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Influence of technological parameters on the properties of sol-gel silica films

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The paper presents the influence of selected technological parameters on the properties of silica films produced in sol-gel processes using the dip-coating method. The influence of water content and catalyst content was investigated as well as the influence of aging time of sols. It was demonstrated that the conditions of film deposition and the content of catalyst have a great influence on the thickness of the films produced. The greatest influence on the refractive index is exerted by molar ratio TEOS:H_2O. Together with the rise of aging time of the sol its properties are changing, and the changes depend on pH.

Keywords: sol-gel, silica film, dip coating.

1. Introduction

Due to their properties, silica films are particularly attractive for planar optics. The advantages of silica films are attributed to their high thermal stability and chemical resistance. Silica films, directly on silicon substrates, can be produced in the processes of thermal oxidation of silicon. In other cases, silica films can be produced with the application of vacuum techniques, such as chemical vapor deposition, sputtering or flame hydrolysis. The sol-gel method can be an alternative for those techniques. It does not require expensive technological installations and its biggest advantage over the conventional deposition methods is that the microstructure of the film being deposited can be modified accordingly [1]. In the sol-gel method glass or ceramics are produced from liquid phase at ambient temperature [1, 2]. Dielectric films produced with the use of sol-gel method are characterized by high homogeneity, and their properties (refractive index, porosity, thickness) are formed by an appropriate selection of technological parameters. Using the sol-gel method we can produce silica films of porous structure, which are characterized by lower refractive indices than dense silica. Such films can be applied in production of sensitive films for chemical amplitude evanescent wave sensors [3–5]. In such cases silica plays the role of a matrix in which indicators are bound. The properties of such sensors are dependant on their porosity and on the indicator applied. Porosity has the influence on the response time and regeneration time of the film. Sensor properties of such layers have been discussed in many publications [5–10], but the influence of technological parameters on their properties has not been thoroughly investigated in the literature.

In the present paper, we present the results of investigations involving the influence of selected technological parameters on the properties of the silica films produced. The films were produced with the application of dip-coating method. The investigations covered the influence of water amount, catalyst and aging time of sol on the thickness of the obtained films and their refractive index.

2. Sol-gel processing

2.1. Chemical basis

The sol-gel technique can be defined as a chemical production method of glass and ceramics from liquid phase. The following stages can be distinguished in sol-gel processes [1, 2]: formation of colloidal system, hydrolysis and condensation, deposition of sol film on the substrate as well as drying and heating of the films being produced. When tetraethoxysilane (TEOS) is applied as silica precursor, the reactions of hydrolysis and condensation are carried out in the following way [2]:

$$\equiv\mathrm{Si{-}OC_2H_5} + \mathrm{H_2O} \Leftrightarrow \equiv\mathrm{Si{-}HO} + \mathrm{C_2H_5OH} \quad \text{(hydrolysis)} \tag{1}$$

$$\equiv\mathrm{Si{-}OC_2H_5} + \mathrm{HO{-}Si}\equiv \Leftrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{C_2H_5OH} \quad \text{(alcohol condensation)} \tag{2}$$

$$\equiv\mathrm{Si{-}OH} + \mathrm{HO{-}Si}\equiv \Leftrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \quad \text{(water condensation)} \tag{3}$$

The reactions of condensation start before the reactions of hydrolysis are finished. In theory, to ensure a full hydrolysis reaction of TEOS it is enough to ensure the ratio H_2O:TEOS at the level of $R = 2$. However, even in excess water ($R \gg 2$), the reaction of TEOS hydrolysis does not go completion [2]. The proportions of the applied output components, kind and amount of the applied catalyst as well as parameters characterizing particular stages of the technological process have the influence on the properties of the films obtained.

2.2. Film formation by dip coating methods

In sol-gel technique the films are produced with the application of three methods: spin coating method, dip coating method and meniscus coating method [2]. In the studies presented the dip coating method was applied, in which substrate withdrawal speed from the sol is the basic parameter having the influence on the thickness of the film. When the sol shows the properties of Newtonian liquid and its viscosity and substrate withdrawal speed are high enough to reduce the curvature radius of meniscus, then the dependence of the thickness d of the sol film being deposited on the substrate withdrawal speed v can be defined by means of the following expression [1, 2]:

$$d = c_1\left(\frac{\eta v}{\rho g}\right)^{1/2} \tag{4}$$

where $c_1 \approx 0.8$, η is the dynamic viscosity of sol, ρ is the concentration of sol and g is the acceleration due to gravity. When the movement of substrate does not result in the reduction of meniscus curvature, the dependence of thickness d of the film being obtained on the speed v of the substrate is expressed by the expression of Landau and Levich [1, 2]:

$$d = 0.94\frac{(\eta v)^{2/3}}{\sigma_{L,V}^{1/6}(\rho g)^{1/2}} \tag{5}$$

where $\sigma_{L,V}$ is the liquid-vapor surface tension.

When deriving the above relations the evaporation of solvents was not considered. The sol films deposited on the substrate are then subjected to drying and heating. In the above processes the films get concentrated whereby their thickness is considerably smaller. This effect can be allowed for by complementing the above expression with a contraction factor [11]. Taking into consideration expressions (4) and (5), the dependence of final film thickness on substrate withdrawal speed from the sol can be written in the following form:

$$d = a\xi v^{\alpha} \tag{6}$$

where $\xi = 1$ (cm/min)$^{-\alpha}$ is a scaling factor (the speed is expressed in cm/min). For a given technological process the factor of proportionality a, and exponent α can be derived empirically. Frequently the relation $d(v)$ is presented in the literature in the logarithmic scale and hence the exponent α is referred to as a slope. With Eqs. (4) and (5) taken into consideration, we can expect that its value is within the range from 0.50 to 0.66.

2.3. Film fabrication

Tetraethoxysilane (TEOS) was the precursor of the silica films produced, and hydrochloric acid (HCl) was used as a catalyst. In all processes described here TEOS was dissolved in ethyl alcohol (EtOH) in constant molar ratio TEOS:EtOH = 1:4. After adding the appropriate volume of water and catalyst the hydrolysis of TEOS was carried out. For all solutions the reactions were carried out for 3 h in a closed glass vessel at a temperature of 50°C with ultrasonic stirring being used. After cooling the sol to the room temperature (18°C) the films were deposited on the glass substrates. The tests were carried out with respect to solutions of different content of water and different amount of the catalyst. In the solutions under investigation the molar ratio H_2O:TEOS was $R = 2$, 4, 8 and 16, respectively. And the molar ratio TEOS:HCl varied from 0.01 to 0.38. The films were deposited on glass substrates by means of controlled withdrawal from the sol. For that purpose, a mechanical system was constructed which allowed the withdrawal of the substrates at a controllable rate. In the investigations the withdrawal rate from 2 to 10 cm/min was applied. The accuracy of withdrawal rate measurement was $\Delta v = 0.02$ cm/min for $v = 2.00$ cm/min and $\Delta v = 0.12$ cm/min for $v = 10.00$ cm/min but the uniformity of the withdrawal rate was considerably better. Microscope slides (Menzel–Glaser) of the dimensions 76×26×1 mm were applied as substrates. Substrate glass was subjected to cleaning procedure which involved the following: mechanical washing in water with detergent, rinsing in deionized water, soaking in the solution of ammonia water, rinsing in deionized water, rinsing in acetone and drying. The sol in which the substrates were immersed was in a beaker, the whole being shielded by a glass cylinder. The application of such a procedure prevented accidental movement of air and, in consequence, ensure homogeneity of the films obtained. The fabricated films were then dried and in each case they were annealed for 2 h at a temperature of 150°C.

3. Measuring method

The thickness and refractive indices of silica films were measured in the ellipsometric way. The ellipsometric method consists in changing the polarization state, which happens to the light beam reflected from the investigated sample [12]. The basic ellipsometric equation has the following form:

$$\rho = \frac{R_p}{R_s} = \tan \Psi \exp(i\Delta), \tag{7}$$

with R_p and R_s indicating the reflection coefficients respectively for the light polarized in parallel (subscript p) and perpendicularly (subscript s) to the plane of incidence. The angles Ψ and Δ are referred to as ellipsometric angles and they generally depend on the film parameters, substrate and the ambient medium. From the measurements of ellipsometric angles, film parameters are determined. The experiments were carried out for the wavelength of $\lambda = 632.8$ nm with the application of a monochromatic ellipsometer Sentech SE400 (Germany). During the measurements the relative humidity in the room was about 40%.

4. Experimental results and discussion

4.1. Effect of water:precursor ratio

The influence of water:precursor ratio R on the properties of the sol obtained was investigated, and then consequently on refractive index and thickness of the silica films produced. Technological processes were carried out in which different water:precursor ratio R was used to prepare the sols. The sols were prepared according to the procedure presented in Sec. 2.3., in which the molar ratio of water to TEOS was $R = 2$, 4, 8 and 12, respectively. The molar ratio TEOS:HCl was 1:0.02 (pH > 2). On the same day

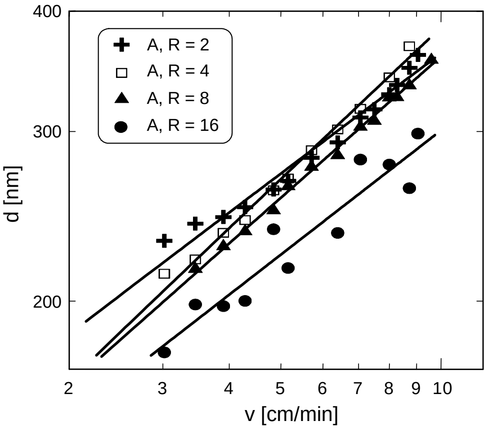


Fig. 1. Dependence of film thickness on the substrate withdrawal speed for different water content *R* (TEOS:EtOH:HCl = 1:4:0.02).

the films were fabricated which, on the next day, were subjected to annealing for 2 h at a temperature of 150°C. The parameters of the films were measured in the ellipsometric way. The dependences of the final thickness of films on the speed of substrate withdrawal from the sol are presented in Fig.1. In the figures the experimental points have been marked. The curves have been determined from the approximation of experimental data using relation (6).

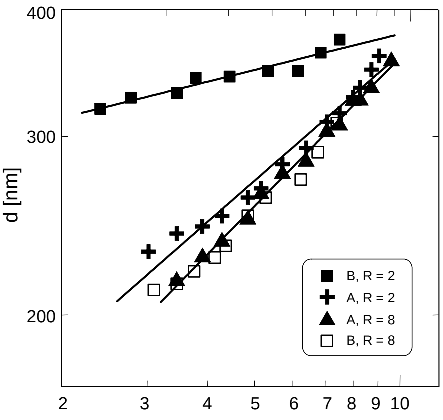
The films were fabricated in room conditions when the sol was placed in a beaker shielded by a glass cylinder, which reduced the movement of air around the beaker. In such a system, there is a high concentration of solvent vapours (mainly of EtOH) in the air inside the cylinder. It has the influence on their evaporation rate from the deposited sol film, and hence on the thickness of the fabricated films. The characteristics reflecting such conditions are additionally marked with the symbol *A*. It can be seen from the dependences presented in Fig. 1 that the content of water in the sol has the influence on their run. For $R > 2$, for a given substrate withdrawal speed from the sol, the thickness of films decreases with the rise of *R*. The solution with the lowest water content ($R = 2$) exhibited different properties. Then, the run corresponding to the highest water content ($R = 16$) is characterized by high dispersion of experimental points. The sols, for which $R < 16$, yielded homogeneous films of good quality. The films fabricated from the sol for which $R = 16$ had heterogeneous thickness. And hence the run corresponding to them is characterized by the highest dispersion of points. This is caused by the fact that with such a high amount of water the surface tension of sol is rising considerably and due to that the wettability of substrate deteriorates.

The technological processes presented here were repeated in the same way, with the conditions of film deposition being slightly changed. The change consisted in raising the cylinder shielding the beaker with sol by a few millimeters to ensure the movement of air around the beaker. In this way, the concentration of solvents in the

Table. Parameters of matching curves.

	α		a [nm]	
	A	*B*	*A*	*B*
$R = 2$	0.404±0.004	0.118±0.004	146.04±0.98	290.58±1.52
$R = 4$	0.514±0.004	0.422±0.004	119.51±0.64	142.84±0.79
$R = 8$	0.485±0.002	0.441±0.005	118.07±0.37	126.47±0.83
$R = 16$	0.428±0.010	0.436±0.011	112.14±2.01	117.78±1.67

vicinity of the beaker with sol decreased, which, in consequence, had influence on their evaporation rate from the films being deposited. The results obtained in such conditions were marked with symbol *B*. For the sake of comparison, the selected characteristics, corresponding to different conditions of film deposition are presented together in Fig. 2, and the parameters of matching curves are given in the Table. We can clearly see the influence involving the change of film deposition conditions on the characteristics obtained. The biggest differences can be observed for $R = 2$. For $R = 4$ the influence involving the change of film deposition conditions is smaller, and for $R = 8$, as can be seen from Fig. 2, the characteristics practically overlap. For $R = 16$ the parameters of matching curves are almost the same. The growing difference between the characteristics with R being decreased is probably caused not only by the change of concentration of solvents present in the atmosphere surrounding the sol but also by water being transferred to the layer of sol by the passing air. Additionally, the flow of air around the film, increasing the evaporation of the catalyst from the sol film, can increase its pH, accelerating in this way the condensation process. Also, in the case of the repeated process, for $R = 16$ the films obtained were of the worst quality. It can be observed from the comparison of matching curves that only for $R = 4$ and for the process *A*, the slope α is within the expected range of values, and the films corresponding to it are characterized in terms of visual assessment by the best quality. For the remaining cases the slope α has the values below expectation. This is indicated by the fact that the sols in the deposited films do not show the properties of Newtonian liquids. It can be seen from the parameters presented in the Table that the flow of air in the vicinity of the beaker with sol has the influence on the properties of sols in the deposited films. The flowing air changes the evaporation rate of solvents (mainly EtOH), but also by transferring water to the film, it affects the processes of hydrolysis and condensation taking place in the film. All results presented below correspond with the conditions of film deposition when the flow of air around the sol was reduced. The influence of water content R in the sol on refractive indices of films is illustrated in Fig. 3. Two runs are presented which correspond with different times of film drying marked in the figure. We can observe from the runs that the lowest refractive index corresponds to $R = 2$. For $R > 4$ the refractive index rises inconsiderably with the rise of water content in the sol. We can also observe that lower values of refractive index correspond also with longer times of film drying. During the drying process the



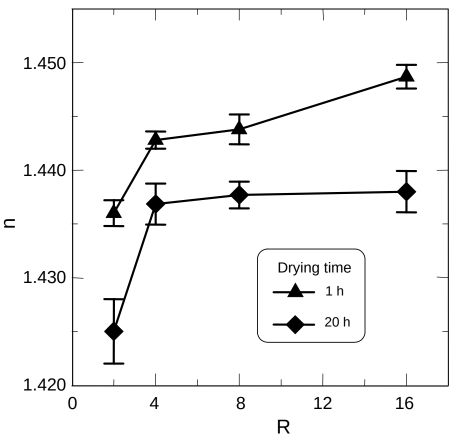


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Fig. 2. Influence of film deposition conditions (*A* – with flow of air around the beaker, *B* – without flow of air around the beaker).

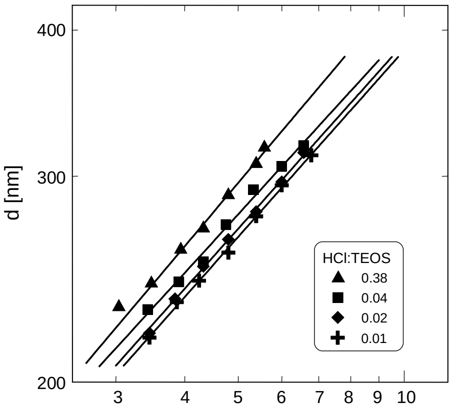
Fig. 3. Refractive index *vs.* water content *R* (TEOS : EtOH : HCl = 1 : 4 : 0.02).

structure of the film material is stiffening, and during the heating process the structure of the film material condenses. The stiffer structure is less susceptible to condensation, and hence the films, which were subjected to drying were characterized by higher thickness and lower refractive index, as presented in Fig. 2.

The results presented above show that when the hydrolysis is carried out in conditions with water excess and pH > 2, then with the rise of *R*, for a given substrate withdrawal speed, the films obtained get thinner and thinner. The excess of water in weakly acidified silica sols accelerates hydrolysis and slows down the condensation, effecting the formation of more furcated polymer networks [13]. The rise of *R* results therefore in higher dissolution of sol and lower condensation level, and then consequently reduced viscosity of sol and in effect smaller thickness of the fabricated films. McDonagh *et al.* [14] have shown that for sols obtained in the conditions of acid hydrolysis (pH < 2) the thickness of films increases with the rise of *R*.

4.2. Effect of catalyst : precursor ratio

The influence of the amount of catalyst on the dependence of film thickness of the fabricated film on the substrate withdrawal speed from the sol is presented in Fig. 4. The results were obtained for the films fabricated from sols of the molar ratio TEOS : EtOH : H_2O = 1 : 4 : 4. The molar ratios HCl : TEOS is marked in the figure. The characteristics presented correspond with the films, which were fabricated on the next day, after the sols had been prepared, *i.e.*, when the sols had been subjected to aging process for 24 h. The dependence of film thickness on the amount of catalyst, for the substrate withdrawal speed from the sol v = 6 cm/min is presented in Fig. 5. The dependences correspond with the films obtained on the day the sol was prepared (dependence *A*) and with the films prepared on the next day (dependence *B*). Higher



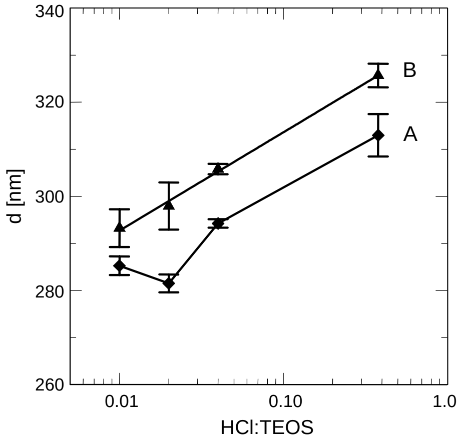


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Fig. 4. Film thickness *vs.* substrate withdrawal speed for different molar ratio HCl:TEOS (TEOS : EtOH : H_2O = 1 : 4 : 4).

Fig. 5. Film thickness *vs.* molar ratio HCl:TEOS. Withdrawal speed v = 6 cm/min, *A* – the films fabricated on the day the sol was prepared, *B* – the films fabricated on the next day.

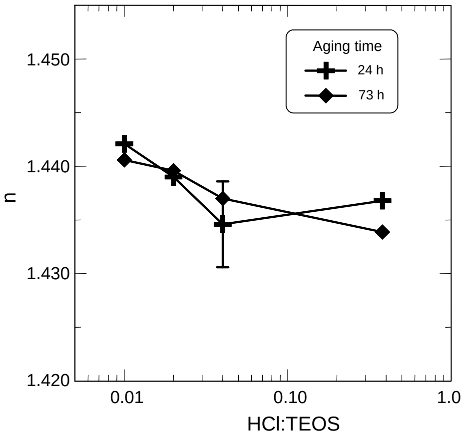


Fig. 6. Refractive index *vs.* molar ratio HCl : TEOS (TEOS : EtOH : H_2O = 1 : 4 : 4).

content of the catalyst in the sol corresponds with higher thickness of films. For the sol subjected to aging for 24 h the dependence of film thickness on log(HCl:TEOS) is linear. The influence of catalyst content on refractive indices of the films, for two selected aging times of sols, is presented in Fig. 6. We can observe a weak dependence of refractive index on the amount of catalyst in the sol. The values of refractive index slightly decrease with the rise of molar ratio HCl : TEOS. These changes are within the measurement error. BRINKER *et al.* [1] have shown that the pH value of the sol, influencing the processes of hydrolysis and condensation, affects the slope α. The problem will be investigated in the next part of the paper.

4.3. Influence of aging time of the sol

The results presented in Sec. 4.2 show that together with aging time of the sol its properties undergo changes. The set of characteristics, which were obtained for different aging times of sols and for different amounts of catalyst are presented in Fig. 7**a** and **b**. From the approximation of experimental points with the relation (6) the slope α was determined whose dependence on aging times of sols of different catalyst concentrations is presented in Fig. 8. We can see three different types of dependence, which are due to the changes taking place in the microstructure of particular sols. The smallest changes are observed for the sol for which the molar ratio TEOS : HCl = 0.04.

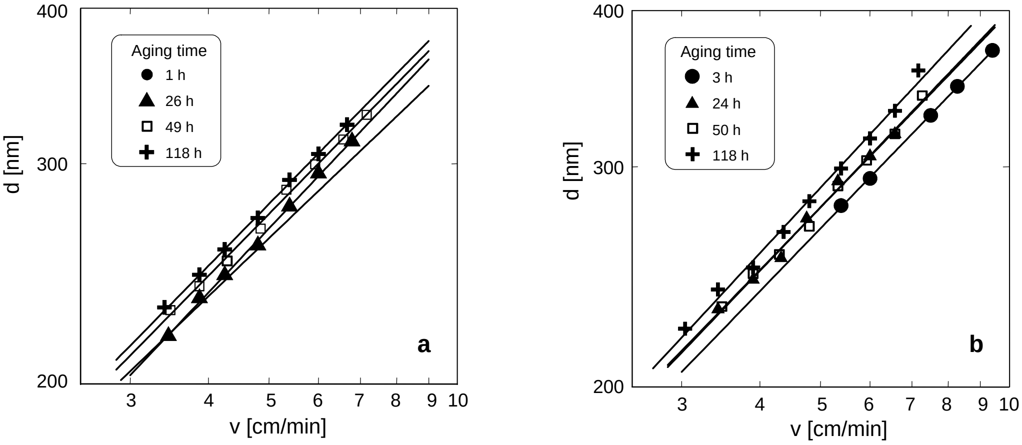
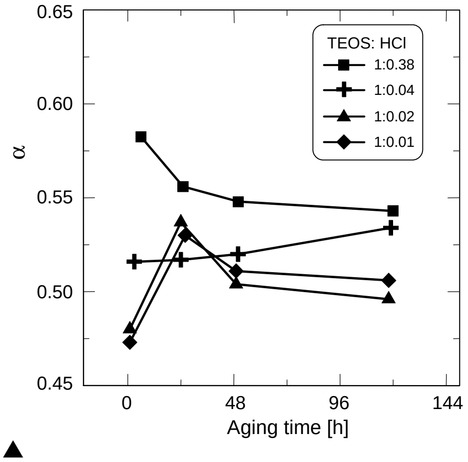


Fig. 7. Dependences of film thickness on the substrate withdrawal speed: **a** – TEOS : EOH : H_2O : HCl = = 1 : 4 : 4 : 0.01, **b** – TEOS : EOH : H_2O : HCl = 1 : 4 : 4 : 0.04.



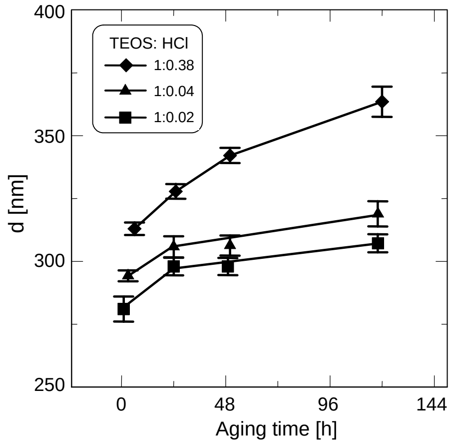


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Fig. 8. Slop *a* *vs.* aging time for different amounts of catalyst (TEOS : EtOH : H_2O = 1 : 4 : 4).

Fig. 9. Influence of aging time on refractive index for different molar ratio TEOS : HCl, *v* = 6 cm/min.

In this case, for a fresh sol $\alpha = 0.516\pm0.001$ and for the sol subjected to aging for 119 hours $\alpha = 0.534\pm0.003$. For this sol pH~2 was measured and hence its properties. For silica sols catalyzed with hydrochloric acid, when pH~2, weakly branched silica sols are deposited and the condensation rate is minimized [2]. And hence the properties of the sol, for which the molar ratio TEOS : HCl = 1 : 0.04, were inconsiderably changing in time. In effect we have small changes of slope α. In the sol with high concentration of catalyst, for which the molar ratio TEOS : HCl = 1 : 0.38 (pH < 2, acid catalysis) the hydrolysis process ran very fast, and the condensation process yielded weakly branched structures, resulting in gradual rise in viscosity and, in consequence, gradual decrease of slope α. In the remaining sols, for which pH > 2, the process of hydrolysis ran slowly and that of condensation was running fast. So, the increase of aging time of the sol resulted in the increase and aggregation of particles. The results obtained show a pronounced change of the sol properties. The slope values show that they have different properties from those of Newtonian liquids. However, after 24 h of aging, their properties changed considerably; slope surpassed the value of 0.5, which might mean that they have the properties of Newtonian liquid. Further elongation of aging time of the sol results in a gradual increase of its viscosity and the reduction of slope α.

The influence of aging time of the sol on the thickness of films for a set substrate withdrawal speed from sols $v = 6$ cm/min is presented in Fig. 9. With the rise of aging time of the sols the thickness of films is rising with a substrate withdrawal speed from the sols. However, this increase is not uniform. The biggest rise can be observed in the first phase of sol aging. For sols with the highest content of catalyst, the strongest dependence is observed, which is then getting weaker with the rise of aging time of the sol. For smaller concentrations of the catalyst the dependence of film thickness on aging time of the sol is becoming a weak dependence when these times are longer than 24 hours. It may be indicative of the fact that the properties of sols get somehow stabilized. The investigations carried out have not proved that there is any influence of aging time of the sols on the refractive index of films.

4.4. Uniformity of films

All films produced from sols, whose molar ratio water : precursor was $R < 16$ were characterized by high homogeneity of thickness. Figure 10 presents the dependence of the thickness d on the location x for the films produced from the sol for which the molar ratio TEOS : EtOH : H_2O : HCl = 1 : 4 : 2 : 0.2. During the production of films, the beaker with sol was shielded by a glass cylinder, owing to which any incidental flow of air around the coated layer was eliminated. The relations presented were obtained from the measurement of film thickness carried out along the sample. The distance between the measurement points was 1 mm. In each case the width of the interval of thickness d, within which the measurement points are located is lower than 3 nm. For the films presented here, the values of standard deviation of the thickness are

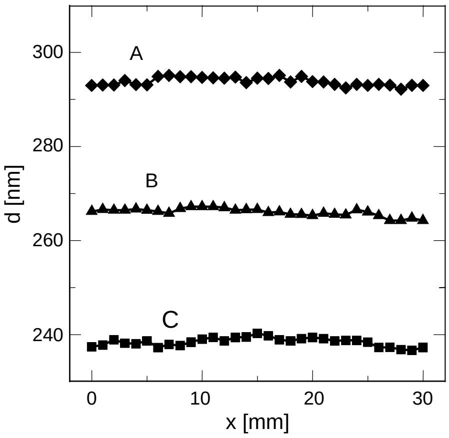

Fig. 10. Distributions of thickness for fabricated silica films.

respectively: $\Delta d = 0.90$ nm for film *A*, $\Delta d = 0.86$ nm for film *B* and $\Delta d = 0.92$ nm for film *C*. As can be seen from the above, by the application of dip-coating method in sol-gel technology, we can produce silica films which are characterized by thickness homogeneity of the order of 1 nm. However, it must be emphasized that the acquisition of such homogeneity of thickness was only possible when we ensured constant withdrawal rate and when any incidental flow of air around the coated film was eliminated.

5. Conclusions

The paper presents the results of investigations involving the influence of selected technological parameters on the properties of silica films fabricated in sol-gel process. We presented the influence of water amount, the influence of the amount of the applied catalyst, the influence of substrate withdrawal speed from the sol and the influence of the conditions of film deposition and aging time of sols on the final parameters of the films fabricated. The results of the investigations show that the application of too much water has a negative influence on the uniformity of the film thickness, but at the same time the processes with the application of high content of water are least sensitive to the changes of conditions involving film deposition. The reduction of water content in the sols as well as longer time of film drying result in the reduction of refractive index of the films. The rise of catalyst amount has influence on the rise of the film thickness with a given substrate withdrawal speed from the sol, but it has inconsiderable influence on the lowering of refractive index. The sols investigated become stable after at least 24 hours. By ensuring constant withdrawal rate and by the elimination of incidental air flow around the sol during the coating process, we can produce silica films of the thickness homogeneity at the level of 1 nm. The results of investigations can be applied in the sensitive film technology for planar chemical evanescent waveguide sensors.

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