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Sol-gel Al_2O_3 antireflection coatings for silicon solar cells

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ABSTRACT

Purpose: This paper presents the results of investigations on morphology and optical properties of the prepared aluminium oxide thin films

Design/methodology/approach: Thin films were prepared with use of sol-gel spin coating method. The changes of surface morphology were observed in topographic pictures performed with the atomic force microscope AFM. Obtained roughness coefficients values were generated with XEI Park Systems software. The thickness distribution were checked with spectroscopic ellipsometry with use of mapping mode. The optical reflection spectra were measured with UV-Vis spectrophotometry.

Findings: Results and their analysis show that the sol-gel method allows the deposition of homogenous thin films of Al_2O_3 with the desired geometric characteristics and good optical properties.

Practical implications: The technology of sol-gel aluminium oxide thin films deposition causes that mentioned thin films are good potential material for optics, optoelectronics and photovoltaics.

Originality/value: The paper presents some results of investigations on aluminium oxide thin films prepared with sol-gel spin coating method on polished monocrystalline silicon.

Keywords: Thin films; Aluminium oxide; Atomic Force Microscope; Spectroscopic ellipsometry; Spectroscopy UV/VIS

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PROPERTIES

1. Introduction

Different methods of thin films deposition allow modifications of their surface morphology for its better properties.

These processes should be provided in required environment/at required technical parameters. In the face of economic aspect the materials applied as thin layers of some structures should be chip enough. It is well known that several most important methods play a big role in world industry – the spin-coating methods (which allow preparation of thin films from solutions, gels) and vacuum techniques like CVD (Chemical Vapour Deposition), PVD (Physical Vapour Deposition), ALD (Atomic Layer Deposition). One of methods which find a lot of applications is sol-gel [1] technique, which is chip and allows modifications of thin films surface. Also this method's joining the sol-gel solution preparation with spin-coating technique. The sol-gel method, known since a long time is still an attractive and modern direction of development of materials science, including primarily surface engineering [2-5].

Sol-gel method includes the preparation of colloidal solutions (sols) by hydrolysis and condensation of the used precursors. Advanced condensation process, combined with the evaporation of the solvent most often leads to gels which can deposited as a thin film of amorphous structure material. The applying of additional heat treatment allows preparation of the materials with more ordered crystalline structure (Fig. 1) [6,7].

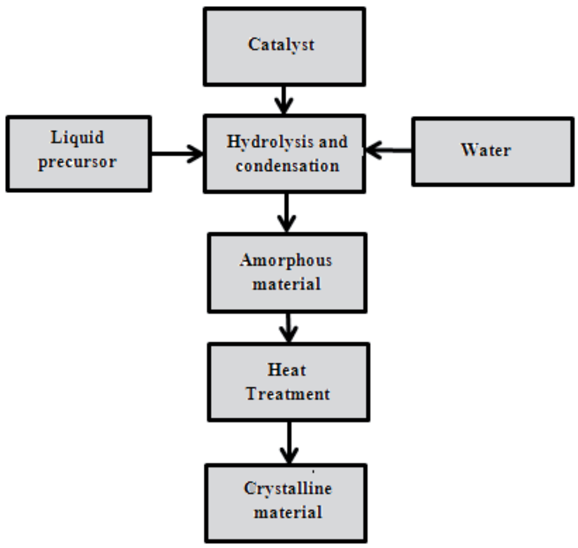

Fig. 1. Schematic representation of the sol-gel method [6,7]

The liquid precursors are really important in sol-gel technology. As a result of hydrolysis and condensation reactions it is possible to obtain gels. For the preparation of glass, monolithic and coating ceramic precursors most frequently used are alkoxides of transition metals (for example $Ti_4(OCH_3)_{16}$, $C_9H_{21}O_3Al$). Alkoxides of these metals are generally very reactive because of their consistent of highly electronegative OR groups. The organic and inorganic compounds can be used as precursors.

The most common used organic precursors are alkoxides of the following alkoxy groups [8, 9]:

- methoxy – OCH_3,
- ethoxy – OCH_2CH_3,
- n-propoxy – $O(CH_2)_2CH_3$,
- n-butoxy – $O(CH_2)_3CH_3$,
- butoxy – $H_3C(-O)CHCH_2CH_3$,
- izobutoxy – $OCH_2CH(CH_3)_2$.

Alkoxides are often used because of the presence of water which makes them more easy hydrolysed. Depending on the concentration of the water and catalyst the hydrolysis may occurs partially or completely. Thin films prepared with sol-gel method can be coated onto different substrates, including glass, ceramic, metal or polymer.

Really important is the roughness and the purity of prepared samples surface. Sol-gel method enables uniform covering the surfaces with low roughness. The thin films manufactured by sol-gel can be applied by various techniques, by dipping, spinning, casting or spraying. Each technique is characterized by selected technological parameters that have a significant effect on the properties and quality of the deposited thin films [8,9]. For example the spin- coating technique bases on speed of rotation of the substrate with droped solution. The technological parameters of spin-coating method are the spin speed and rise time [10]. Sol-gel method is used mainly for the production of oxide ceramics (e.g. SiO_2, TiO_2, Al_2O_3). This kind of thin films can be applied as the protection of the glasses from the effects of corrosive agents (protective thin films), to improve strength properties to impart specific optical properties of the substrate (reflection coating, antireflection, coloured, luminescent, etc.) and also to modify the conductivity of thin films (conductive and semi-conductive). Multicomponent coatings also can be used as the protection of metal substrates in acidic and aqueous environments. From the other hand the multicomponent oxide systems are used in the manufacture of glass fibres exposed to alkaline environments. Moreover, are also used as protection of aluminium foil from the effects of HCl acid at room temperature. Sol-gel method allows to obtain carbon ceramic nanopowders (e.g. NbC, TaC, Cr_3C_2, ZrC, SiC, TiC, VC). Non-oxide ceramic thin films deposited by the sol-gel method can be used as a ceramic protective thin film, including ceramic tool [11-25].

In the presented work the aluminium oxide thin films prepared by sol-gel method have been examined. This paper presents the results of investigations on the changes in surface morphology, roughness, thickness and optical reflection of Al_2O_3 thin films, by the atomic force microscope, and spectrometer UV/VIS as dependent on conditions of the thin films preparation.

2. Materials and methodology

Aluminium tri-sec butoxide (TBA) was used as a precursor to obtain Al_2O_3. It was mixed in appropriate proportions with anhydrous alcohol and acid to prepare Al_2O_3 solutions. Aluminium alkoxide was dissolved in anhydrous ethyl alcohol (molar ratio 1:4) and homogenized with a magnetic stirrer through 180 minutes at 25°C temperature. After that time the nitric acid has been added to the solution (molar ratio of 255:1) and later has been homogenized again through 180 min. The prepared solutions were aged at room temperature for 72 hours. The aluminium oxide solutions prepared by sol-gel method were applied for Al_2O_3 deposition with use of spin coating method. Technological parameters like centrifugation time, rise time (time to reach the spin speed) and the range of spin speed were chosen basing on preliminary experiments. The technological conditions are showed in Table 1.

Table 1.
Technological conditions of deposition process

No.	Spin speed, rpm	Rise time, s	Centrifugation time, s	Heat treatment, °C
1	1000	5	60	-
2	2000	5	60	-
3	3000	5	60	-
4	1000	5	60	100
5	2000	5	60	100
6	3000	5	60	100
7	1000	5	60	200
8	2000	5	60	200
9	3000	5	60	200
10	1000	5	60	300
11	2000	5	60	300
12	3000	5	60	300

3. Results and discussion

Thin films of Al_2O_3 were deposited with use of spin-coating method from aluminium oxide solution onto silicon substrates. We have checked the influence of technological parameters (like spin speed) on morphology of Al_2O_3 thin films and it has been noticed that morphology structure doesn't depend on spin speed significantly.

The topographic images taken with AFM microscopy (Figs. 2-4) showed that small atoms aggregations which size is less than 20 nm are visible on the surface. Thin film deposited with a 1000 rpm substrate spin speed was characterized by the RMS (root mean square) and R_a (arithmetic average of absolute values) coefficients, respectively, 0.27 and 0.22 nm. Topographic images of thin film deposited at 2000 and 3000 rpm allowed to observe values of RMS=0.26 and R_a=0.2 nm which were in nearly coincidence with coefficients of the first one (Table 2). Thin film deposited with spin speed equal to 2000 rpm on polished silicon substrate was additionally annealed in temperature equal to 200°C and 300°C. The AFM topographic analysis showed that temperature influences the surface morphology including size of atoms aggregations.

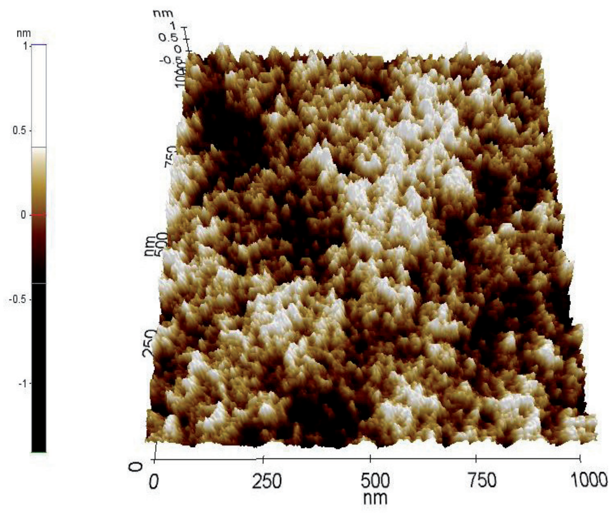

Fig. 2. AFM 3D image of the surface topography of Al_2O_3 thin film deposited with a 1000 rpm spin speed without heat treatment

It can be seen that size of atoms aggregations has been decreased after heat treatment. Size of aggregations after heating in 200°C was at about 0.5 μm (Fig. 5) and after heating in 300°C was at about 0.25 μm (Fig. 6). Also the values of RMS and R_a coefficients after annealing has been decreased. The RMS and R_a after heating in 200°C was equal to 0.19 nm and 0.14 nm respectively and after heating in 300°C has been decreased to 0.18 nm and 0.13 nm (Table 2). If we compare roughness coefficients presented in Table 2 can be observed that spin speed doesn't influences on the morphology of samples surface significantly, cause the RMS and R_a coefficients values are in nearly coincidence. The temperature of heat treatment influenced rather the size of aggregations.

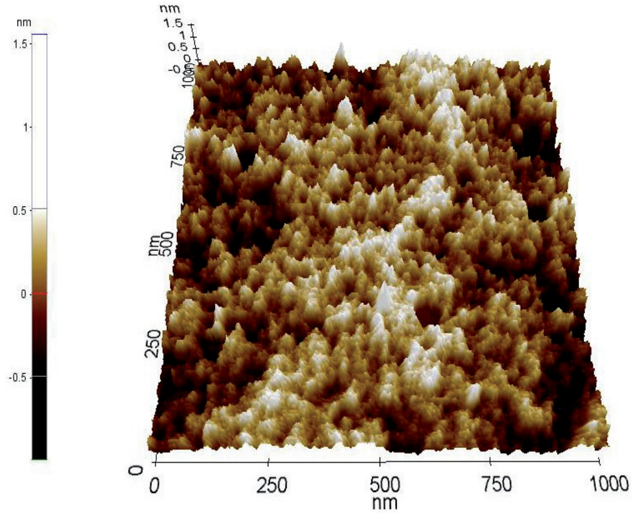

Fig. 3. AFM 3D image of the surface topography of Al_2O_3 thin film deposited with a 2000 rpm spin speed without heat treatment

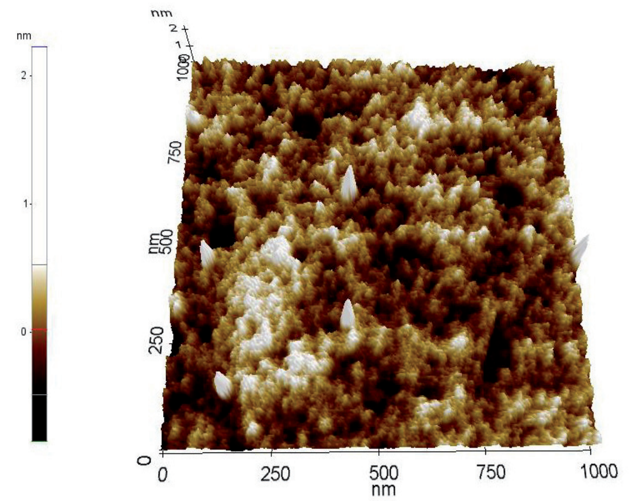

Fig. 4. AFM 3D image of the surface topography of Al_2O_3 thin film deposited with a 3000 rpm spin speed without heat treatment

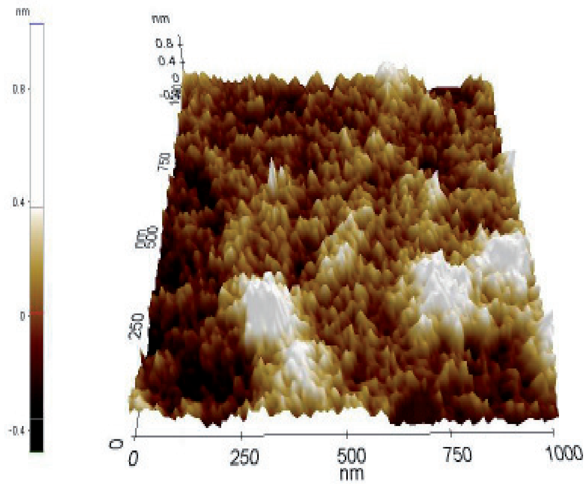

Fig. 5. AFM 3D image of the surface topography of Al_2O_3 thin film deposited with a 2000 rpm spin speed and with a 200ºC heat treatment

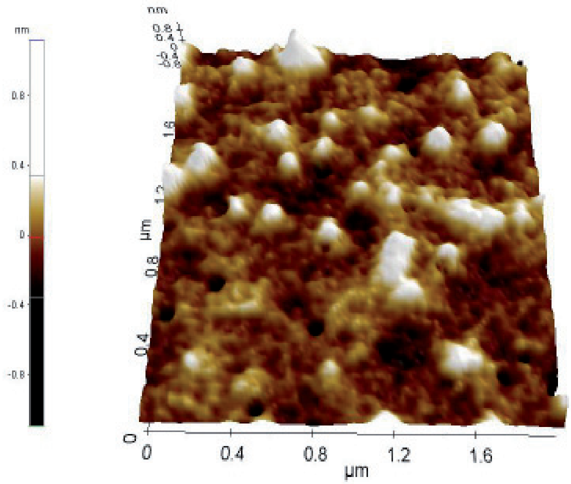

Fig. 6. AFM 3D image of the surface topography of Al_2O_3 thin film deposited with a 2000 rpm spin speed and with a 300ºC heat treatment

Table 2.
Calculated values of the RMS and R_a of Al_2O_3 thin films

No.	Spin speed, rpm	Additional heat treatment, °C	Value of RMS, nm	Value of R_a, nm
1	1000	-	0.27	0.22
2	2000	-	0.26	0.20
3	3000	-	0.26	0.20
4	2000	200	0.19	0.14
5	2000	300	0.18	0.13

Besides of morphology also the quality of prepared thin films was investigated with spectroscopic ellipsometry. The thickness distribution maps were performed with multipoint mapping mode of SENTECH SE 850 E spectroscopic ellipsometer. The measurements were carried out in room temperature under angle 70°. The Psi ad Delta measurements were performed on pure polished silicon substrate in the first step and on substrate with deposited thin film in the further step. The thickness value was determined with Spectra Ray 3 software basing one used model.

The used model included several layers (Silicon/SiO_x/Al_2O_3/air), where the parameters of individual layers were fitted step by step (in the first step just for substrate and in the second step for substrate with deposited film). The thin film of Al_2O_3 was fitted with Cauchy layer.

The mapping mode is working just with model, where individual parameters are fitted in different areas of sample. It's possible to get thickness and roughness distribution maps. The thickness distribution maps taken on prepared samples are showed in Figs. 7-11.

Basing on performed maps it has been noticed that quality of coated thin films is good enough. It's also visible that variation of thickness is not very high and surface of recorded area is rather smooth. One can see that surface of thin film deposited with spin speed equal to 1000 rpm (Fig. 7) is smooth and uniform and the maximum value of thickness is 162 nm and minimum value is 156 nm. The area with thickness equal to 161 nm reaches 96% of recorded area.

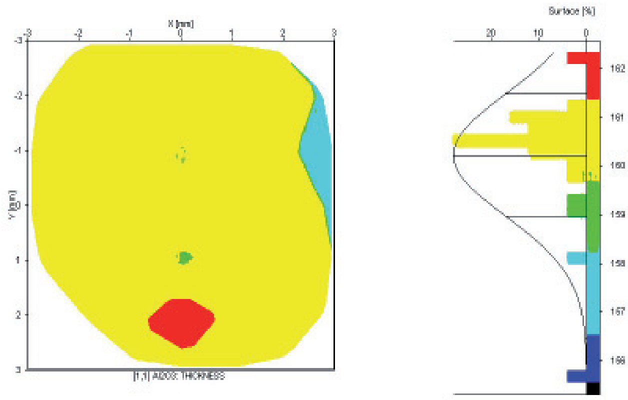

Fig. 7 The thickness distribution map of Al_2O_3 thin film deposited with a 1000 rpm spin speed without heat treatment

The thickness of thin film deposited with 2000 rpm (Fig. 8) spin speed was about 100 nm and the deviation from this value is not higher than 2 nm. The percent of thickness equal to 100 nm reaches 90% in recorded area. The surface is little more smooth than surface of sample deposited with 1000 rpm spin speed. It shows that thin film deposited with 3000 rpm without heat treatment (Fig. 9) has the best quality of presented samples. Its thickness has the smallest value equal to 84 nm where the percent of surface with the same value reaches 85% of recorded area.

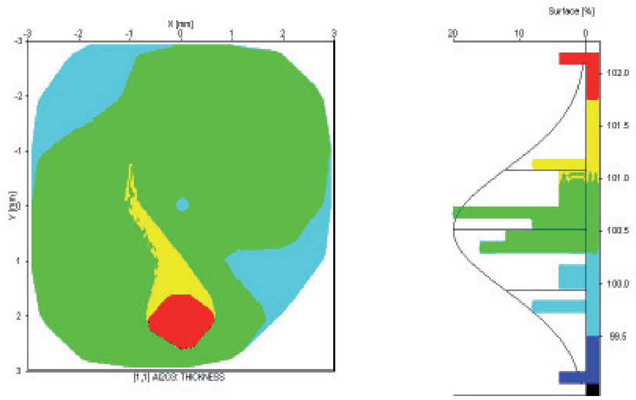

Fig. 8. The thickness distribution map of Al_2O_3 thin film deposited with a 2000 rpm spin speed without heat treatment

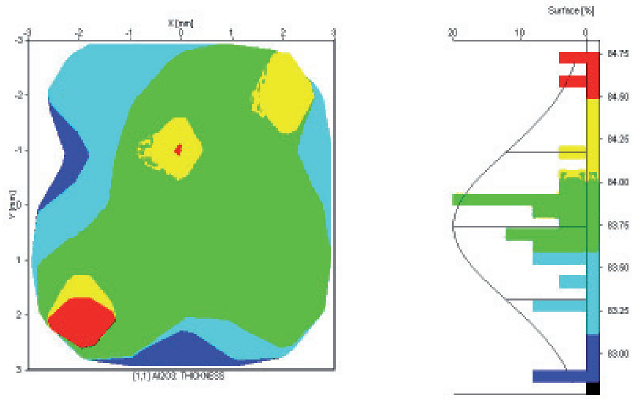

Fig. 9. The thickness distribution map of Al_2O_3 thin film deposited with a 3000 rpm spin speed without heat treatment

The analysis of obtained thickness values showed that higher spin speed determines small variation of the thickness value. The distribution maps of thin film deposited with 2000 rpm, annealed in 200ºC and 300ºC are showed in Figs. 10-11.

It can be seen that percent of surface with equal thickness decreases with the spin speed, but if we compare thickness variations – its value is lower with spin speed increase. The thickness variation of thin film deposited with 3000 rpm is not higher than 1.75 nm.

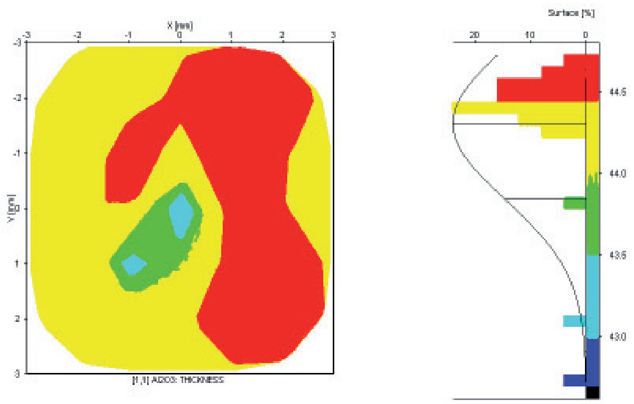

Fig. 10. The thickness distribution map of Al_2O_3 thin film deposited with a 2000 rpm spin speed and with a 200ºC heat treatment

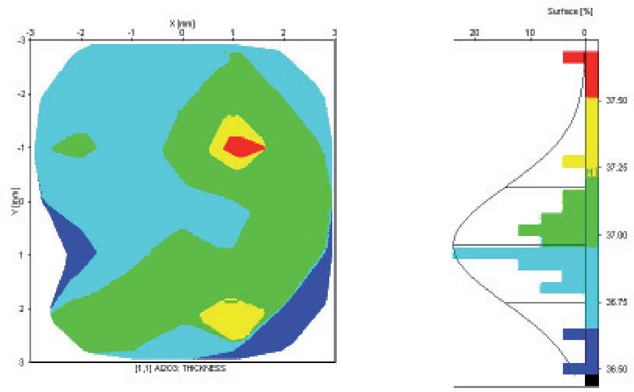

Fig. 11. The thickness distribution map of Al_2O_3 thin film deposited with a 2000 rpm spin speed and with a 300ºC heat treatment

The distribution map visible in Fig. 10 shows that thickness variation in all performed area is not higher than 1.5 nm and its average thickness has decreased from 100 nm to 44 nm. Also the surface is very smooth and flat. It has been found that thickness of the same sample has been decreased again after annealing in 300°C and is about 37 nm. The variation of thickness value is similar and isn't higher than 1.5 nm what means that change if thickness is the same in all surface area.

Basing on results performed with spectroscopic ellipsometry we can conclude that the spin speed and heat treatment reduce the sample thickness and its surface which is more smooth.

Thickness distribution maps showed in Figs. 7-11 are in good coincidence with reflectance spectra taken in 300-700 nm wavelength range (Fig. 12). The reflectance spectra of the thin films of Al_2O_3 deposited with spin-coating method were analysed focusing on variation of spin speed associated with reduction of film thickness. It has been observed that there is significant impact of the spin speed of the substrate on the reflection spectra.

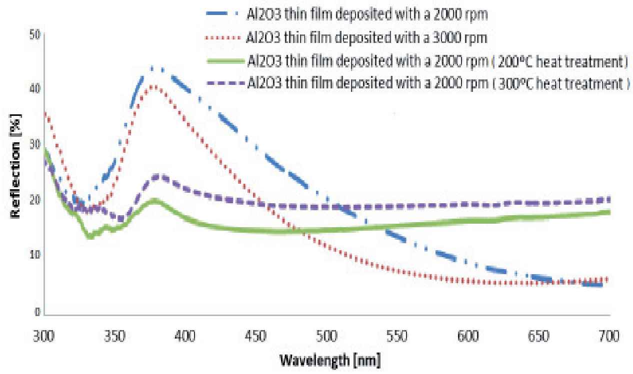

Fig. 12. The spectrum of reflection for the Al_2O_3 thin films deposited by sol-gel method

The intensities and the shapes of reflection bands depend on technological parameters of deposition process and on value of treatment temperature. The maxima of bands are placed at about 370 nm and 365 nm for thin films deposited with 2000 rpm and 3000 rmp spin speed respectively. The maxima of annealed films obtained with the same spin speed are placed at about the same wavelength values. The maximum of band in spectrum of thin film annealed in higher temperature is shifted more to higher values of wavelength. The intensity of reflection spectrum has been decreased with change of technological parameters in all cases and its value depends on spin speed. In first case the intensity of band is lower for thin film deposited at 3000 rpm and in the second case is lower for thin film treated in temperature 300°C. The changes of presented spectra are connected with thickness value which always will be lower in case of films deposited at higher values of spin speed. The treatment temperature influenced the crystalline structure of deposited layer, which is expected that will be more ordered with higher temperature and can also connected with change of thickness value. From the other hand the reflectance spectra are the confirmation of ellipsometric measurements. All obtained results showed that temperature treatment changed thickness, morphology and the properties of the same sample. In case of temperature treatment the structure is more ordered what's in good coincidence with topographic pictures and roughness coefficients values.

It's expected that chip and easy sol-gel method connected with heat treatment is the best technique for Al_2O_3 thin films deposition.

4. Conclusions

The Al_2O_3 solutions were prepared with sol-gel method and thin films were deposited with use of spin-coating.

The investigations on Al_2O_3 thin films included analysis of AFM topographic images, thickness distribution maps performed with ellipsometer mapping mode and reflection spectra.

The sol-gel method connected with spin-coating method allows the deposition of homogenous thin films with the desired thickness and good antireflective properties.

Basing on AFM topographic images we can conclude that technological parameters like spin speed doesn't significantly influence the surface morphology, where the molecules aggregations are visible. However, the aggregation size has been decreased after temperature treatment.

Thickness distribution maps analysis showed that surface of thin films obtained with mentioned method were uniform and smooth enough and the differences between thickness values in different areas of samples weren't higher than 7 nm.

The spectroscopic investigations performed on prepared samples shows that thin Al_2O_3 films have high transparency which value is over 90%. It correspond with very good antireflection properties (what's connected with low reflectance in a wide spectral range). Also additional heat treatment influences the reflection spectra of deposited films, where the intensity of reflection band was lower in the case of annealed sample.

All obtained results showed that antireflective properties and quality of obtained thin films are good enough for applying in industry.

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