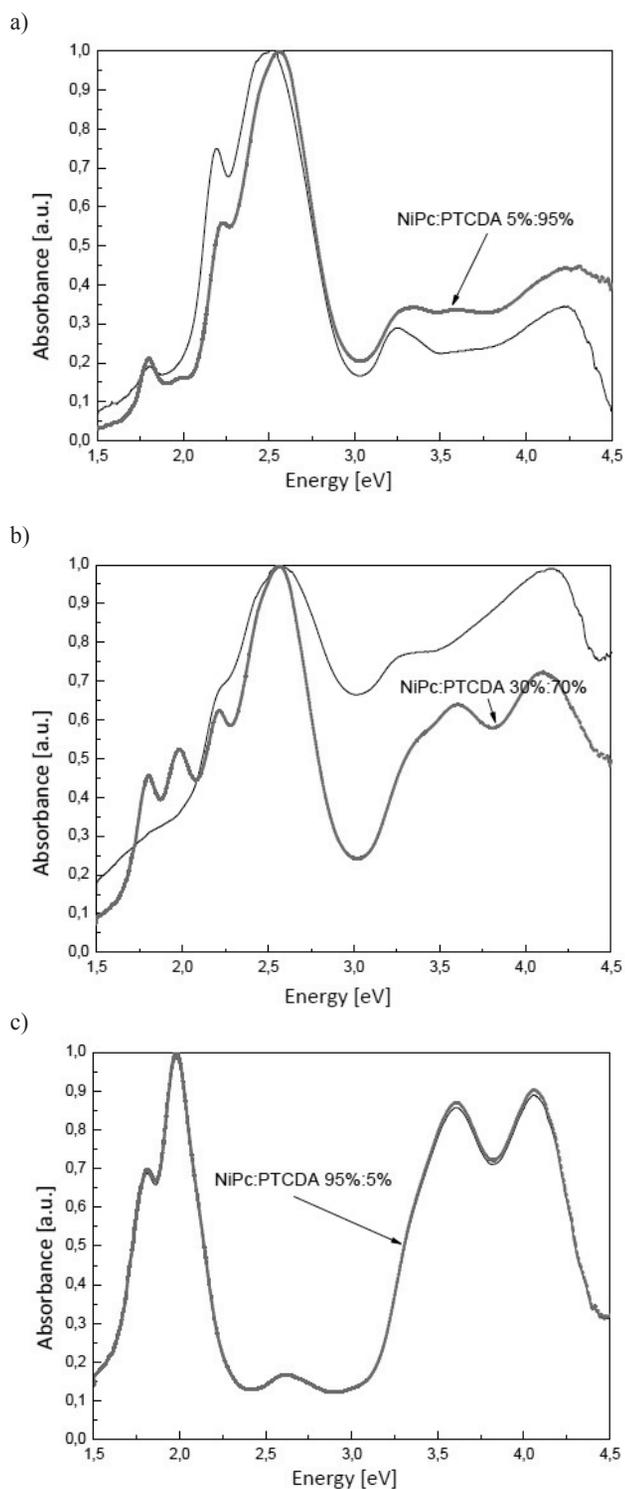


Fig. 7. Absorption spectrum of the organic thin film formed on the substrate at temperature of 100°C from two sources at a temperature of: a) 350°C for PTCDA, and 300°C for NiPc, b) 350°C for PTCDA and 350°C for NiPc, c) 350°C for PTCDA and 400°C for NiPc, obtained using a UV-Vis spectrophotometer

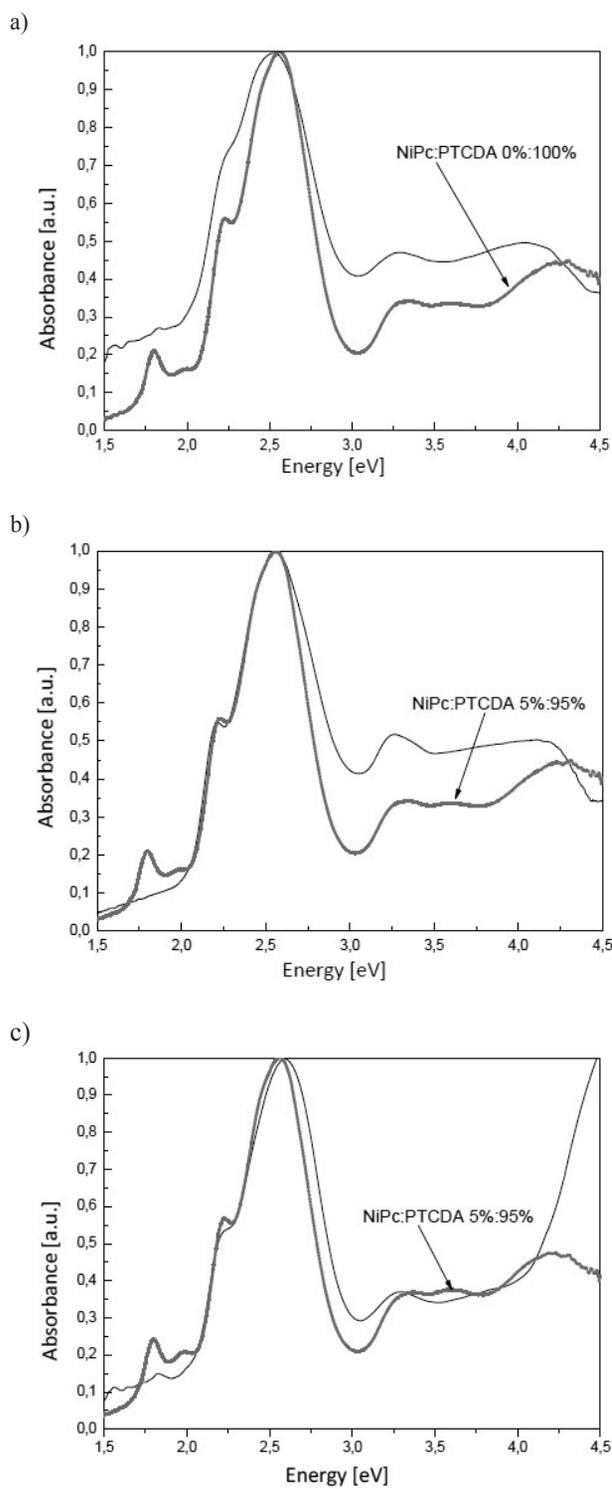


Fig. 8. Absorption spectrum of the organic thin film formed on the substrate at temperature of 100°C from two sources at a temperature of: a) 400°C for PTCDA, and 300°C for NiPc, b) 400°C for PTCDA and 350°C for NiPc, c) 400°C for PTCDA and 400°C for NiPc, obtained using a UV-Vis spectrophotometer

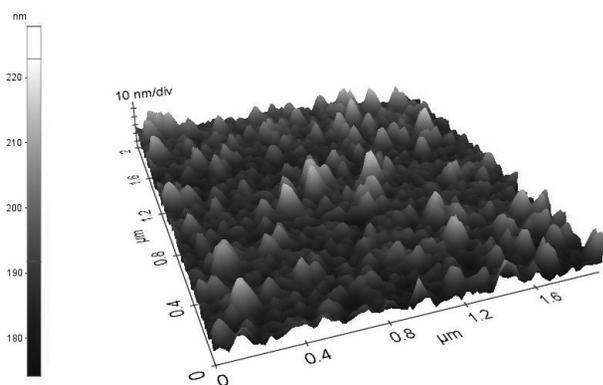


Fig. 9. Topographic image of the surface of the organic thin film formed on the substrate at room temperature by vapor deposition from two sources with a temperature of 300°C for PTCDA and at 300°C for NiPc

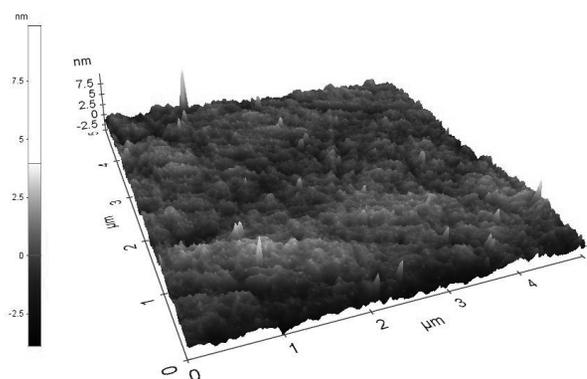


Fig. 12. Topographic image of the surface of the organic thin film formed on the substrate at room temperature by vapor deposition from two sources with a temperature of 350°C for PTCDA and at 300°C for NiPc

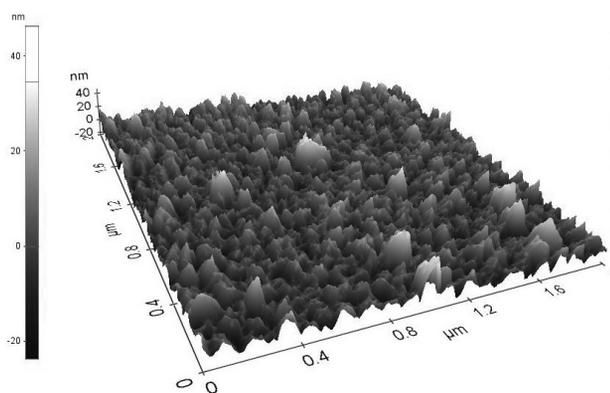


Fig. 10. Topographic image of the surface of the organic thin film formed on the substrate at room temperature by vapor deposition from two sources with a temperature of 300°C for PTCDA and at 350°C for NiPc

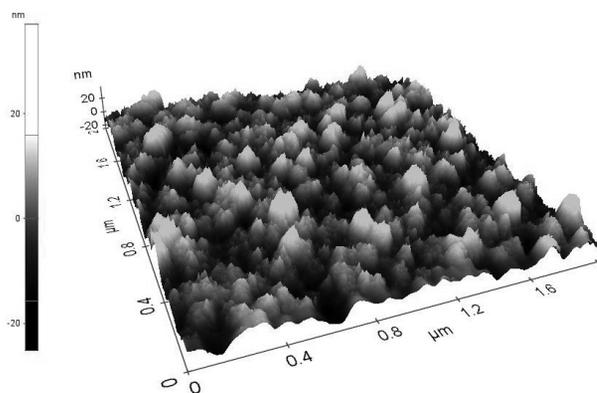


Fig. 13. Topographic image of the surface of the organic thin film formed on the substrate at room temperature by vapor deposition from two sources with a temperature of 350°C for PTCDA and at 350°C for NiPc

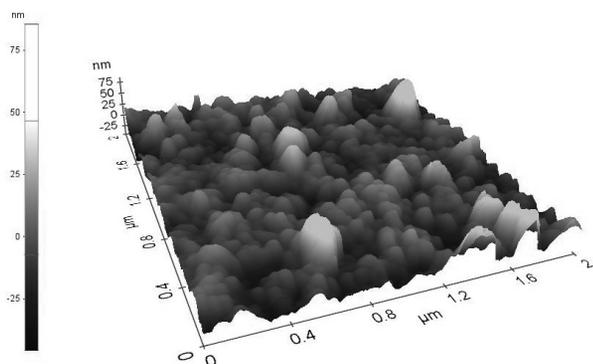


Fig. 11. Topographic image of the surface of the organic thin film formed on the substrate at room temperature by vapor deposition from two sources with a temperature of 300°C for PTCDA and at 400°C for NiPc

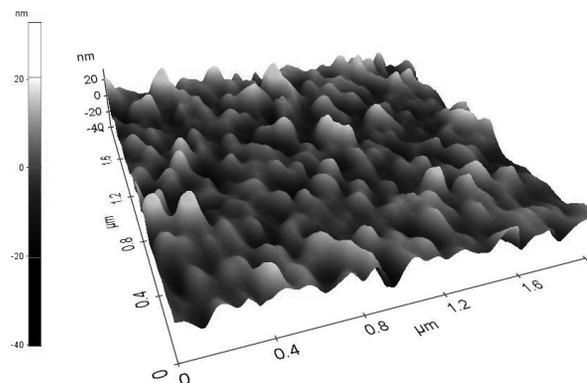


Fig. 14. Topographic image of the surface of the organic thin film formed on the substrate at room temperature by vapor deposition from two sources with a temperature of 350°C for PTCDA and at 400°C for NiPc

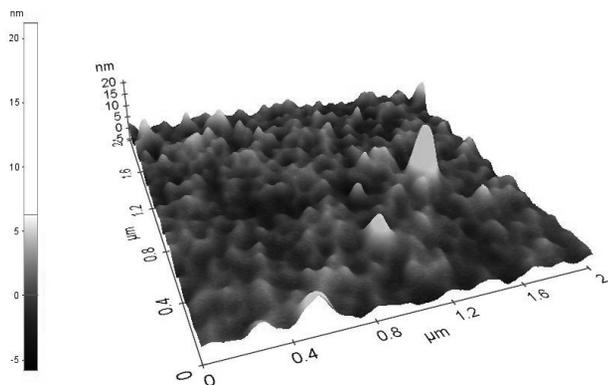


Fig. 15. Topographic image of the surface of the organic thin film formed on the substrate at room temperature by vapor deposition from two sources with a temperature of 400°C for PTCDA and at 300°C for NiPc

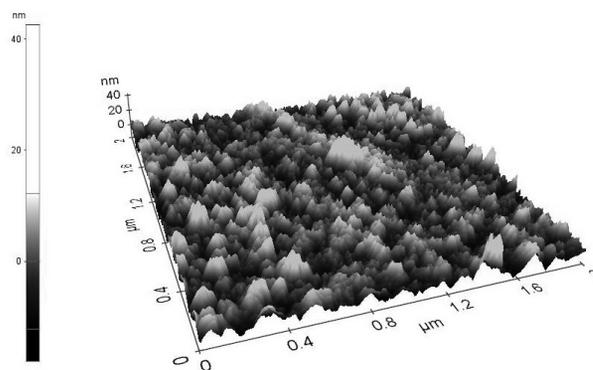


Fig. 18. Topographic image of the surface of the organic thin film formed on the substrate at temperature of 100°C by vapor deposition from two sources with a temperature of 300°C for PTCDA and at 300°C for NiPc

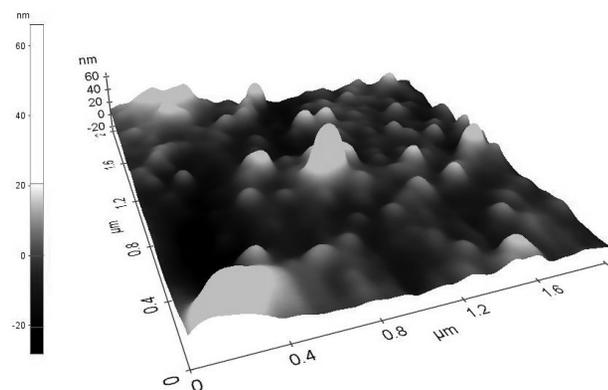


Fig. 16. Topographic image of the surface of the organic thin film formed on the substrate at room temperature by vapor deposition from two sources with a temperature of 400°C for PTCDA and at 350°C for NiPc

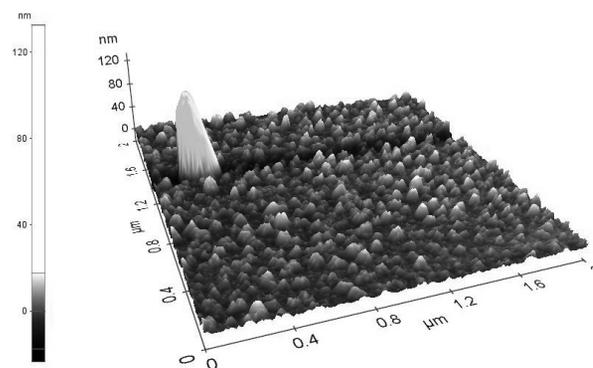


Fig. 19. Topographic image of the surface of the organic thin film formed on the substrate at temperature of 100°C by vapor deposition from two sources with a temperature of 300°C for PTCDA and at 350°C for NiPc

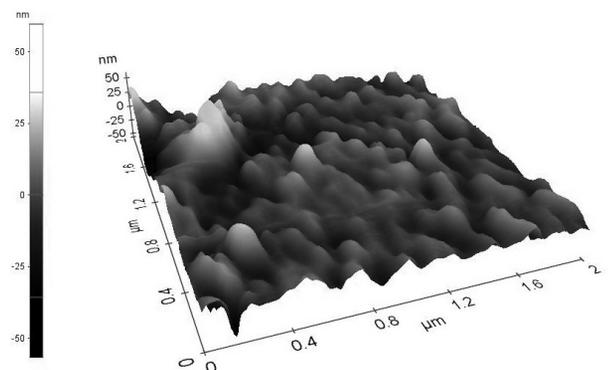


Fig. 17. Topographic image of the surface of the organic thin film formed on the substrate at room temperature by vapor deposition from two sources with a temperature of 400°C for PTCDA and at 400°C for NiPc

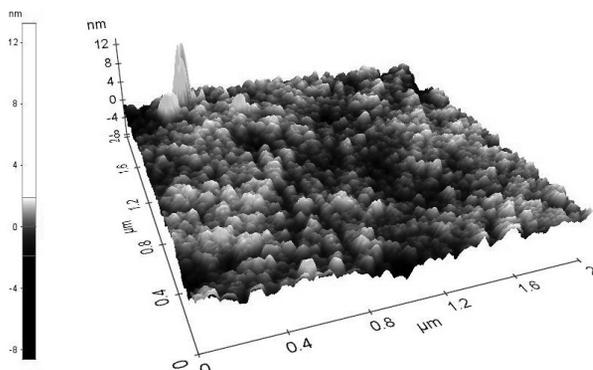


Fig. 20. Topographic image of the surface of the organic thin film formed on the substrate at temperature of 100°C by vapor deposition from two sources with a temperature of 300°C for PTCDA and at 400°C for NiPc

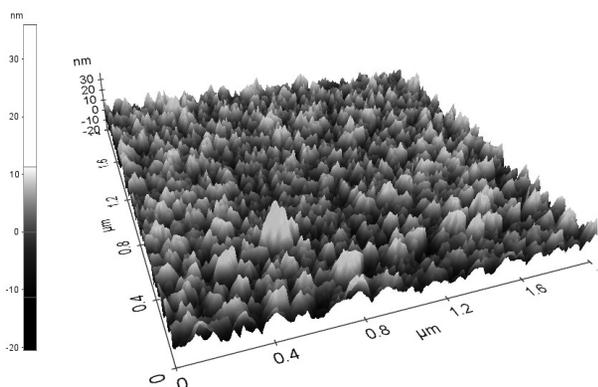


Fig. 21. Topographic image of the surface of the organic thin film formed on the substrate at temperature of 100°C by vapor deposition from two sources with a temperature of 350°C for PTCD A and at 300°C for NiPc

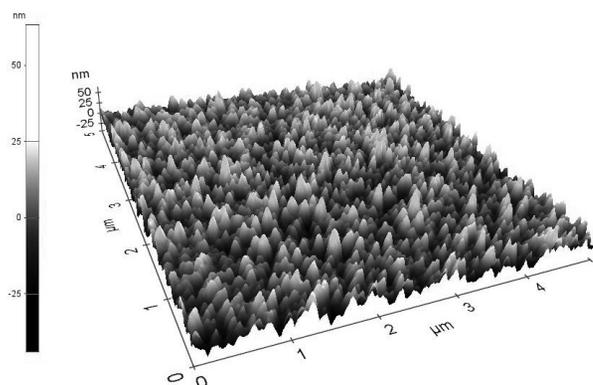


Fig. 24. Topographic image of the surface of the organic thin film formed on the substrate at temperature of 100°C by vapor deposition from two sources with a temperature of 400°C for PTCD A and at 300°C for NiPc

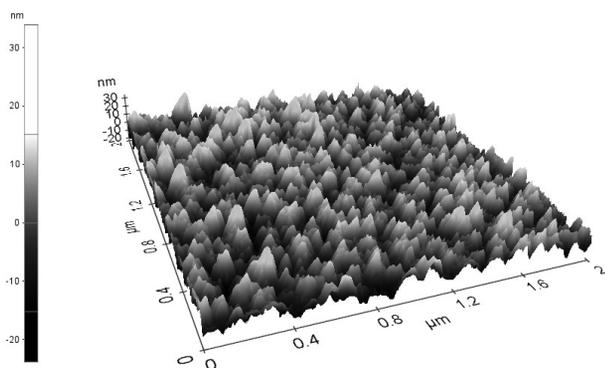


Fig. 22. Topographic image of the surface of the organic thin film formed on the substrate at temperature of 100°C by vapor deposition from two sources with a temperature of 350°C for PTCD A and at 350°C for NiPc

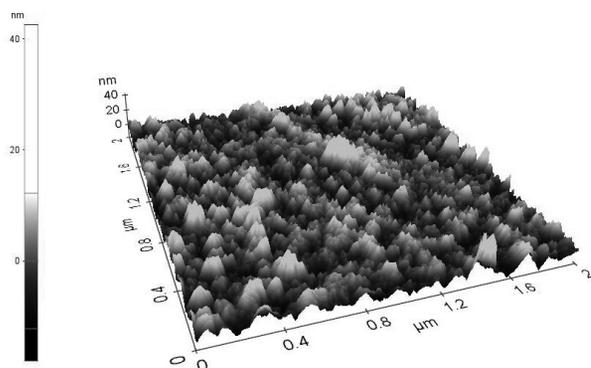


Fig. 25. Topographic image of the surface of the organic thin film formed on the substrate at temperature of 100°C by vapor deposition from two sources with a temperature of 400°C for PTCD A and at 350°C for NiPc

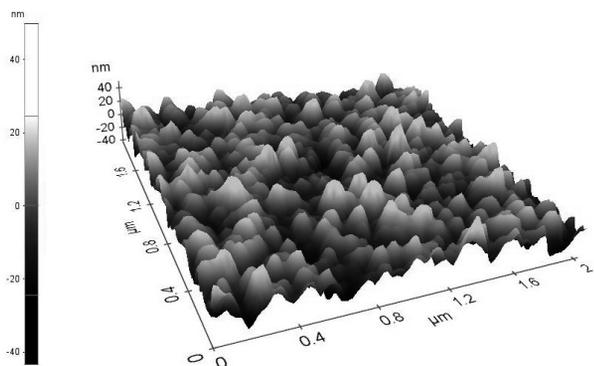


Fig. 23. Topographic image of the surface of the organic thin film formed on the substrate at temperature of 100°C by vapor deposition from two sources with a temperature of 350°C for PTCD A and at 400°C for NiPc

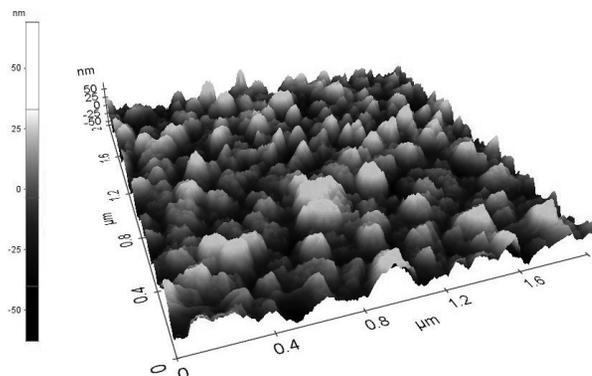


Fig. 26. Topographic image of the surface of the organic thin film formed on the substrate at temperature of 100°C by vapor deposition from two sources with a temperature of 400°C for PTCD A and at 400°C for NiPc

Layers of PTCDA:NiPc blends deposited from 2 sources of temperature 300°C (Fig. 3a) show the absorption maxima characteristic for NiPc (for energy of 1.7 eV, 1.9 eV, 3.5 eV, 4.0 eV) and PTCDA (for energy of 2.3 eV, 2.5 eV). The course of the absorption spectrum of the layer is characterized by a high intensity characteristic for PTCDA and virtually no noticeable absorption maxima characteristic for NiPc. Analysis of the absorption spectrum leads to the conclusion about the absence of the NiPc component in layer.

Layers deposited from sources of temperature 300°C for PTCDA and 350°C of NiPc (Fig. 3b) shows the increase of the absorption maxima intensity of the energy characteristic for NiPc, and reducing the intensity of the absorption maxima at the energy characteristic for PTCDA. Higher temperature of NiPc source causes the increase of the absorption intensity of energy maxima at the value characteristic for NiPc. The estimated content of components are respectively 30% for PTCDA and 70% for NiPc.

Thin films evaporated from PTCDA source of temperature of 300°C and 400°C for NiPc source (Fig. 3c) shows intensive absorption maxima characteristic for NiPc and practical disappearance of the absorption maxima characteristic for PTCDA. In this case content of components has been defined as 10% for PTCDA and 90% for NiPc.

Spectra of the thin films deposited by thermal evaporation from 2 sources with temperatures of 350°C of PTCDA source and 300°C for NiPc source (Fig. 4a) show high intensity of absorption peaks characteristic for PTCDA and low intensity of absorption peaks characteristic for NiPc. The estimated content of components are respectively 90% for PTCDA and 10% for NiPc.

Vapor-deposited layer from two separate sources of PTCDA and NiPc at the same temperature of 350°C (Fig. 4b) shows the maxima of the absorption spectra characteristic for PTCDA and NiPc with slightly reduced intensity of PTCDA maxima and a slight increase in the intensity of the band NiPc. In this case the estimated contents of components indicates a slightly higher content of NiPc with a value of 15%.

In the case of vapor-deposited thin film from the source of PTCDA at temperature of 350°C and NiPc source at temperature of 400°C (Fig. 4c) intensity of the absorption maxima of spectrum characteristic for NiPc have been increasing. The intensity of the absorption maxima of PTCDA decreased significantly below the intensity of the bands of NiPc what suggest lower content of PTCDA in layer, estimated at 25%.

The PTCDA source temperature of increasing to 400°C with NiPc source equal to 300°C (Fig. 5a) results in increase of the intensity of maxima of absorption characteristic for PTCDA and the low intensity of absorption maxima characteristic for NiPc. The estimated composition of the layer indicates the presence of only PTCDA.

Thin film deposited from PTCDA source at temperature of 400°C (Fig. 5b) and NiPc source at temperature 350°C shows maxima of the absorption spectra characteristic energy for PTCDA and NiPc, but maxima characteristic of PTCDA demonstrated a much higher intensity. The content of NiPc has been estimated at 5%.

Similarly to previous case thin film deposited from sources PTCDA and NiPc at temperature of 400°C (Fig. 5c), followed by increase in the intensity maxima of absorption characteristic for NiPc, compared with thin film deposited from a NiPc source at a lower temperature. In this case the estimated content of NiPc increased to 10%.

The vapour-deposited of thin film from the two separate sources PTCDA and NiPc at uniform temperature of 300°C, on the substrate heated to temperature of 100°C (Fig. 6a) shows the strong intensity of absorption maxima characteristic for NiPc and weak maxima intensity characteristic for PTCDA.

Increasing the temperature of NiPc source to temperature of 350°C while maintaining the PTCDA source temperature equal to 300°C (Fig. 6b) increases intensity of absorption maxima characteristic for NiPc. The PTCDA source temperature of 300°C and a source temperature of NiPc about 400°C (Fig. 6c) results in increasing the intensity of absorption maxima characteristic for NiPc and virtually lack of absorption maxima characteristic for PTCDA. Content of NiPc are estimated respectively 15% for NiPc source temperature of 300°C, 30% for NiPc source temperature of 350°C and 95% for NiPc source temperature of 400°C.

Thin films of PTCDA evaporated from source at 350°C and NiPc source of temperature equal to 300°C (Fig. 7a), on a substrate heated to temperature of 100°C shows absorption maxima characteristic for PTCDA and low intensity of absorption maxima characteristic for NiPc.

For the sources temperature of both materials 350°C (Fig. 7b) thin film characterized by a spectrum of high-intensity absorption maxima characteristic for NiPc.

NiPc evaporation from source at temperature of 400°C with a temperature of PTCDA source of 350°C (Fig. 7c) results in a high-intensity absorption maxima characteristic for NiPc reaching the higher value than the intensity of maxima corresponding to PTCDA. Content of NiPc are estimated respectively 15% for NiPc source temperature of 300°C, 30% for NiPc source temperature of 350°C and 95% for NiPc source temperature of 400°C.

Estimated content of NiPc in deposited thin films has been increasing depending on the temperature of the source of NiPc, from 15% for temperature of source having a value 300°C, to 95% for temperature of source having a value 400°C.

Vapor-deposited layer at source temperature of 400°C for PTCDA source and the source of NiPc at a temperature of 300°C at a substrate heated to a temperature of 100°C (Fig. 8a) demonstrated absorption maxima of high intensity characteristic for PTCDA and practically not occurring maxima characteristic for NiPc. That indicates a minimum content of NiPc in thin film.

Increase the NiPc evaporating temperature to 350°C with the temperature of the PTCDA source 400°C (Fig. 8b) results in rising of the intensity of absorption peaks characteristic for NiPc (estimated content of NiPc 30%), as in the case of vapor deposited layers on the substrate at room temperature. However in the spectra of these layers still the value of the intensity of absorption maxima characteristic of PTCDA are higher than the values of absorption maxima of NiPc.

Thin film evaporated from the two separate sources PTCDA and NiPc at uniform temperature of 400°C (Fig. 8c), on the substrate heated to temperature of 100°C shows the strong intensity of absorption maxima characteristic for NiPc and weak maxima intensity characteristic for PTCDA. That indicates a significantly higher content of NiPc estimated to 5%.

Changing the evaporation temperature of mixture components NiPc: PTCDA also affects the surface morphology of the layers. All layers have formed granular structure on the surface. The increase of evaporation temperature of components affects the growth surface roughness, the number of defects and large size of granular structures on the layers surface evidenced by the high values of the RMS and Ra both the layers applied to the substrate at room temperature and elevated temperatures up to 100 (Table 2).

Table 2.

RMS and  $R_a$  coefficient values for the NiPc:PTCDA layers deposited from two sources

No.	Temperature of PTCDA source, °C	Temperature of NiPc source, °C	RMS coefficient, nm	$R_a$ coefficient, nm
substrate at room temperature				
1	300	300	7.145	5.310
2	300	350	7.495	6.125
3	300	400	10.793	9.872
4	350	300	2.02	1.211
5	350	350	7.00	5.889
6	350	400	7.152	5.513
7	400	300	5.020	3.856
8	400	350	10.478	9.087
9	400	400	14.355	12.503
substrate at temperature of 100°C				
1	300	300	6.286	5.050
2	300	350	9.354	8.008
3	300	400	13.209	10.890
4	350	300	6.569	5.002
5	350	350	8.010	6.990
6	350	400	12.489	11.000
7	400	300	6.907	6.052
8	400	350	9.273	7.994
9	400	400	12.658	10.045

#### 4. Conclusions

Results of absorption measurement of layers deposited from two sources show that the source temperature variation of the components affects the composition of the layer, which is expressed in the course of the absorption spectra by changing the intensity of the peaks characteristic of the deposited materials. The occurrence of distinct peaks characteristic for PTCDA and NiPc in the absorption spectra of the thin films, evaporated from sources at the same temperature and from a source at a different temperature, demonstrates the ability to controlled change the course of absorption of NiPc: PTCDA layers.

The substrate temperature increased to 100°C has an impact on the course of the spectrum. However in this case, as in the case of layers deposited on substrates at room temperature, absorption spectra have a shape corresponding to the content of components of the layer and, it is possible to change the course of the absorption spectrum by control of temperature of sources during the physical deposition.

Due to the possibility of using layers as components of photovoltaic cells, a sufficiently low surface roughness of the active layers is an important aspect of technology what allows to get a good contact with the electrode active layer.

Simultaneously, the surface texture of the layer can influence on the improvement in the absorption of light.

In the case of the layers in photovoltaic devices inequalities and their uneven distribution can cause a decrease in absorption, which adversely affects the possibility of a bulk layer p-n junction creating.

Heterogeneity of layer may cause the exciton distance to the p-n junction becomes much greater than 10 nm, which along a low mobility of carriers in organic materials causes a reduction in the photovoltaic effect.

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