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Influence of aging and annealing on the properties of silica films produced with sol-gel method

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The paper presents the results of investigations involving the influence of aging and annealing of the sol films on the final parameters of the obtained silica films. Both technological process and measurement method were described. The changes of refractive index were presented as well as the changes of film thickness of sols deposited on glass substrates during their aging under ambient conditions. The influence of the annealing process of films on their final parameters was examined. Silica films on glass substrates were deposited using dip coating method.

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, created 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 accordingly modified [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 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 indexes than that of dense silica. Such films can be applied for the production of sensitive films for chemical amplitude evanescent wave sensors [3–5]. In such cases silica is playing the role of a matrix in which indicators are bound. The properties of such sensors are dependant on both their porosity and the applied indicator. Porosity has the influence on the response time and regeneration time of the film. Sensor properties of such films were discussed in many papers [5–10], but the influence of technological parameters on the film properties has not been investigated thoroughly enough in the literature.

The work [10] presents the influence of the amount of water and catalyst on the properties of the produced silica films. Also, the influence of the change of film deposition conditions on their final parameters is there presented. Here we show the results of investigations involving the time of sol films aging and the influence of sol films annealing on the thickness and refractive index. We also study the changes of thickness and refractive index of the films during their aging. The films were produced using the dip coating method.

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 a sol film on the substrate as well as drying and annealing of the produced films. In the formation process of silica, the hydrolysis and condensation are respectively described by the following reactions [2]:

$$\equiv\text{Si–OC}_2\text{H}_5 + \text{H}_2\text{O} \Leftrightarrow \equiv\text{Si–HO} + \text{C}_2\text{H}_5\text{OH} \quad \text{(hydrolysis)} \tag{1}$$

$$\equiv\text{Si–OC}_2\text{H}_5 + \text{HO–Si}\equiv \Leftrightarrow \equiv\text{Si–O–Si}\equiv + \text{C}_2\text{H}_5\text{OH} \quad \text{(alcohol condensation)} \tag{2}$$

$$\equiv\text{Si–OH} + \text{HO–Si}\equiv \Leftrightarrow \equiv\text{Si–O–Si}\equiv + \text{H}_2\text{O} \quad \text{(water condensation)} \tag{3}$$

The reactions of condensation start before the reactions of hydrolysis were finished. In the described investigations the tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS) was applied as the silica precursor. In theory, to ensure a full hydrolysis reaction of TEOS it is sufficient to ensure that the ratio $H_2O:TEOS$ is at the level of $R = 2$. However, even in excess water, when $R \gg 2$, 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 obtained films.

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 [11] and meniscus coating method [2]. In the present investigations 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 obtained film. When the sol shows the properties of Newtonian liquid, the theoretical dependence of the thickness d of the obtained film on the withdrawal speed v can be written down as follows [10]:

$$d = a\xi v^{\alpha} \tag{4}$$

where $\xi = 1$ (cm/min)$^{-\alpha}$ is a scaling factor (the speed has dimension of cm/min). For a given technological process the factor of proportionality a and exponent α can be determined 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 [8].

2.3. Film fabrication

Tetraethoxysilane (TEOS, obtained from Aldrich) was the precursor of the produced silica films, while hydrochloric acid (HCl) was used as catalyst. In all processes described here TEOS was dissolved in ethyl alcohol (EtOH) in constant molar ratio TEOS : EtOH = 1 : 4. After adding an appropriate volume of both 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 the temperature of 50°C with ultra sonic stirring being used. After cooling the sol to the room temperature (18°C) the films were deposited using the dip coating method. The already mentioned work [10] presents the influence of the amount of water and catalyst on the properties of the produced silica films. Here, we present the results of investigations involving silica films obtained from the sols in which the molar ratio of components took the following values: TEOS : EtOH : HCl = 1 : 4 : 0.02. The results are shown for three different molar ratios of water and TEOS ($R = H_2O$: TEOS) being respectively equal to $R = 2$, $R = 4$ and $R = 8$. The films were deposited on glass substrates by means of controlled dip coating from the sol. Microscopic glass (Menzel–Glaser) of the dimensions 76×26×1 mm^3 was applied as substrate. Substrate glass was subjected to cleaning procedure which involved the following treatments: 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 from which the substrates were dip coated was in a beaker and the whole was shielded by a glass cylinder. The application of such a procedure ensured that accidental movement of air could be avoided, and, in consequence, the obtained films were of suitable homogeneity. The fabricated films were then dried and annealed.

3. Measurement method

The thickness and refractive indexes of silica films were measured in the ellipsometric way. The ellipsometric method is based on the change of polarization state, which is happening to the light beam reflected from the investigated sample [12]. The basic ellipsometric equation has the following form:

$$\rho = \frac{R_p}{R_s} = \tan\Psi \exp(i\Delta) \tag{5}$$

where R_p and R_s are combined reflection coefficients for the light polarized in parallel way (subscript p) and perpendicular way (subscript s) to the incidence plane, respectively. The angles Ψ and Δ are referred to as ellipsometric angles and they generally depend on the film parameters, the substrate used and the surrounding 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

The influence of the water content and the amount of catalyst as well as the influence of aging time of sols of different composition on the properties of silica films was extensively reported in work [10]. Here, we study the influence of aging time and annealing of the produced films on both their thickness and refractive index. We examine also the changes of the thickness and refractive index during the aging process of films, which were not subjected to annealing.

4.1. Aging of the sol

The dependence of the thickness on the substrate withdrawal speed for different aging times of sol is presented in Fig. 1. Experimental points, being approximated with solid lines defined by the Eq. (4), are marked in this figure. The characteristics were obtained for the sol of the molar ratio TEOS : H_2O : EtOH : HCl = 1 : 4 : 0.02. After their deposition on the substrate the films were dried for 1 hour under room conditions and then they were annealed for two hours at 150°C. It can be observed that with the rise of aging

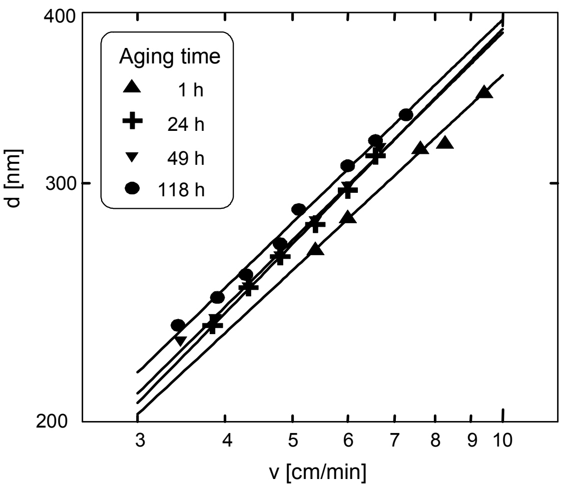

Fig. 1. Dependence of the thickness on the substrate withdrawal speed for different aging times of sol (TEOS : H_2O : EtOH : HCl = 1 : 4 : 4 : 0.02).

time of the sol the same substrate withdrawal speeds *v* correspond to higher thickness values of the obtained film. During the aging process of sol the processes of hydrolysis and condensation are continued. The structure of the sol is changing and its viscosity is growing. Hence, for longer times of sol aging, for the same substrate withdrawal speed, the films obtained are thicker and thicker. The strongest changes of sol properties are taking place in the initial stage of its aging [10]. For the later aging times of the sol the changes are smaller. We did not observe any influence of aging time of the sol on the refractive index of the produced films. The values of the refractive indexes of the obtained films (Fig. 1) were within the range from 1.4354 to 1.4418.

4.2. Aging of the films

The time changes of film thickness of the sol due to their aging are shown in Fig. 2. The results were obtained for the films which were produced at substrate withdrawal speed of $v = 4.1$ cm/min. In this case the structures were not subjected to annealing. The structures were kept in glass vessels in room conditions, with relative humidity within the range from 40% to 50%. At definite time intervals the thickness and refractive index of the films were measured. The figure presents the results corresponding to three different molar rations *R* of water to TEOS. It can be observed that in the whole range of aging time, higher contents of water *R* correspond to lower thickness values of films. This dependence is typical for sols for which pH > 2 [13]. It can be observed that with the rise of aging times of the films their thickness is decreasing. For the films obtained from the sols of water content being $R = 4$ and $R = 8$, the contraction of thickness along the whole aging period was respectively 18.7% for $R = 8$ and 13.5% for $R = 4$. The highest changes of thickness took place in the first 6 days of the aging process and were respectively 14% for $R = 8$ and 10% for

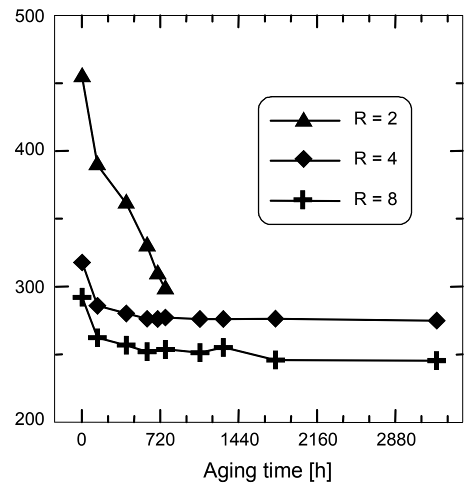

Fig. 2. Changes of thickness of the sol films during their aging for different water content *R*. Lines are drawn as guides for eye.

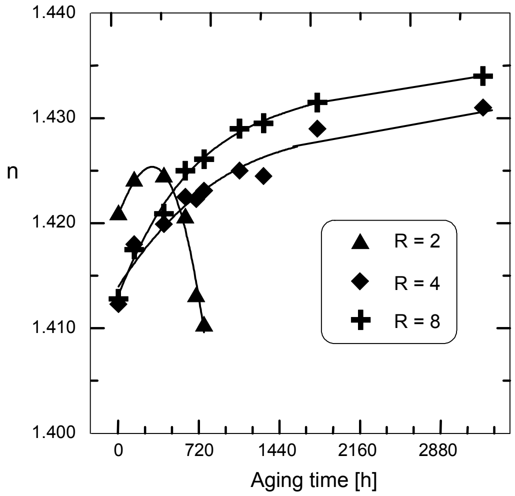

Fig. 3. Changes of refractive index of the films during their aging.

$R = 4$. During the aging of films under ambient conditions, when water from the air is delivered to the film, the processes of hydrolysis and condensation are continued. The process of hydrolysis is facilitated by the water being delivered from the environment. There are two effects competing with each other during the process of film aging; stiffening of the material structure of the film and condensation of the film material. As it can be observed from the presented results, in the initial period of film aging ($R > 2$) the film thickness decreases considerably, which proves that the condensation of material structure of the film is the dominating effect. Then, for longer aging times (above 140 h), the changes of film thickness are very slow. It results from the rise of stiffness of material structure of the film. The strongest and at the same time the most uniform changes of thickness are observed for the films produced from the sol of the molar ratio of water to TEOS being $R = 2$. During 768 h of aging, the thickness of the film decreased by about 30%, after which its destruction took place. The changes of refractive index of the films during their aging are presented in Fig. 3 For short aging times, lower values of R correspond to higher values of refractive index. For both $R = 4$ and $R = 8$, the refractive index is growing with the rise of aging time. It is the effect of film thickness contraction and condensation of its structure. The dependence of refractive index on the aging time of film produced from the sol of water content being $R = 2$, has a different character. In this case we observe initially the rise of refractive index and then its drop down to the value of about 1.410 for the aging time of 768 h. With the next attempted measurement destruction of the film was observed. The microscopic image of the destructed structure obtained with the use of differential interference is presented in Fig. 4. We can observe distinct sol drops on the glass substrate, which means that the film lost its continuous character.

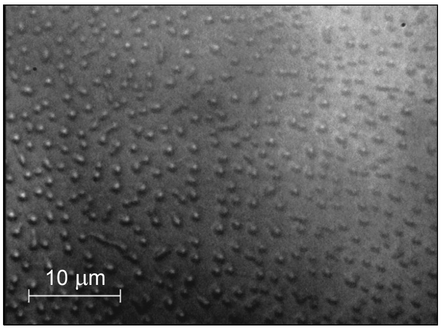

Fig. 4. Microscopic image of the structure after being aged for 1085 h in ambient conditions. Molar ratio TEOS : H_2O : EtOH : HCl = 1 : 2 : 4 : 0.02.

It proves at the same time that the films deposited on glass substrate, which were not subjected to annealing, have the properties of liquid films for very long time during their aging.

The results obtained for the films, which were subjected to aging for different periods of time and then to annealing for 2 h at 150°C are presented in Figs. 5 and 6. Each of the measurement points shown on the charts was obtained from the series of 8 samples. The corresponding molar ratio of the components in the sol was TEOS : H_2O : EtOH : HCl = 1 : 4 : 4 : 0.02. Figure 5 presents the dependence of refractive index on aging time of the films which were produced with substrate withdrawal speed of v = 5 cm/min. In this case the films were kept at 18°C and relative humidity of 66%. It can be observed that with longer time of aging the refractive index decreases. First, we observe strong influence of aging time of films on the value of their refractive index. For longer aging times of films this influence is diminishing. This dependence results from the rise of stiffness of silica structure during the aging. The material of films, which were subjected to aging over shorter times is less stiff and therefore more susceptible to condensation and contraction of thickness during annealing. Hence, for the films, which were not subjected to aging, we obtained the highest refractive indexes and the lowest thickness values. The silica structure of films subjected to longer aging is more stiff, and lower contraction of their thickness is taking place during the annealing at 150°C. In effect, the refractive index of these films after the annealing is fixed at lower level while their thickness values are higher. Comparing the results presented in Fig. 3 for the films produced from the sol of the molar ratio TEOS : H2O : EtOH : HCl = 1 : 4 : 4 : 0.02 with those shown in Fig. 5 we can observe that in both cases for the maximum times of aging the refractive indexes reached the same level of value. For the film not subjected to annealing (Fig. 3), for the aging time being 3260 h, the refractive index of the film was n = 1.4310. For the films subjected to aging for 392 h and then annealed for 1.5 h at 150°C, the value of refractive index was $n = 1.4300 \pm 0.0014$. We can see from

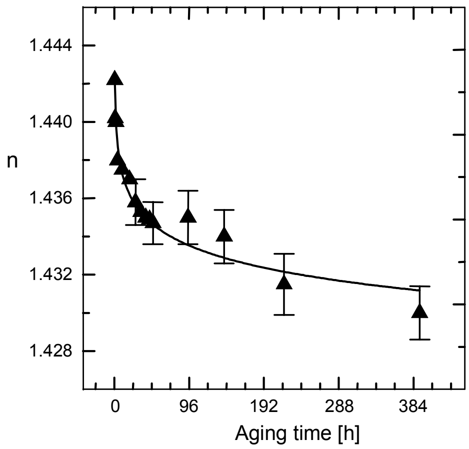

Fig. 5. Influence of aging time of the sol films on final refractive index. Films were aged at 18°C and relative humidity of 66% and than were annealed at 150°C for 2 h. Substrate withdrawal speed $v = 5.0$ cm/min.

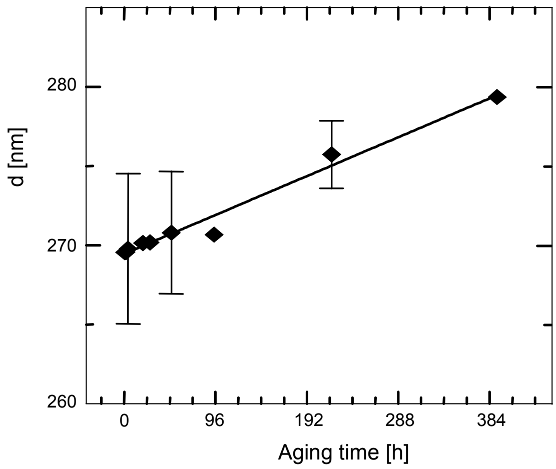

Fig. 6. Influence of aging time of the sol films on final thickness.

the above that in effect of long-lasting aging of the films, their refractive index is fixed at the same level as for the films subjected to shorter aging and then annealed at 150°C. A relatively low refractive index of silica films obtained in this way is effected by their porosity. We should emphasize here that this is the refractive index in the air of the relative humidity of 40%. The porosity and distribution of pores can be determined using molecular probe ellipsometry [13]. Introductory estimates show that the porosity of the films of the lowest values of refractive index surpasses 10%. Such films can be applied in technology of sensor layers for optical evanescent waveguide chemical sensors. High porosity of sensor films facilitates the exchange of gases with the environment. We can therefore expect that such films will be reacting faster to the concentration changes of measured substance than the films of low porosity.

4.3. Annealing

The final properties of materials produced using the sol-gel method are formed in the annealing process. In this process the removal of both the remainder of solvents the residual reaction products and is taking place. At the same time, at higher temperatures, the condensation of structure is taking place, which leads in effect to the lowering of porosity of material structure and to the increase of refractive index. The influence of annealing temperature on the final thickness of the obtained films is illustrated in Fig. 7. The figure presents the relations $d(v)$ obtained for the films which after the deposition on substrates were kept for 1 h at 18°C and relative humidity of 66% and then they were annealed at appropriate temperature for 2 h. There are experimental points marked in Fif. 7 which were approximated with the curves described by the relation (4). With the rise of annealing temperature the characteristics $d(v)$ are getting arranged lower and lower. The effects involving the decrease of film thickness and the rise of refractive index are illustrated in Fig. 8. Figure 8**a** presents the dependence of film thickness on annealing temperature. The experimental points were marked on these figures, in the form approximated with the polynominal curve. Each of the points corresponds to different film which was obtained at substrate withdrawal speed $v = 5.4$ cm/min. We can observe strong influence of annealing

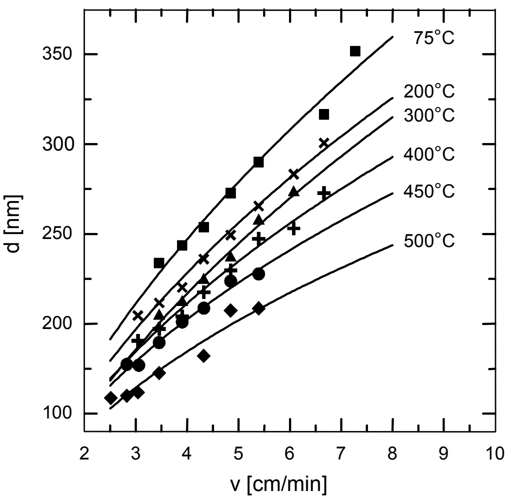

Fig. 7. Dependence of film thickness on the substrate withdrawal speed for different annealing temperatures.

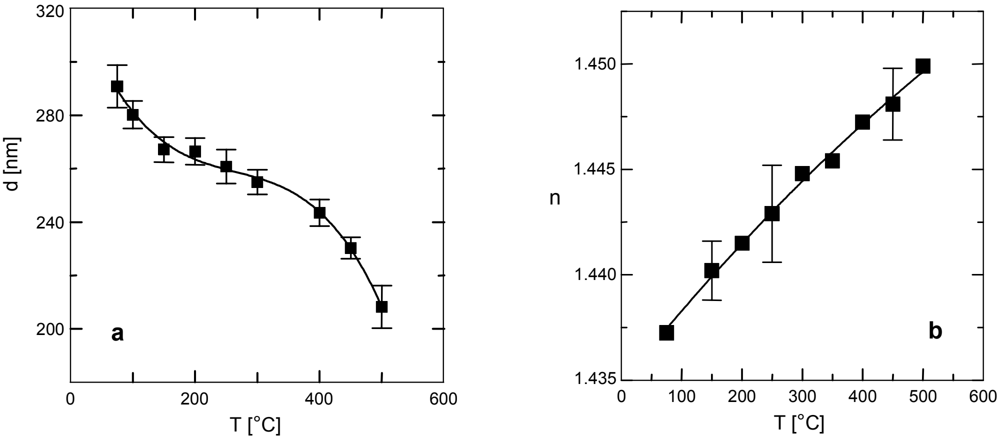

Fig. 8. Influence of annealing temperature: on the final film thickness (**a**), on refractive index (**b**).

temperature on the final thickness of the obtained films. The final thickness of the film annealed at the temperature of 500°C is by almost 30% lower than that of the film annealed at the temperature of 75°C. The dependence of refractive index on annealing temperature is illustrated in Fig. 8**b**. The films annealed at higher temperatures are characterized by higher refractive index and lower porosity. The measurements of refractive index were carried out at the relative humidity of 40%.

5. Conclusions

The paper presents the results of investigations concerning the influence of aging process and annealing of silica films on their parameters. The applied technological processes were described as well as the measurement method. The change of both the refractive index and the film thickness of the sol deposited on glass substrates during their aging under ambient conditions was presented, and the influence of annealing process of the films on their final parameters was shown. We presented also the influence of aging time of the sol on the thickness of the obtained silica films produced with the use of dip coating method.

During the aging process of sol films, their thickness is contracted and the refractive index rises. The strongest changes are taking place in the initial stage of film aging. The investigations show that the films produced from the sol of low water content ($R = 2$) have the properties of a liquid over long time. When such films are not subjected to annealing process, they undergo destruction. The films produced from the sol of higher water content can be subjected to aging over long time. By the application of aging process of films followed by their annealing, we can obtain silica films, which are characterized by relatively low refractive indexes and high porosity. Eventually, the refractive index of silica films is formed in annealing process. By the application of lower annealing temperature we can obtain strongly porous silica films. By the application of high annealing temperatures, we obtain silica films of the refractive index close to the refractive index of solid silica and minute porosity. Such films can be applied as buffer layers or masking layers. Porous films can be applied in the technology of sensor films for optical waveguide chemical sensors.

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