

Synthis and Phisical And Chemical; Properties of $\text{SiO}_2 - \text{B}_2\text{O}_3$ and $\text{SiO}_2 - \text{P}_2\text{O}_5$ Thin Film Systems and Powders

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Abstract. The $\text{SiO}_2 - \text{B}_2\text{O}_3$ and $\text{SiO}_2 - \text{P}_2\text{O}_5$ films were synthesized by using film forming solutions having a P_2O_5 content of up to 30% and B_2O_3 up to 40%. Properties of the film-forming solutions and binary oxides were examined. The physical and chemical processes occurring in the solution during the heat treatment of films were examined. The conditions for producing films of different thicknesses were determined. The kinetic parameters were calculated.

1. Introduction

Currently, a lot of studies are devoted to inorganic silicate materials with a focus on their applications and functional uses. Available results relating to the synthesis and study of physical and chemical properties of materials allow us to design and develop thin-film based materials and devices for use in various industries, including mechanical engineering. A substance of thin films in the solid phase is a special state, and its properties are different from those of the same substance in the bulky state. The difference lies in the fact that such systems are characterized by a range of particle dimensions that dominates most of the physical and chemical properties [1,2]. The properties of thin-film materials sharply contrast with the properties of materials in the bulky state due to their specific features of macrostructure, which is very dependent on processes occurring during the formation of film systems. For various applications in modern machinery and tool manufacturing industries, products surfaces made of glass, ceramics, porcelain or other materials are often required to be hydrophobic and have wetting resistance to acidic or saline solutions and organic liquids. For this purpose it is often sufficient to apply a thin film of a specific chemical nature. Such films are designed for applications where it is important to maintain transparency, expand functionality of devices under particular severe weather conditions, and extend their service life. A variety of organic-silicone compositions are the most frequently used as hydrophobic coatings [3,4].

The aim of this work is to obtain thin films of $\text{SiO}_2 - \text{B}_2\text{O}_3$ and $\text{SiO}_2 - \text{P}_2\text{O}_5$ systems and study physical and chemical processes behind the synthesis as well as their properties. In the course of this work, the properties of film-forming solutions based on tetraethoxysilane, ethyl alcohol,



orthophosphoric and boric acids were investigated; ranges of stable film forming properties were studied; The physical and chemical processes of forming oxides during the heat treatment were examined; the optimal conditions for the formation of $\text{SiO}_2 - \text{B}_2\text{O}_3$ and $\text{SiO}_2 - \text{P}_2\text{O}_5$ films were determined; the physical and chemical properties of the obtained films were studied.

2. Experimental part

To obtain thin films of a specified composition, we used film forming solutions (FFSs), prepared on the basis of 96% ethanol, tetraethoxysilane, boric and orthophosphoric acids. The films were prepared on silicon and glass substrates. Two methods were used for obtaining: the processes of centrifugation at 3000 - 5000 rev/min and stretching at 1 - 5 mm/s. Samples were thermostatically controlled at a temperature of 333K for 30 minutes. The final formation of the film was made at temperatures of 473-873K for 1 hour. A glass viscometer ($d = 0,99 \text{ mm}$) was used to measure viscosity of solutions. The dried FFSs were analyzed by a NETSCHSTA 499C (in air; standard - calcined $\alpha - \text{Al}_2\text{O}_3$) in a temperature range of 25 to 1000 °C. The refractive index and thickness of films were measured at 5 points of each sample using laser ellipsometers LEF-3M and "SE400advanced". The morphology of the film surface was examined by a scanning electron microscope (SEM) HITACHI-3000.

3. Results and Discussion

The process of forming double oxides is complex and its processing history is influenced by conditions of preparing FFSs. For this purpose, during the first phase we studied the influence of adding boric and orthophosphoric acids on properties of FFSs. Since the main processes of forming FFSs are hydrolysis and polycondensation, a criterion for film-forming ability is viscosity of solutions. A detailed study of the system shows that the viscosity of the solution with orthophosphoric acid added is higher at the initial moment of time. However, the time to solution aging remains the same as the time to aging solutions without adding H_3PO_4 , i.e. for two days. Subsequently, the viscosity in the orthophosphoric acid – added system changes more significantly than in the plain system, and this points to the fact that H_3PO_4 accelerates hydrolysis and polycondensation, reducing a solution's expiration time.

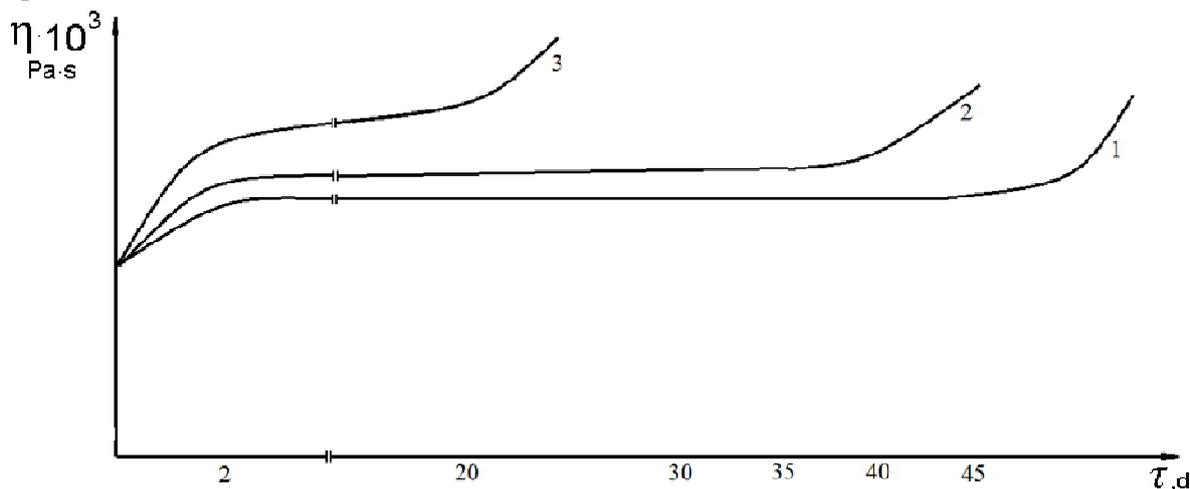


Figure 1. Time – dependent changes in viscosity of the FFSs with orthophosphoric acid added: 1 P_2O_5 – 10% by wt.; 2 P_2O_5 – 20% by wt.; 3 P_2O_5 – 30% by wt.

FFS without adding H_3PO_4 becomes a gel after 45 days after its preparation; FFS with adding orthophosphoric deteriorates after 35 days, moreover, the higher concentration of H_3PO_4 , the more the solution is subject to the aging process. The dependency of FFS viscosity on time is shown in Figure 1 [5, 6].

The film-forming properties of FFS with adding boric acid were measured by a viscometric method. The addition of boric acid has a less effect on the plain system than orthophosphoric acid, as H_3BO_3 ($pK_1=9,2$) is much weaker than H_3PO_4 ($pK_1=2,1$). The time to solution aging remains the same, i.e. two days. FFSs with boric acid added deteriorates in 43-44 days, and in this case, a concentration of boric acid does not cause a substantial change in viscosity, consequently, the time to expiration of the solution (Figure 2).

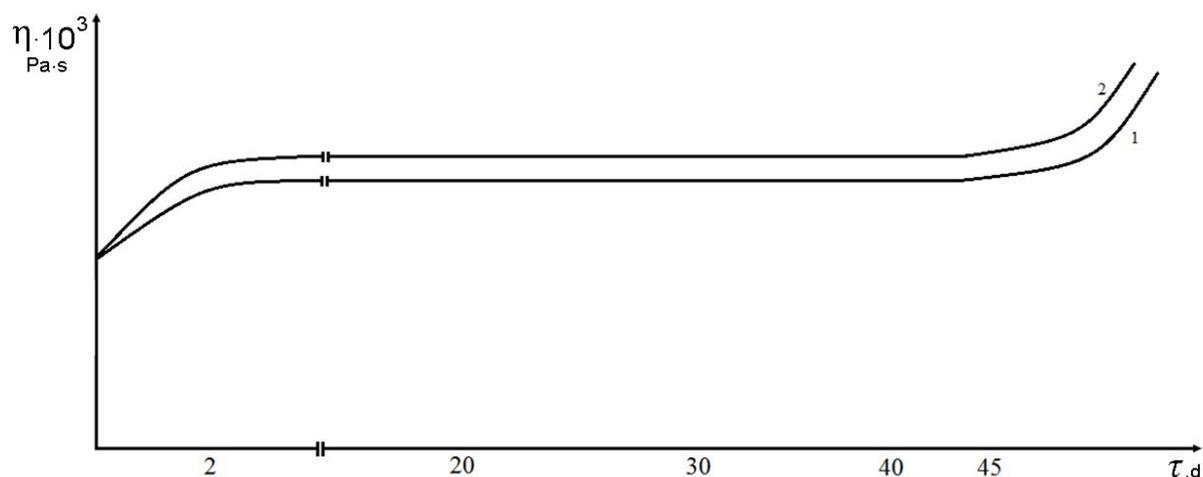


Figure 2. Time-dependent changes in viscosity of the FFSs with boric acid added: 1 B_2O_3 - 10% by wt.; 2 B_2O_3 - 30% by wt.

As a result, we established limits for a range of stabilized film-forming properties with regard to FFSs with H_3BO_3 and H_3PO_4 additions. The maximum content of B_2O_3 in the film reaches 40 % by weight. A further increase in boric acid concentration is limited by poor solubility in ethanol. The maximum content of P_2O_5 in the film is 90 % by weight. However, FFSs are not self-sustaining; the time to their aging varies 5 to 10 days at high concentrations of orthophosphoric acid in FFSs. The hydrolysis process rapidly flows at high concentrations of H_3PO_4 , resulting in the formation of glass-like polymer that is not suitable for producing films. Accordingly, FFSs with a content of P_2O_5 up to 30% in the film is classified as most technically possible.

The process of forming $SiO_2 - P_2O_5$ oxides is complicated and undertakes several phases. When comparing thermal micrographs of powders in the SiO_2 and $SiO_2 - P_2O_5$ systems, it can be noted that the addition of phosphoric acid to FFS reduces a decomposition temperature to 873K in comparison with the plain system – 973K. The formation process proceeds in three steps, as evidenced by the presence of three peaks in the DTA - curve (Figure 3). The first phase takes place at a temperature of up 433K and corresponds to the process of polycondensation. In this case, the polycondensation process is faster than in the plain SiO_2 system, this is indicative regarding a smaller value of activation energy (Table 1). The second phase starts at 473K and ends at 523K. This results in the decomposition process of polyorganosiloxanes, with the simultaneous processes of phosphoric acid decomposition and P_2O_5 oxide formation. Energetically, these processes are constrained, and the energy of activation is the highest at this phase (Table 1). During the third phase, an intermediate is formed according to equation 1 with subsequent break-down to $SiO_2 - P_2O_5$.

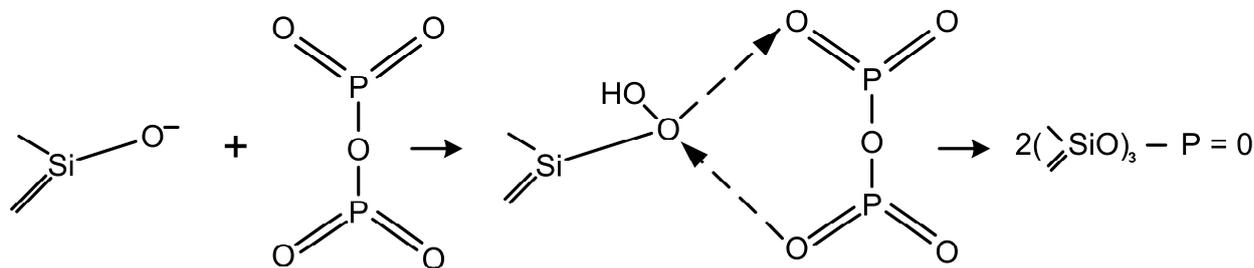


Table 1 Energy of Activation for the processes of obtaining powders

System	Phases	T, K	E _a , kJ/mol
SiO ₂	1	333 – 433	48,9
	2	433 – 973	70,4
SiO ₂ – P ₂ O ₅	1	333 – 433	42,6
	2	433 – 523	81,9
	3	523 – 873	32,0
SiO ₂ – B ₂ O ₃	1	333 – 433	54,2
	2	433 – 823	37,9

From scientific literature it is known that the energy required for breaking bonds P - O and Si - O have very high values of 597 kJ/mol and 408 kJ/mol respectively [7,8,9]. But the energy of activation in the third phase is not high, and it can be assumed that this occurs due to the formation of an intermediate, reducing the temperature of decomposition by 100K. We can also assume that the formation of SiO₂ – P₂O₅ oxides in the thin film state will proceed in the same way, in three stages. Therefore, a three step-wise process is required to ensure the formation of uniform structured films: first, drying at 333K for 15-20 minutes, then annealing at 523K for 30 min and final annealing at 873 K.

If we compare the thermal micrographs of SiO₂, SiO₂ – P₂O₅ and SiO₂ – B₂O₃ powders [10], it can be observed that adding boric acid to FFSs reduces a temperature of decomposition to 823K, which is 50 K lower than the temperature of decomposition when orthophosphoric acid is added. The process of forming oxides in the SiO₂ – B₂O₃ system develops in three phases as well, there are only two peaks observed in the DTA-curve (Figure 4). At a temperature of 433K two processes take place simultaneously: the decomposition of boric acid and polycondensation, both having the highest value of activation energy (Table 1). During the next phase, an intermediate is formed according to equation 2, which decomposes to SiO₂ – B₂O₃.

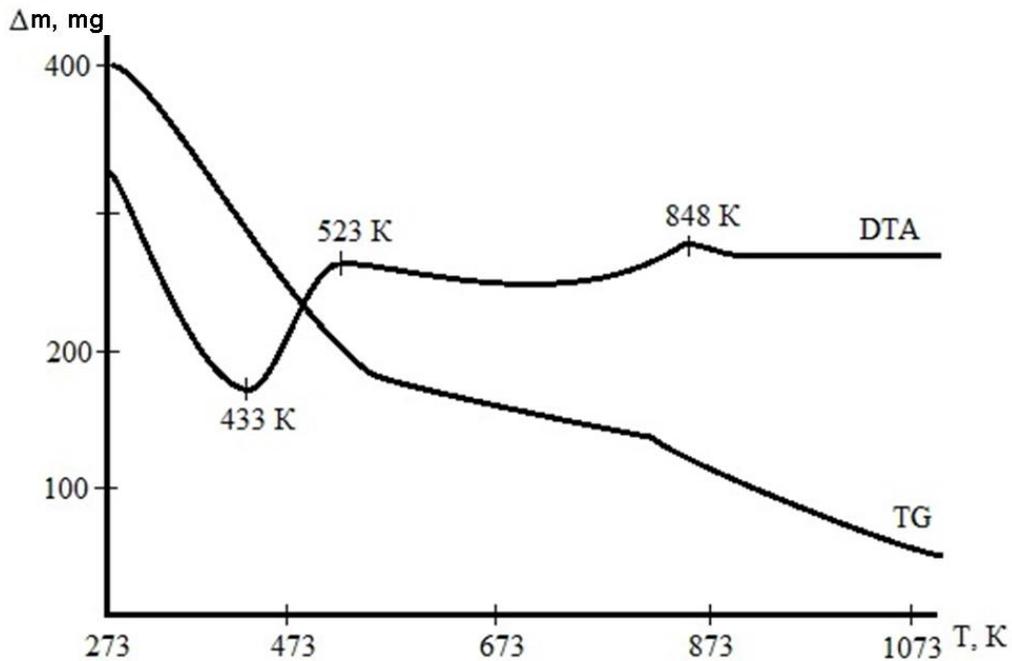
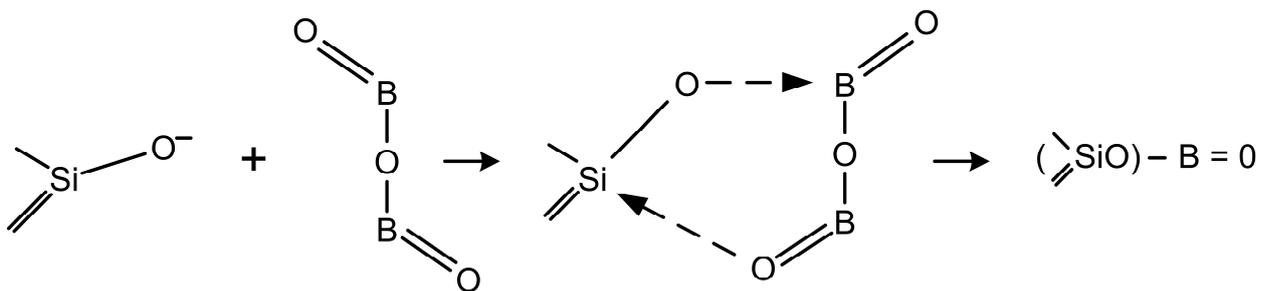


Figure 3. Thermogram of the $\text{SiO}_2 - \text{P}_2\text{O}_5$ formation by decomposing FFS based on tetraethoxysilane and orthophosphoric acids

The formed intermediate leads to a reduction in the energy of activation, as compared with the plain system, although it is higher than the energy of activation in the orthophosphoric acid added system. This apparently relates to the fact that the energy of B – O bond breaking is as high as 807 kJ/mol, so the process of breaking the intermediate takes place with difficulty and followed, accordingly, by an increase in the energy of activation. We can assume that the formation of $\text{SiO}_2 - \text{B}_2\text{O}_3$ oxides in the thin film state will proceed similarly in three stages. Therefore, a step-wise process is required to ensure the formation of uniform structured films: first, drying at 333K for 15-20 minutes, then annealing at 433K for 30 min and final annealing at 823K.



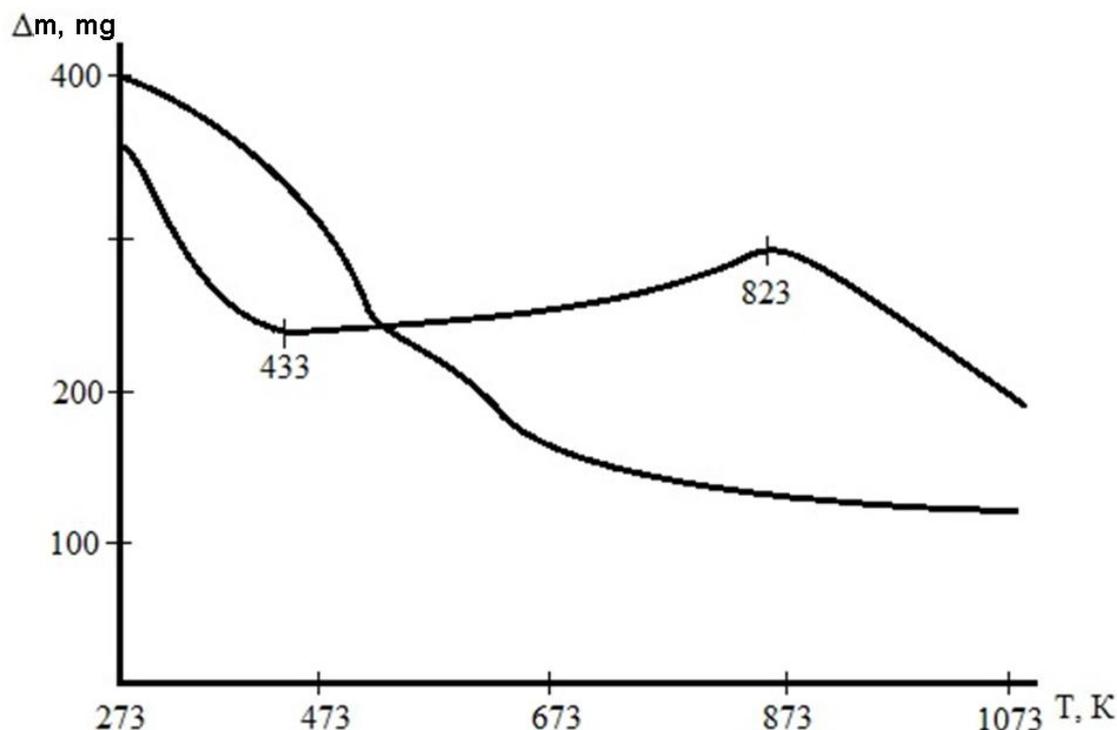


Figure 4. Thermogram of the $\text{SiO}_2 - \text{B}_2\text{O}_3$ formation by decomposing FFS based on tetraethoxysilane and boric acid

The study of physical and chemical properties of thin films allows us to make conclusions on possible uses of films with a specified composition. The $\text{SiO}_2 - \text{P}_2\text{O}_5$ films received from FFSs are nonporous, homogeneous and have a good adhesion to the substrate ($F = 0,993 \text{ kg/mm}^2$) (Figure 5). The values of refractive index are shown in Table 2 depending on the time to FFS aging, the rate of stretching and centrifugation.

Table 2. Dependencies of refractive indices and $\text{SiO}_2 - \text{P}_2\text{O}_5$ film thicknesses on the film forming processes

Property	Time to solution aging, day			A rate of stretching, mm/s			Centrifugation, rev/min		
	2	10	20	1	3	5	3000	4000	5000
n	1,378	1,476	1,536	1,463	1,474	1,431	1,479	1,473	1,415
d, nm	55,28	107,36	274,14	224,63	286,4	198,92	167,77	156,56	196,60

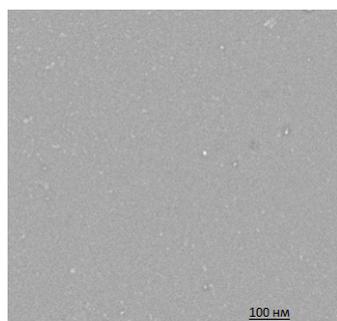


Figure 5 A micrograph of the $\text{SiO}_2 - \text{P}_2\text{O}_5$ film

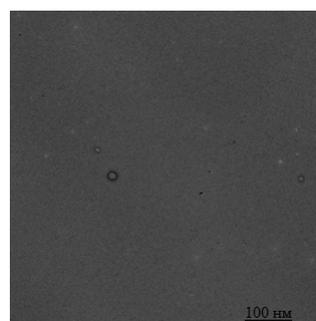


Figure 6 A Micrograph of the $\text{SiO}_2 - \text{B}_2\text{O}_3$ film

It should be noted that the film thickness and refractive index grow with increasing the time to solution aging. Apparently, the hydrolysis and polycondensation processes are faster when H_3PO_4 is added, causing the viscosity of the solution to increase that results in the increased thickness and refractive index.

The obtained $SiO_2 - B_2O_3$ films are nonporous and have a good adhesion ($F = 0,981 \text{ kg} / \text{mm}^2$) (Figure 6). The optical properties of the $SiO_2 - B_2O_3$ films are presented in Table 3.

Table 3. Dependencies of refractive indices and $SiO_2 - B_2O_3$ film thicknesses upon the film forming processes

Property	Time to solution aging, day			A rate of stretching, mm/s			Centrifugation, rev/min		
	2	10	20	1	3	5	3000	4000	5000
n	1,431	1,464	1,473	1,415	1,438	1,436	1,467	1,434	1,456
d, nm	198,92	224,63	286,4	167,77	178,32	193,24	198,87	177,83	181,77

In contrast to the $SiO_2 - P_2O_5$ films, the refractive index for the $SiO_2 - B_2O_3$ films does not increase noticeably with the time to FFS aging. This is explained by the fact that the viscosity of FFS with boric acid added does not change significantly.

4. Conclusions

Based on the results of research, the following conclusions can be made: using the viscometry methods, the influence of boric and orthophosphoric acids additives on the FFS properties were analyzed; the ranges of the solutions' stabilized film-forming properties were established. Application of H_3BO_3 is limited to 40% by wt. because of poor solubility of boric acid in ethanol, and H_3PO_4 is limited due to the fact that an increase in adding orthophosphoric acid reduces the expiry time of the solution up to 10 days. Therefore, the technologically usable solutions are those with acid additives up to 30% by wt. The mechanism for the formation of complex $SiO_2 - B_2O_3$ and $SiO_2 - P_2O_5$ oxides was studied; the optimal conditions for the formation of films are as follows: for $SiO_2 - P_2O_5$: 15-20 min at 333K, 30 min at 523K and 30 min at 873 K, and for $SiO_2 - B_2O_3$: 15-20 min at 333K, 30 min at 433K and 20-25 min at 823K.

The structure and physicochemical properties of the films were studied. The refractive index for the $SiO_2 - P_2O_5$ films varies from 1.38 to 1.53; the film thickness depends on the time to solution aging. The refractive index for the $SiO_2 - B_2O_3$ films varies from 1.41 to 1.47; the film thickness is practically independent of the aging time. The films with the specified compositions can be recommended as protective coatings in microelectronic and optic application.

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