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Studying of polyoxadiazole with Si atom in the backbone

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ABSTRACT

Purpose: The aim of this paper is to show properties of spin-coated thin films of new polymer having silicon atom in the backbone. This amorphous polymer has appeared to be applied as active films in organic devices (as OLED).

Design/methodology/approach: Thin films of 4-(diphenyl(4-(4-(5-(p-tolyoxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyloamino)methyl)-phenyl)silyl)-1-methylbenzamide (Oxad–Si-B) were obtained by spin-coating method. The methodology of preparing was changing of technological parameters such as solution concentration and spinning rate V. The films were deposited with five spinning rates.

Findings: Such technological parameters as spinning rate and solution concentration has appeared to influence optical properties of thin films. These parameters were found to influence surface morphology and UV-Vis absorption spectra of thin films.

Research limitations/implications: The optical properties of obtained films will allow further researches of this polymer. Its optical properties allow carrying of electrical measurements, which will be carried out in the nearest time.

Practical implications: The value of Oxad-Si (B) energy gap suggests its luminescent properties and applications of this material as active film in optoelectronic devices.

Originality/value: The goal of this paper is to show optical properties of thin films prepared with most optimal technology conditions.

Keywords: UV-Vis spectroscopy; AFM microscopy; IR spectroscopy; Spin-coating method; Organic polymer

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MATERIALS

1. Introduction

An application of organic polymers as thin films in optoelectronic devices is wide enough. The most common in this area are semiconducting polymers as polyparaphenylenevinylene (PPV) [1] and polyparaphenylene (PPP).

Most frequently used deposition methods for preparing polymer thin films for optoelectronic applications are chemical vacuum deposition (CVD) [2-5] and spin-coating technique [12,13].

Spin-coating deposition methods are based on spinning several droplets of polymer solution put onto glass substrate. Amongst many solvents most widely used ones are trichlomethane (chloroform), tetrahydrofuranum (THF) and methanol.

Polyoxadiazoles are organic polymers whose backbone comprises oxad group, composed of furan-like cycle containing two nitrogen, two carbon and one oxygen atoms [6-7]. Nitrogen and carbon atoms are linked together by double bond in oxad fragment. Oxad-Si-B is one of silicon-containing polyoxadiazoles [8].

2. Experimental

Thin films of poly 4-(diphenyl(4-(4-(5-(p-tolyoxy)phenyl)-1,3,4-oxadiazol2-yl)phenyloamino)-methyl)-phenyl)silyl)-1-methylbenzamide (Oxad-Si-B) were deposited onto quartz and glass substrates.

The Oxad-Si-B polymer, which is shown in Fig. 1 was synthesized in Institute of Macromolecular Chemistry of Romanian Academy Sciences in Iasi, Romania.

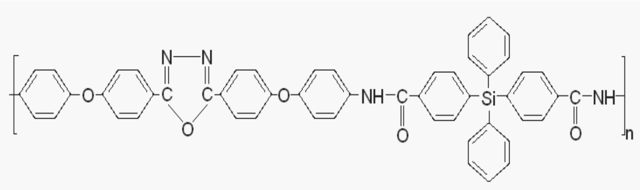

Fig. 1. The scheme of Oxad-Si-B polymer

Three different concentrations of Oxad-Si-B solution in THF were used to prepare its thin films by spin-coating. The three concentrations C equal to 0.77%, 1.4% and 2.0% and other technological parameters are given in Table 1.

Table 1.
Technological parameters of spin-coating method

C[%]	V [rpm]	t [s]
0.77	3000	15
	4000	
	5000	
	6000	
1.40	3000	15
	4000	
	5000	
	6000	
2.00	3000	15
	4000	
	5000	
	6000	

Thin films were deposited with five spinning rates V: 3000, 4000, 5000 and 6000 rpm at the same rise time t [15 s]. During the deposition process substrates were fixed to the holder by succion. Spin-coating is the method based on spinning several droplets of polymer solution put onto the substrate. Procedures to prepare polymer solution were the same and various polymer quantities were dissolved in the same volume of tetrahydrofuran.

The optical measurements of UV-Vis absorbance spectra were performed on thin films of Oxad-Si-B with the use of Ocean Optics HR4000 spectrophotometer, covering the wavelength range spreading over from 200 to 1000 nm.

The morphology of the as-prepared thin films was examined based on topographic and sensor images performed with Atomic Force Microscope (AFM). IR absorption spectra were recorded with IR spectrophotometer SPECORD M-80 within 200-4000 cm^{-1} range. All measurements were performed at room temperature.

3. Results

3.1. UV-Vis results

The absorbance spectra of Oxad-Si-B thin films deposited onto glass substrates with spinning rate equal to 3000, 4000, 5000 and 6000 rpm are shown in Figs. 2-5, respectively.

The strength of the absorbance spectrum of thin film deposited from 1,40% solution appears to be the highest, as it is seen in Fig. 2. The intensity of absorption bands is seen to be dependent on concentration of THF-polymer solution. Then, the intensity increase following the solution concentration is observed in Figs. 3-5. One can see that the absorption bands cover the wavelength range 300-350 nm in each spectrum. In case of thin films prepared with the spinning rate V=3000 rpm the maxima of the absorption band from the solution with concentrations 0.77% and 1.40% are at about 311 nm, while for concentration 2.1% the maximum is at about 319 nm (Fig. 2).

The maxima of spectra performed with spinning rate V=4000 rpm are at 310 nm for thin film from 0.77% solution and 312 nm for Oxad-Si-B deposited from 1.4% and 2.1 % solutions.

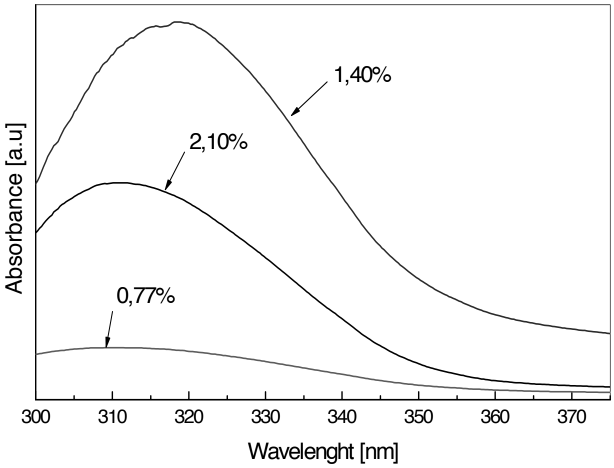

Fig. 2. UV-Vis absorption spectra of Oxad-Si-B deposited with 3000 rpm spinning rate

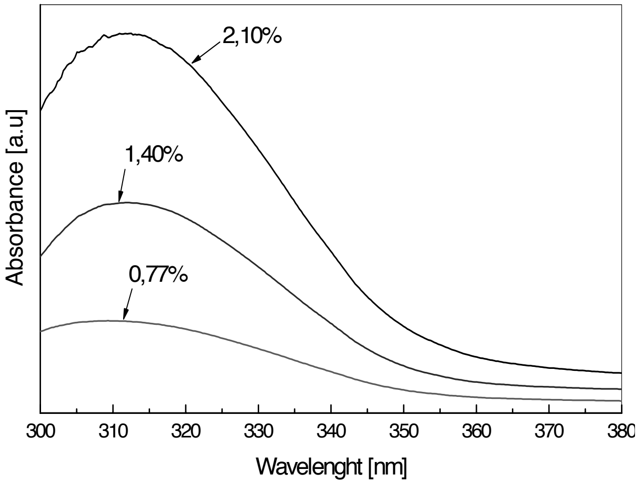

Fig. 3. UV-Vis absorption spectra of Oxad-Si-B deposited with 4000 rpm spinning rate

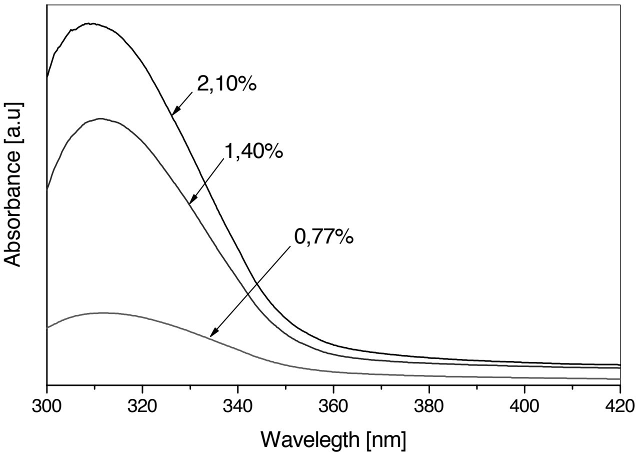

Fig. 4. UV-Vis absorption spectra of Oxad-Si-B deposited with 5000 rpm spinning rate

The absorbance spectra of thin Oxad-Si-B films, which were deposited onto glass substrates with 5000rpm and 6000 rpm spinning rate for three concentrations are shown respectively on Figs. 4-5, respectively. The absorption maxima in the spectra of Oxad-Si-B thin films deposited with the spinning rate V=5000 rpm are at 312 nm for the films deposited from 0.77% and 1.4% solutions and at about 310 nm for the film deposited from 2.1% solution. The strength of optical absorbance is seen to increase with concentration of polymer - THF solution in both graphs.

The absorption maxima in the spectra taken on Oxad-Si-B thin films spin-coated with the spinning rate V=6000rpm, appear at 308, 318 and 319 nm when solution concentrations were equal to 0.77%, 1.40 % and 2.10%, respectively.

One can see in Fig. 2 that peak of the absorption band is the strongest when the film was spin-coated from 1.4% solution and the weakest for 0.77% solution, while that from 2.1% solution being in the middle. When spinning rates were equal to 4000 and 5000 the intensity was proportional to the solution concentrations. For 6000 rpm rate the intensity sequence is like in Fig. 2, but the absorbance strength for 2.1 % solution, being compatible with 1.4% solution, in contrast to the case shown in Fig. 2.

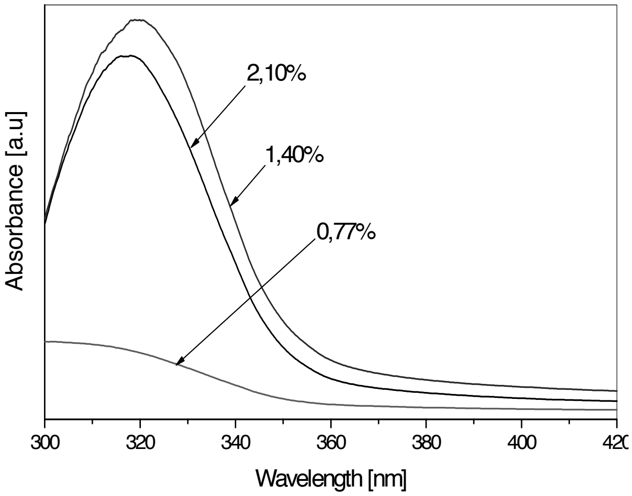

Fig. 5. UV-Vis absorption spectra of Oxad-Si-B deposited with 6000 rpm spinning rate

3.2. IR results

IR absorption spectrum taken within the wave number range 400-4000 cm^{-1} on Oxad-Si-B thin film deposited on KBr pastille is shown in Fig. 6. The strongest peak is seen at about 1487 cm^{-1}. The other strong peaks are seen at 509, 698, 1229, 1605 and 1665 cm^{-1}. The weak peaks are seen at about 1012, 1109, 2596 and 3069 cm^{-1} wave numbers.

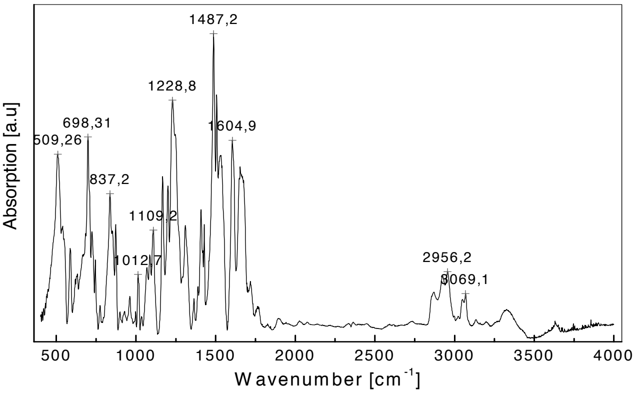

Fig. 6. IR absorption spectrum of Oxad-Si-B thin film deposited onto KBr pastille

3.3. AFM results

The topographic images of Oxad-Si-B polymer films deposited with the spinning rate V=5000 rpm from solutions with three concentrations 0.77%, 1.40% and 2.10% are shown in Figs. 7-9.

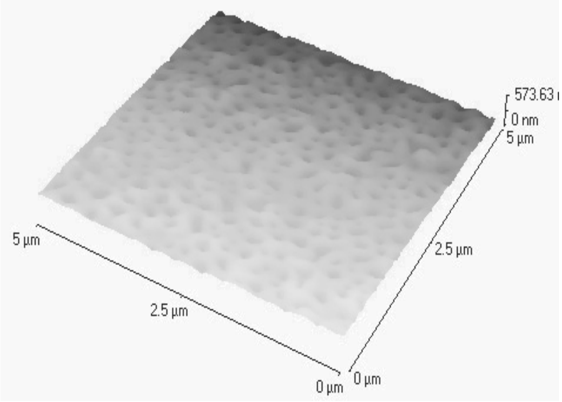

Fig. 7. Topographic image of Oxad-Si-B polymer thin film deposited rom 0.77% solution

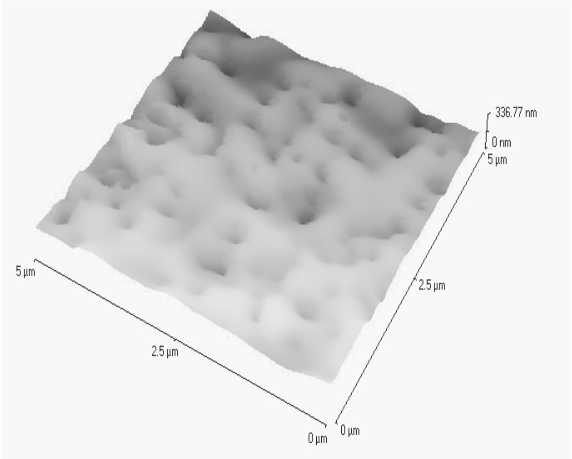

Fig. 8. Topographic image of Oxad-Si-B polymer thin film deposited from 1.40 % solution

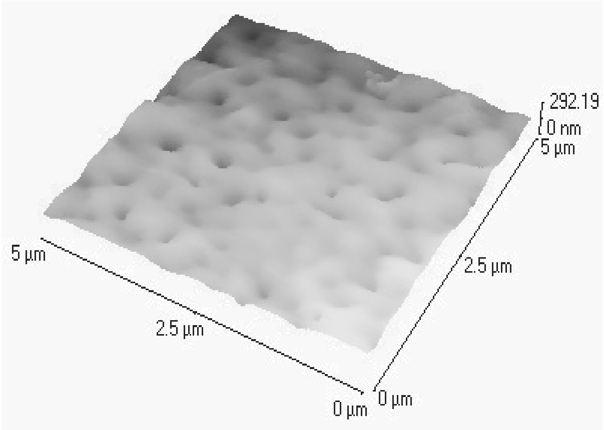

Fig. 9. Topographic image of Oxad-Si-B polymer thin film deposited from 2.20 % solution

One can see that the spread of the film surface roughness is the highest in the case of thin film spin-coated from the most diluted solution of 0.77% and it is the smaller, the higher the spinning rate is. The morphology of the film surface seems to be most homogenous in the case of thin films spin-coated with the lowest spinning rate. One can see the largest holes in the image taken on the film prepared from the 1.4% solution.

4. Discussion

The IR absorption spectrum taken on Oxad-Si-B thin films covering wave number range 400 – 1800 cm^{-1} is shown in Fig. 10. It is expected that Oxad-Si-B thin films have amorphous character, but they built-up of polymer chains, so that the backbone vibrations should have impact on the shape of infrared spectrum. As the repeating unit of Oxad-Si-B polymer contains two ether groups formed by two oxygen atoms linked to two phenyl rings, separated by the oxadiazol group. Then, the feature at about 1228 cm^{-1} is attributed to C-O-C vibrations and the feature at about 1247 cm^{-1} overlapped with the former band is expected to be due ether group vibrations [12,13]. The shape of this band may be related to vibrations of polymer chains of various lengths.

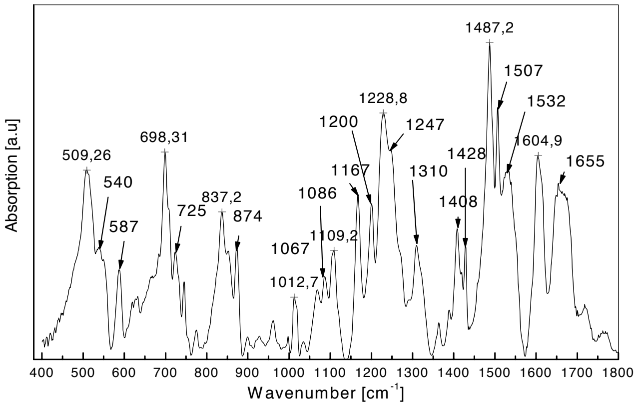

Fig. 10. The IR spectrum of Oxad-Si-B thin film in range 400-1800 cm^{-1} wave number

Features peaking at about 509, 698, 725, 837 and 874 cm^{-1} are attributed to ring out-of –plane deformation vibrations. Origin of bands with frequencies in the vicinity of 1100 cm^{-1} can be difficult to attribute unambiguously, but they can be attributed to ring in-plane CCH bending vibrations as well as to C-O vibrations of ether linkages.

The features overlapped with 1229 cm^{-1} band are expected to be due to C-O-C ether linkages vibrations. Their frequencies are expected to be influenced by chain conformation and conjugation effects [9-10].

The strongest peaks between 1487 and 1532 cm^{-1} are attributed to benzene ring stretching vibrations and their high absorption strength is thought to indicate there are rather short conjugated fragments in the polymer backbone. The peaks at about at 1408 and 1428 cm^{-1} are attributed to Si-phenyl ring vibrations. While analyzing Oxad-Si-B chain conformation one may expect that peak at about 1604 cm^{-1} might be due to vibrations of benzene ring linked to Si atom. The peak at 1655 cm^{-1} is attributed to C=N vibrations in the oxadiazol groups. Additionally, the feature peaking at about 1247 cm^{-1} may be related to amid groups in the backbone, which is thought to be confirmed by the presence of 3300 cm^{-1} feature (Fig. 6). There are also seen peaks at about 2867, 2928 and 2956 cm^{-1}, which are attributed C-H vibrations in phenyl rings.

Thin films of Oxad-Si-B were spin-coated onto glass substrate, so that the spectra presented in Figs. 2-5 cover photon energy ranging 3.2 to 4.2 eV, the upper limit being imposed by glass absorption edge. For the aims of this paper this range of UV-Vis spectra is sufficient, moreover this is an area where the band attributed to interband transitions connecting delocalized states of the electronic structure of conjugated polymers with short conjugated segments is observed. This is the case for Oxad-Si-B thin films because it is clearly seen in Fig. 1 that the longest conjugated segment is comprised within unit cell limits together with other ones consisted of individual phenyl rings. According to the spectra given in Figs. 2-5 the thickness of the spin-coated film depends on the solution concentration and spinning rate.

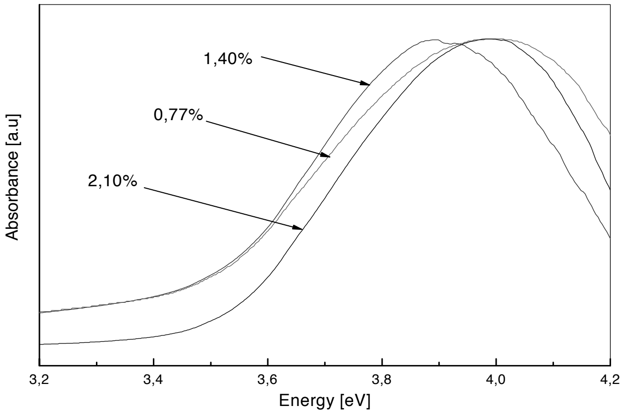

Fig. 11. Normalised UV-Vis absorption spectra of Oxad-Si-B thin films deposited with 3000 rpm spinning rate

For the rates of 3000 and 6000 rpm one can see that the films from 1.4% solutions are the thickest, while for 4000 and 5000 rpm the film is the thicker, the higher concentration is. The normalised UV-Vis absorption spectra shown in Figs. 11-14 show additionally how technological condition influence the shape and location of the absorption band. It can be seen in Fig. 11 that the film spin-coated with the rate 3000 rpm from the 1.4% solution has more planar conjugated fragments than the two other films, as the absorption maximum is moved towards lower energies to 3.9 eV. One can see,that normalized maxima of absorption bands are located at 3.96 eV for thin films deposited from 0.77% and 2.10 % solutions. While the spinning rate is equal to 4000 rpm the shape and position of all the three absorption bands nearly coincide and their conjugation lengths are supposedly shorter than this is the case for 3000 rpm rate (Fig. 12).The spectra taken on the films spin-coated with the rate of 5000 rpm are similar to the former rate. Absorption spectra of Oxad-Si-B thin films deposited with V=6000 rpm spinning rate are shown in Fig.13, where one can see that those prepared from 1.4 and 2.1 % solutions have peaks at about 3.9 eV, the former one slightly moved towards lower energy. The maximum of the film prepared from 0.7% solution is pushed above 4.2 eV, beyond the spectral range.

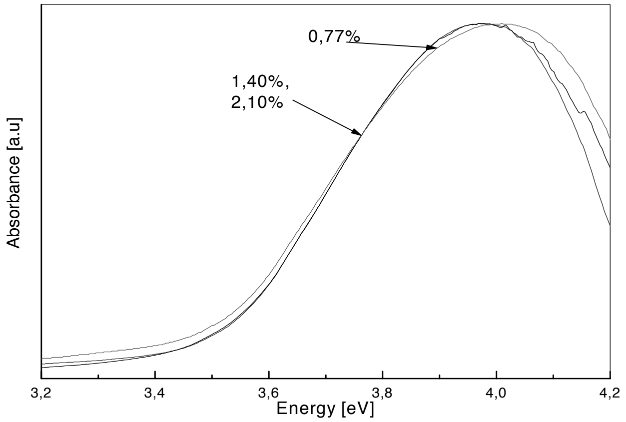

Fig. 12. Normalised absorption spectra of Oxad-Si-B film deposited with V=4000 rpm spinning rate

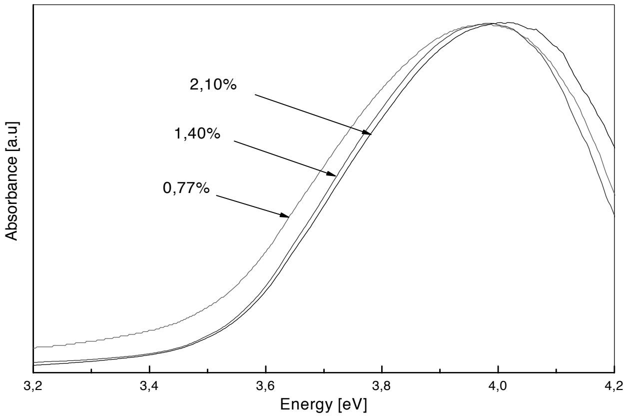

Fig. 13. Normalised UV-Vis absorption spectra of Oxad-Si-B thin films deposited with 5000 rpm spining rate

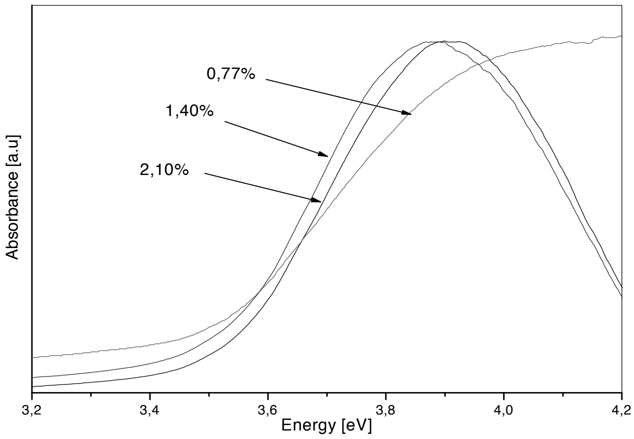

Fig. 14. Normalized UV-Vis absorption spectra of Oxad-Si-B thin films deposited with 6000 rpm spinning rate

The RMS coefficients [8] were performed with AFM microscope software to characterize the roughness of Oxad-Si-B thin films morphology are given in Table 2. The RMS coefficients were done for thin films deposited onto quartz substrates from three solutions 0.77%, 1.40% and 2.10 % with the spinning rate of 5000 rpm. The RMS coefficients [11,14] are shown in Table.2.

Table 2.
The RMS coefficients

C[%]	V [rpm]	RMS[nm]
0.77	5000	103
1.40		50
2.10		40

The average diameter of surface grain are shown in Table 3.

The average diameter of grains upon the film surface revealed with AFM topographic and sensor images are shown in Table 4.

Table 3.
The averge diameter of holes in surface

C[%]	V [rpm]	d [μm]
0.77	5000	0.2
1.40		0.4
2.10		0.6

Table 4.
Average deep of surface defects

C[%]	V [rpm]	h[nm]
0.77	5000	100
1.40		180
2.10		150

To describe influence of solution concentration on film morphology they were spin-coated onto quartz substrate with the rate of 5000 rpm, while other technological parameters being the same those given in Table 1. The topographic images taken on thin films deposited onto glass substrate were shown in Figs. 7-9. To examine thin film roughness horizontal profiles were performed with Topometrix SPMLab Nt Ver.5.0, which are shown in Fig. 15-17.

One can see that there are seen numerous holes in the surface of the film prepared from 0.77% solution. As it can be seen in Fig. 15 holes are distributed rather regularly upon the film surface. However, the distribution of holes, their diameter and depth is seen to change with the solution concentration. While analyzing data in Tables 2-4, it can be seen that RMS and hole depth decrease as the concentration increases, while otherwise behave hole diameter. Profiles which were performed on topographic images show, that surface of polymer film deposited from 2.1% solution concentration is smoother than the surface of thin film deposited from 1.4% solution. Average holes diameter is increasing with solution concentration. It is about 0.2 μm, 0.4 μm and 0.6 μm for 0.77%, 1.4% and 2.10% solution concentrations, respectively. Roughness coefficients of thin films is decreasing with higher solution concentration. RMS coefficients depend on the height of points signed on the surface [5], that is the reason why that two different topographic images could have two equal RMS coefficients. Comparing profiles made for sensor images of thin films shown in Figs. 15-17, which are illustrated in Figs. 18-20 one can see that on the average thin film deposited from the 0.77% solution reveals the smallest depth variations (Fig. 18), in contrast to the films prepared from 1.4 and 2.7% solutions, as it is seen in Figs. 19 and 20, respectively. Topographic images of Oxad-Si-B thin films surface are consistent with optical measurements.

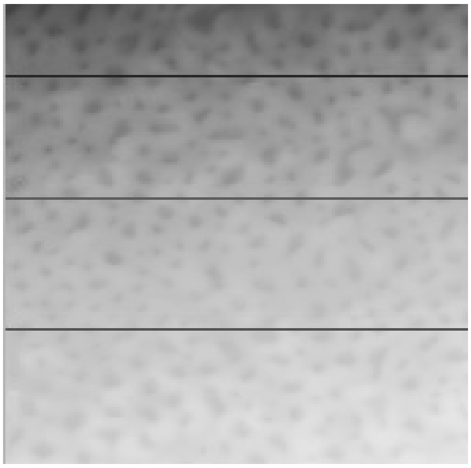

Fig. 15. Sensor image of Oxad-Si-B thin film deposited from 0.77% solution concentration with signed profiles

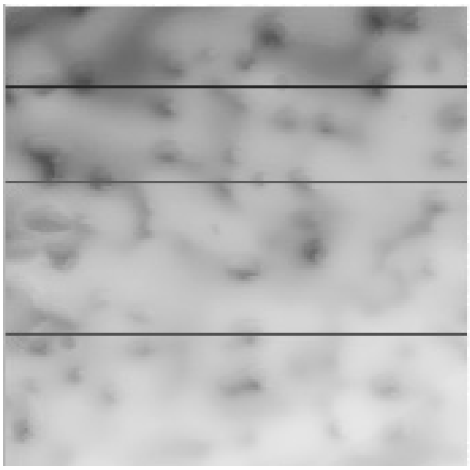

Fig. 16. Sensor image of Oxad-Si-B thin film deposited from 1.40% solution concentration with signed profiles

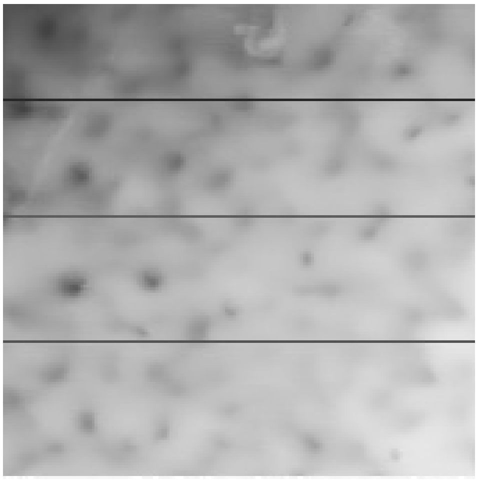

Fig. 17. Sensor image of Oxad-Si-B thin film deposited from 2.10% solution concentration with signed profiles

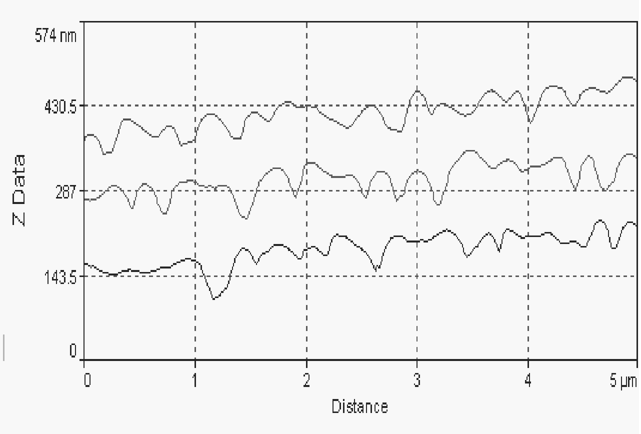

Fig. 18. Example surface profiles performed on sensor image 5x5 µm of Oxad-Si-B thin film deposited from 0.77% concentration solution

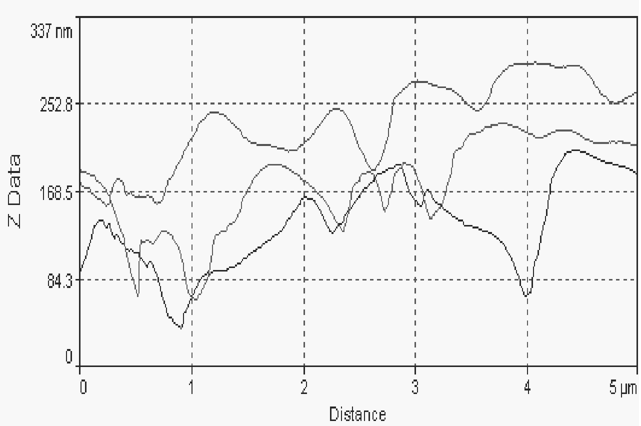

Fig. 19. Example surface profiles performed on sensor image 5x5 µm of Oxad-Si-B thin film deposited from 1.40% concentration solution

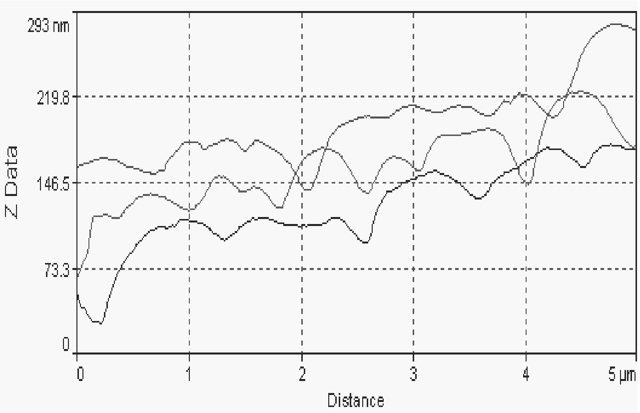

Fig. 20. Example surface profiles performed on sensor image 5x5 µm of Oxad-Si-B thin film deposited from 2.10% concentration solution

5. Conclusions

Thin films of Oxad-Si-B polymer were spin-coated with four spinning rates (3000, 4000, 5000 and 600 rpm) from three THF solution concentrations (0.77%, 1.40%, 2.10%) at room temperature. The strength of the absorbance spectra for thin films prepared from 0.77% solution was in each case the smallest. Absorbance strength of UV-Vis spectra taken on thin films prepared with spinning rates V=3000 rpm and V=6000 rpm from 2.1% solution have appeared to be weaker than in the spectra of thin films deposited from 1.4% solution. The films deposited with 3000 and 6000 rpm rates from 1.4% solution reveal the better conjugation than the others.

There are seen holes randomly distributed on AFM topographic images taken on as-deposited thin films. Average diameters of seen holes are in range 0.2-0.6 µm and roughness coefficients are in range 40-103 µm. RMS coefficient is decreasing with higher concentration of THF-Oxad-Si-B solution. Average diameter of holes is increasing with solution concentrations. The numerous of holes in topographic images is lower for higher concentration. The surface is smoother for 1.4% and 2.1% concentration.

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