

Studying of spin-coated oxad-Si properties

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Properties

ABSTRACT

Purpose: The major aim of this paper was describing technical conditions of polymer thin film deposition by spin-coating techniques.

Design/methodology/approach: Thin films of about nanometres thickness were prepared by spin-coating and their properties were studied. As a material for preparing polymer thin films oxad-Si was used. The thin films were deposited with various spinning velocity from solution of different concentration. Thin films were deposited on BK7 glass and quartz substrates.

Findings: The obtained results describe influence of the solution concentration and spinning velocity on morphology and optical properties of spin-coated oxad-Si thin films.

Research limitations/implications: The obtained results confirm the oxad-Si availability for optoelectronic application to be stipulated.

Practical implications: The morphology and optical properties of Oxad-Si polymer thin films were described. This paper include also description of the influence of deposition conditions on properties of polymer thin films.

Originality/value: The value of this paper is defining the optimal parameters of spin-coating technology for preparing oxad-Si thin film with the best properties for optoelectronics appliances. This paper describes new experimental polymeric material for spin coating technology. Results of these researches enable to develop the spin-coating technology.

Keywords: Oxad-Si; Thin films morphology; AFM microscopy; Spin coating; Absorbance

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1. Introduction

Nowadays polymer materials appear to be more competitive with widely used inorganic materials in many technical fields. The chain structure of polymer materials makes them to have unique physicochemical properties. Since discovering that conjugated polymers are conducting materials intensive progress has been achieved and new fields of polymer materials applications appeared, optoelectronics in particular [1,2,3].

To main features of polymer materials one should count their low weight, flexibility and low costs of their manufacturing and processing, which is widely used nowadays [1].

Conducting conjugated polymers are used to manufacture organic light emitting diodes and photovoltaic cells. As OLED or polymer LED have layered structure great efforts are put to identify ways to control properties and process ability and costs connected with preparing polymer thin films having structure, morphology and properties adequate to the role they play in such optoelectronic application [4-6].

Continuous progress in manufacturing polymer thin film devices is a result of continuously developing and progressing technologies of organic, molecular and polymer thin film deposition.

Most widely used technologies of preparing polymer thin films appear to be [1-3]:

- chemical vapour deposition (CVD)
- physical vapour deposition (PVD)
- spin coating

Spin coating technology and its derivatives seem to be one of the most important technologies applied to deposition of polymer and organic thin films [5].

This paper describes the results of the research of the most promising polymer for optoelectronic application.

2. Materials

Polymer thin film have been prepared from solution of poly(oxydiazole). Poly(oxydiazole) is called oxad-Si and its formula is shown in Fig.1.

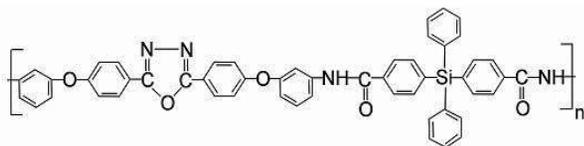


Fig. 1. Oxad-Si constitutional formula

THF is organic solvent belonging to the group of cyclic ethers, which can be mixed in any proportion with water and it dissolve most organic chemical compounds. THF is very often used as a solvent while preparing polymer thin films by spin coating technology

Thin films of oxad-Si were prepared by spin coating technique by putting a droplet of solution (concentration: 0.7 - 0.9 weight %, 1.3 - 1.7 %, and 2.1 - 2.2 weight % respectively) onto spinning BK7 glass and quartz substrate kept at room temperature.

3. Experimental

Technological conditions applied to the spin coating deposition process are given in Tab. 1. One can see that for each concentration range four different spinning velocities have been used, 3000, 4000, 5000 and 6000 [rpm] for thin films spin-coated onto BK7 glass substrate, while one velocity of 5000 [rpm] was used for thin films deposited onto quartz substrate. It can be seen in Tab.1, that the start-up time, the time needed for the preset spinning velocity. Start - up time was the same for each case and was equal 15 s. For the thin film deposition the spinning time was taken to be equal 20 s. Other start-up times were also examined but thin films prepared under such conditions were not of satisfactory structure. The time equal 15 s has appeared to be the most suitable for preparing oxad-Si thin films by spin coating.

The substrates was cleaned following technological procedure to remove any impurities on it surface and then fixed by vacuum on spin coater holder (Fig. 2). Then, droplets of concentrated polymer solution have been put with a pipette onto the spinning substrate (glass or quartz). The rotation was stopped automatically after a preset time 35 s of deposition process.

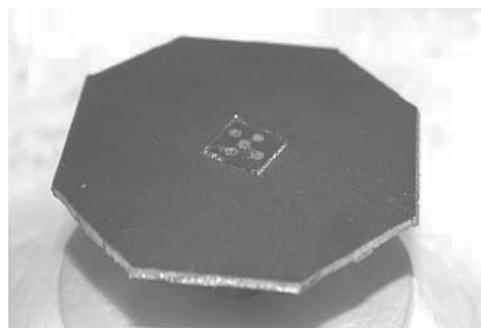


Fig. 2. Spin-coater holder

Thickness of deposited films was examined by means of an interferometer microscope using Tolansky method. On the surface of each layer a thin scratch was cut. Relevant arrangement of interferometer microscope allowed to obtain the picture with visible interference fringes. By measuring the fringes distance ΔL and distance between fringeless L (Fig. 3), thickness of thin film was determined [10, 11].

For every organic thin film 5 reading was done, the arithmetical mean of results gave the final result of thickness measurement.

Table 1.
Oxad-Si spin coating specification

Oxad-Si			
M = 810,89 g/mol			
Suspension volume = 2 cm ³		Polymer mass = 0,0100 g	
C _p = 0.71 %		C _m = 6.2 mmol/dm ³	
substrate	Spinning velocities [rpm]	Start-up time [s]	Spinning time [s]
BK7	3000	15	20
BK7	4000	15	20
BK7	5000	15	20
BK7	6000	15	20
quartz	5000	15	20
Suspension volume = 1 cm ³		Polymer mass = 0.0100 g	
C _p = 1.40 %		C _m = 12.3 mmol/dm ³	
substrate	Spinning velocities [rpm]	Start-up time[s]	Spanning time [s]
BK7	3000	15	20
BK7	4000	15	20
BK7	5000	15	20
BK7	6000	15	20
quartz	5000	15	20
Suspension volume = 1.5 cm ³		Polymer mass = 0.0290 g	
C _p = 2.10 %		C _m = 23.8 mmol/dm ³	
substrate	Spinning velocities [rpm]	Start-up time[s]	Spanning time [s]
BK7	3000	15	20
BK7	4000	15	20
BK7	5000	15	20
BK7	6000	15	20
quartz	5000	15	20

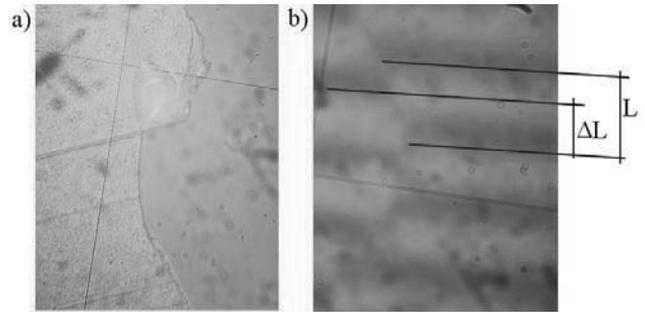


Fig. 3. Picture of a thin film layer taken on interferometer microscope MII - 4 with 490x zoom; a) image of scratch on thin film surface, b) image interference fringes displacement

Topographic images of surface morphology of polymer oxad-Si thin films were made with Topometric atomic force microscope (AFM) (Fig. 4).

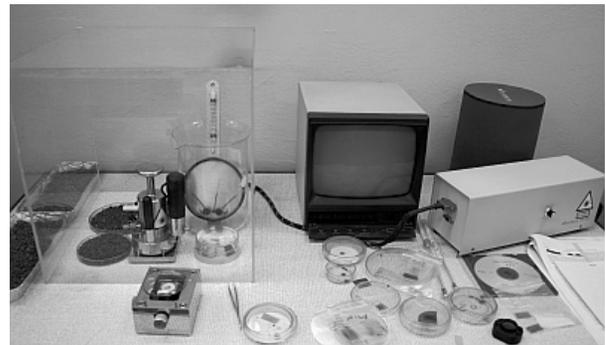


Fig. 4. Atomic force microscopy AFM

Each of as-prepared films was examined by means of HR 4000 spectrophotometre by taking their transmission spectra T. They were then used to deduce their absorbance according to its definition:

$$A = \log 1/T \tag{1}$$

where:
T- transmittance value

Absorbance UV-Vis spectra are thought to be suitable way for comparing the ones taken on different thin films, as by definition they depend on thickness of a film. If compared with absorption coefficient spectrum, the absorbance is a product of absorption coefficient and a film thickness divided by 2.303 (relation between natural logarithm and decimal one [12]). Measurements were performed also for thin films deposited on quartz substrate obtained at the same condition as BK7.

3. Results and discussion

Thickness of thin films spin-coated onto BK7 glass and quartz substrates were measured with interferometer and analysed. The as-determined thicknesses of oxad-Si films deposited onto quartz substrate from the three solutions with 5000 rpm spinning velocity are shown in Fig. 5.

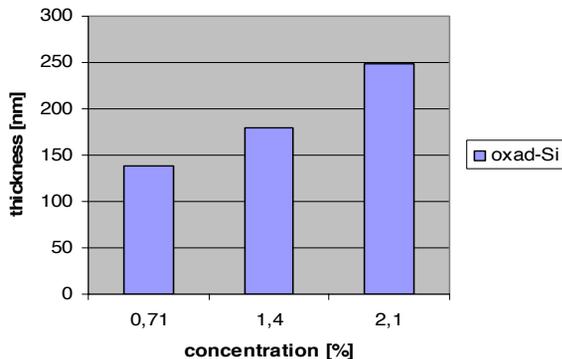


Fig. 5. Diagram of thicknesses for thin films deposited on quartz substrate for three oxad-Si concentrations in THF solution and for 5000 rpm of spinning velocity

The thickness of thin films deposited on the quartz substrate with fixed spinning velocity of 5000 rpm is seen to grow with higher concentration of solution.

Thicknesses of thin films deposited onto the BK7 glass substrate from solutions of 0.71, 1.4 and 2.1 wt% concentrations of oxad-Si for spinning velocities from 3000 to 6000 rpm are shown in Figs. 6-9.

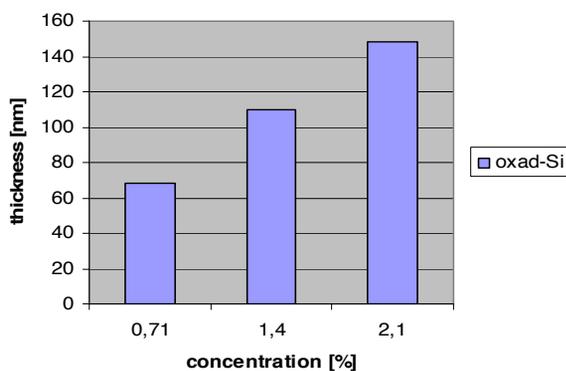


Fig. 6. Diagram of thicknesses of oxad-Si polymer thin films spin-coated onto BK7 glass substrates for the three solutions with 3000 rpm spinning velocity

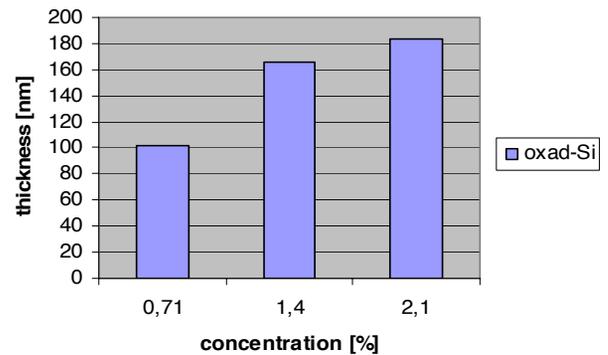


Fig. 7. Diagram of thicknesses of oxad-Si thin films spin-coated onto BK7 glass substrate for the three concentrations with 4000 rpm spinning velocity.

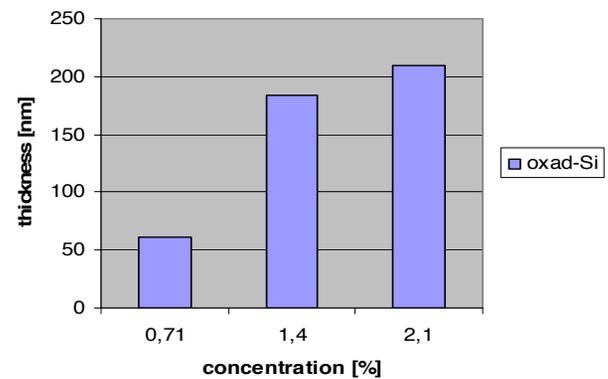


Fig. 8. Diagram of thicknesses of oxad-Si thin films spin-coated onto BK7 glass substrate for the three concentrations with 5000 rpm spinning velocity

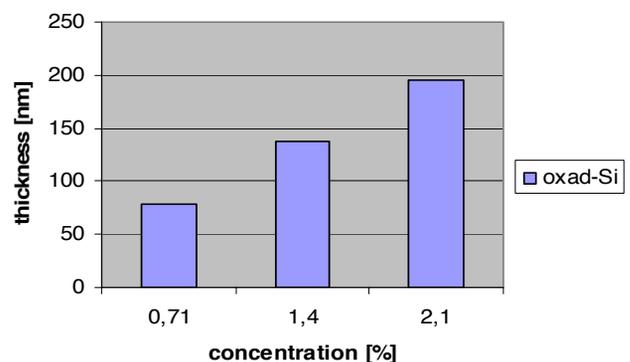


Fig. 9. Diagram of thicknesses of oxad-Si thin films spin-coated onto BK7 glass substrate for the three concentrations with 6000 rpm spinning velocity

The thickness of as-prepared oxad-Si thin films on the BK7 glass substrate depend on concentration of solution. The highest values of film thickness were obtained for thin films deposited with 5000 rpm spinning velocity.

Topographic images of oxad-Si thin films deposited from solutions of different concentrations onto quartz substrate are shown in Figs. 10-12.

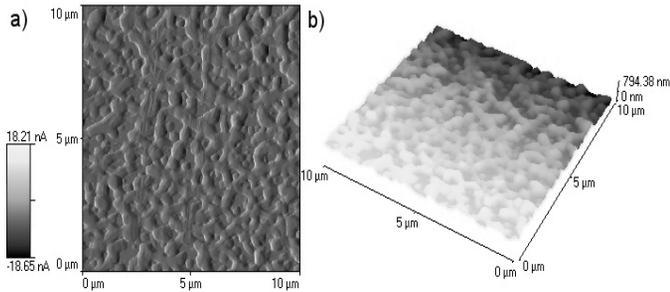


Fig. 10. AFM images of oxad-Si film prepared from the solution 0.71wt%, a) 2D image, b) topographic 3D image

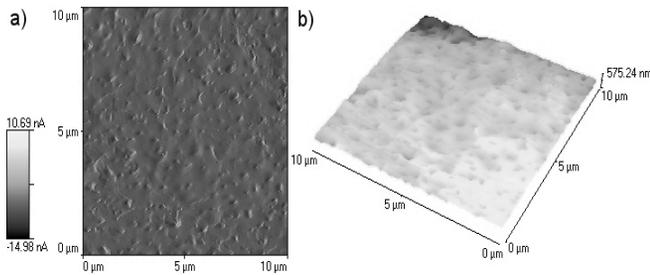


Fig. 11. Image of oxad-Si polymeric layer surface for 1.40 wt% concentration; a) 2D image, b) topographic 3D image

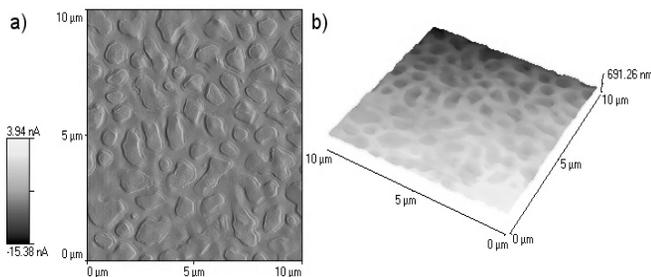


Fig. 12. Image of oxad-Si polymeric layer surface for 2.10% of concentrate a) 2D image, b) topographic 3D image

While comparing AFM images taken on thin films deposited onto quartz under 5000 rpm with different spinning velocity the morphology of films are similar. However the thin film prepared from 1,4% is seen to be more homogenous than the others. One

can see that thin films deposited with low concentration and medium concentration of solution reveal granular morphology with more overlapped grains. The morphology of a thin film prepared from the high concentration solutions reveals same “melted” character if wetness of the substrate were stronger than in case of thin film deposited from the solution of the lower concentration.

To characterize roughness of thin films surface morphology the RMS (Root Mean Square roughness) coefficient was used [13] (2) :

$$RMS = \sqrt{\frac{1}{n} \cdot \sum_{i=1}^n (Z_i - \bar{Z})^2} \text{ [nm]} \quad (2)$$

were:

n - is the number of sampled points,

Z_i - is the height of each point and

\bar{Z} - the mean height value

The values of RMS coefficients are shown in Table 2. The value of roughness coefficient of sample prepared with spinning velocity equal to 5000 rpm and with concentration 0.71 % is higher then roughness coefficients of samples prepared with the same velocity and concentration equal to 1.4 and 2.1 %.

Table 2.

The values of RMS coefficient

No.	oxad-Si concentration C[%]	RMS [nm]
1	0.71	52.7
2	1.40	24.6
3	2.10	26.7

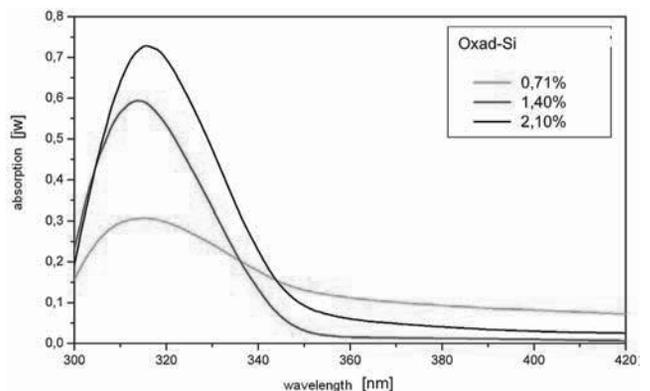


Fig. 13. Absorbance spectrum of thin films prepared with 3000 rpm spinning velocity on BK7 substrate for three concentrations of the oxad-Si solution.

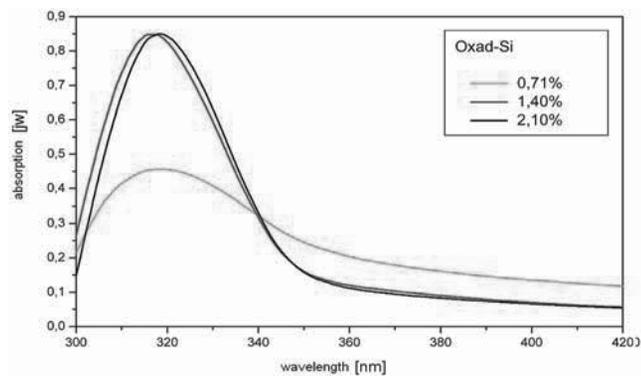


Fig. 14. Absorbance spectrum for three concentrations of oxad-Si solution in THF for 4000 rpm of spinning velocity (BK7 background)

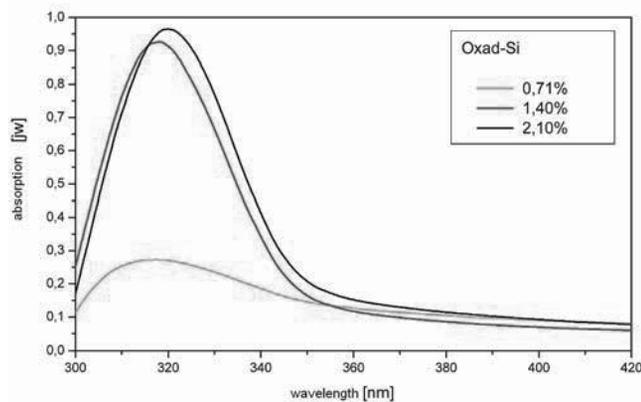


Fig. 15. Absorbance spectrum for three concentrations of oxad-Si solution in THF for 5000 rpm of spinning velocity (BK7 background)

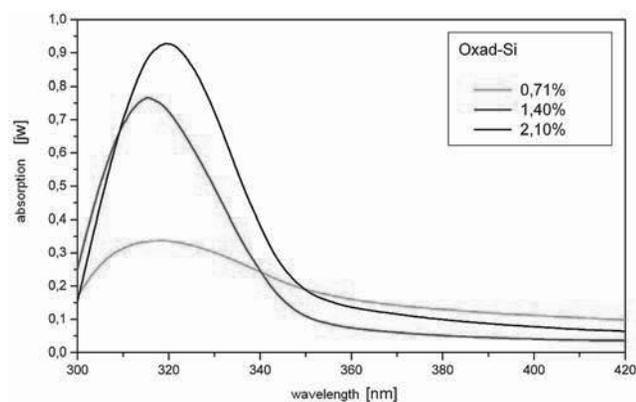


Fig. 16. Absorbance spectrum for three concentrations of deposited oxad-Si solution in THF for 6000 rpm of spinning velocity (BK7 background)

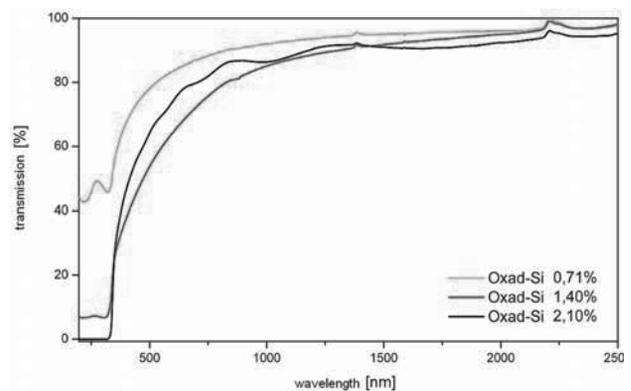


Fig. 17. Transmission spectrum for three concentrations of oxad-Si solution in THF (quartz substrate).

Absorbance spectra taken on thin films of Oxad-Si deposited onto glass substrate from 0.71, 1.4, and 2.1 wt.% solutions with spinning velocities equal to 3000, 4000, 5000 and 6000 rpm are shown in Figures 13-16. It is visible that the absorbance level of films prepared from 1.4 and 2.1 wt. % solutions is nearly twice as high as that of thin film prepared from the dilute solutions of 0.71 wt. %. The absorption band appears to be the most smoothed out while thin film prepared from the most dilute solutions and its maximum is slightly moved towards shorter wave lengths.

For 3000 and 6000 rpm spinning velocities the absorption maxima are seen to shift towards shorter wavelength when the more dilute solution was used.

However, thin films prepared from medium and high concentration solutions with 4000 and 5000 rpm velocities reveal absorption bands of nearly the same absorbance level and nearly coinciding peak positions.

For chosen spinning velocity equal to 5000 rpm on quartz substrate the transmission spectra is shown in Fig. 17. All thin films have nearly coinciding absorption edges. The strongest absorption at spectral range below 500 nm is observed for thin film deposited from the high concentration solution 2.1 wt. %. Thin film prepared from solution of medium concentration has appeared to reveal higher transmission level below 500 nm than the former one.

When analysing the recorded absorbance spectra it is thought that thin films prepared from the 0.71 wt% oxad-Si solution have slightly shorter conjugation lengths than it was the case for films prepared from higher concentration solutions.

Additionally, one can suppose that thin films prepared from the highest concentration solutions are built up of polymer chains more planarized with longer conjugation length than the others. The observed coincidence of the absorption maxima is thought to indicate that viscosities of the two solutions are similar.

4. Conclusions

Obtained results for each of using spinning velocity and substrates confirm that film thickness is depending on solution concentration. Thin films of oxad-Si solutions spin-coated with 4000 and 5000 rpm have nearly the same thickness. Our research indicates that that quartz substrate is more wettable than glass BK7 substrate.

References

- [1] L.A. Dobrzanski, Fundamentals of material science and physical metallurgy, WNT, Warsaw, 2006.
- [2] M. Żenkiewicz, Adhesion and topcoat modification of high-molecular plastics, WNT, Warsaw, 2000.
- [3] J. Tyczkowski, Thin films of plasma polymers, WNT, Warsaw, 1990.
- [4] W. Przygocki, A. Włochowicz, Polymers physics, PWN, Warsaw, 2001.
- [5] L. Wu, Thermal effects on liquid film dynamics in spin coating, Sensors and Actuators A: Physical A 134 (2007) 140-145.
- [6] H. Galina, Polimers physicochemistry, Rzeszow University publishing house, Rzeszow 1998.
- [7] S. Kulaszewicz, Thin transparent electro conducting layers, using, properties, Bialystok University publishing house, Bialystok 1994.
- [8] S. Połomiński, Polymer physical chemistry, Lodz University publishing house, Lodz 2001.
- [9] J. Raczkowska, P. Cyganik, A. Budkowski, A. Bernasik, J. Rysz, I. Raptis, P. Czuba, K. Kowalski, Composition Effects in Polymer Blends Spin-Cast on Patterned Substrates, Macromolecules 38 (2005) 8486-8493.
- [10] W. Przygocki, Physical methods of polymers researching, PWN, Warsaw 1990.
- [11] M. Pluta, Microinterferometry in polar light: physical rudiments of birefractive microinterferometry, alliance and application, WNT, Warsaw 1990.
- [12] A. Cygański, Spectroscopic method in analytical chemistry, WNT, Warsaw 2002.
- [13] B. Hajduk, J. Wieszka, J. Jurusik, Influence of LCVD technological parameters on properties of polyazomethine thin films, Journal of Achievements in Materials and Manufacturing Engineering 36/1(2009) 41-48.