Optica Applicata, Vol. XLV, No. 1, 2015
DOI: 10.5277/oa150112

Chemical resistance of SiO_2 layers obtained by the sol–gel technique on a glass substrate

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The paper analyses the influence of heat treatment parameters on SiO_2 coatings obtained by the sol–gel technique. Their adhesion to the glass substrate and corrosion resistance were studied. The changes in thickness and porosity with the firing temperature and time of sintering for the systems of 1, 2 and 3 layers in case of SiO_2 layers were studied. It was shown that the sufficient durability of the SiO_2 coating on the glass substrate can be achieved only by the appropriate selection of thermal treatment parameters. The results confirmed that higher sintering temperature is required for multilayer systems, as compared with a one-layer system.

Keywords: sol–gel, antireflection coating, sintering parameters.

1. Introduction

Sol–gel technology enables the preparation of coatings with a precisely controlled chemical composition without sophisticated and expensive devices. It is therefore an inexpensive technique to produce coatings of optical quality. The advantage of the sol–gel technique is that it is often used for the preparation of antireflective [1–3], reflective [4], hydrophobic [5] and hydrophilic [6, 7], photocatalytic [8], and many other types of coatings [9, 10]. However, although in case of the synthesis of various coatings, an extensive literature is available, there are only a few works in the field of long-term stability of the sol–gel coating. There is a number of publications on the adhesion of the gel layers to the glass substrate but these studies are mainly focused on measuring techniques [11, 12] or mechanical properties of the sol–gel coatings [13], however, they do not refer to the effect of heat treatment on adhesion and corrosion resistance of the coating. Yet, this problem is important as the durability and corrosion resistance of the coating is essential from the practical application point of view. Sol–gel coatings are characterized by open porosity, what leads to the uptaking of water vapor from the environment. When the humidity is high, water vapor condensates inside the pores resulting in an increase in the volume of the coating. The effect is reversible, *i.e.*,

a reduction in the thickness of the coating at low ambient humidity takes place. The process is known as "breathing of the coating" [14]. When the porosity is high with many big pores, the structure of the coating is mechanically weak and the interaction with water vapor leads to its destruction. To obtain a stable coating under varying humidity conditions, it is necessary to adapt the sintering process to match the type of a the substrate with the chemical nature of the layer. SiO_2 layers are particularly interesting because, on the one hand, they have found wide practical applications as antireflective coatings and, on the other hand, the process of formation is relatively easy and well understood.

The results of the corrosion resistance and adhesion of SiO_2 layers obtained by the sol–gel on a glass substrate as a function of sintering parameters are presented in the paper. Variations in the layer thickness and the porosity depending on the firing temperature and sintering time were also analyzed. The tests were performed on single and multilayer systems (up to 3 layers).

2. Experiment

2.1. Sol preparation

To prepare the sol, the following reagents were used: tetraethyloortosilicate (TEOS) – Sigma-Aldrich, ethanol, hydrochloric acid and 2-propanol – Polish Chemicals (POCH). Chemical composition of the sol is shown in Table 1. The sol prepared from TEOS, alcohol, water and HCl as a catalyser was diluted by propanol. The synthesis procedure is shown in Fig. 1.

2.2. Film preparation

Soda lime glass samples with the dimension of 3×7×2 mm were used as a substrate. The samples were washed in distilled water with detergents addition in an ultrasonic

T a b l e 1. Chemical composition of the sol.

	Chemical composition	Density [g/cm^3]	Atomic mass [g/mol]	Molar composition
TEOS	$C_8H_{20}O_4Si$	0.934	208.30	1.0
Ethanol	C_2H_5OH	0.789	46.07	2.05
Propanol	C_3H_7OH	0.786	60.10	8.0
HCl	HCl	–	36.45	0.9
Water	H_2O	1.000	18	3.0

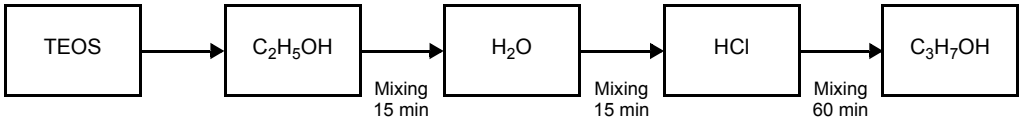

Fig. 1. Sol preparation procedure.

bath during 10 min; then they were thoroughly sluiced in distilled water and dried. Next, the samples were washed in propanol vapor [15].

The sol was applied on the glass substrate by the dip coating method. Withdrawing speed of the samples from the sol was 12 cm/min Wet samples were dried at room temperature and next at 150°C in a drier. In case of a multilayers system, the second and third layer were obtained in the same manner.

2.3. Characterization methods

Films were characterized by spectroscopic ellipsometry type PhE-102 Angstrom Advanced, Inc., reflectance spectroscopy – CM-2500d Konica–Minolta. The adherence of the film to the substrate was tested using the micro-hardness method – PMT-3. According to IEC 61215-2005, corrosion durability of the sol–gel films is advised to be evaluated by a damp heat test at water vapor conditions at 85°C and 85% RH during 1000 h [16]. In these studies we applied the boiling water test. Samples were treated by the immersion in boiling distilled water. The boiling water test is very severe and is advised for the sol films used outside in the countries with high summer temperatures. In such conditions, the glass surface can reach 100°C and even higher temperatures so the working conditions (during a rainfall) are very similar to the boiling water test.

3. Results

3.1. Sintering at 400°C

Prepared samples have antireflective properties, what is seen from the reflectance spectra in Fig. 2**a**. The influence of sintering time on the thickness of the films sintered at 400°C is shown in Fig. 2**b**. The initial thickness of the samples is decreasing with the sintering time due to the removal of the residual alcohol and water and next due to the shrinkage of pores.

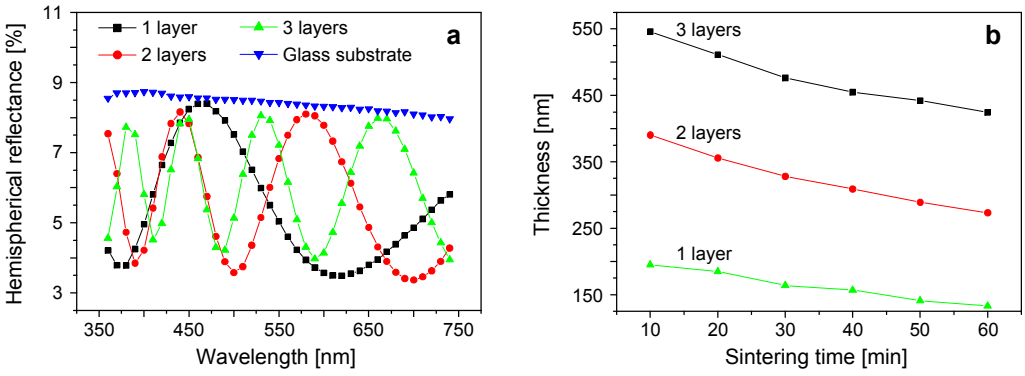

Fig. 2. Reflectance spectra of the samples after drying at 150°C (**a**). Thickness of the samples with 1, 2 and 3 layers depending on the sintering time (**b**).

Changes in the porosity with the sintering time were calculated basing on the changes in the refractive index measured by the spectroscopic ellipsometry. The relationship between the refractive index and the porosity is depicted by the following equation [17, 18]:

$$n_{pc} = \left[\left(1 - \frac{P}{100}\right)(n_{dc}^2 - 1) + 1\right]^{1/2} \tag{1}$$

where n_{pc} and n_{dc} are the refractive indexes of porous and dense coating material, respectively, and P is the porosity percentage. The rearrangement of the above equation allows us to calculate the porosity of the coating as

$$P = 100 - \frac{(n_{pc}^2 - 1) \times 100}{n_{dc}^2 - 1} \tag{2}$$

The changes in the refractive index with the sintering time for the sample with 3 layers are shown in Fig. 3**a**. Basing on the change in the refractive index at 550 nm porosity, the change with the sintering time was calculated – Fig. 3**b**. The refractive index of fully dense SiO_2 n_{dc} was assumed to be 1.46.

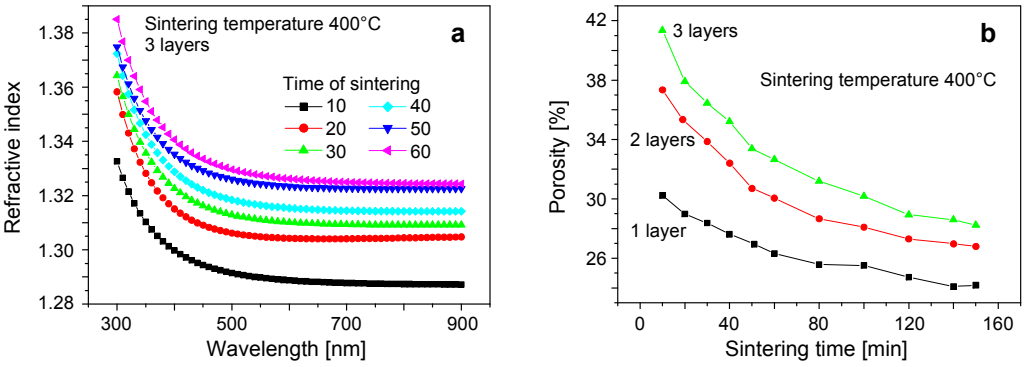

Fig. 3. Changes in the refractive index with sintering time in case of samples with 3 layers (**a**). Changes in porosity with sintering time (**b**).

Porosities of the samples after 10 min sintering were 30%, 37% and 41% for 1, 2 and 3 layers samples, respectively. Porosity decreases with sintering time. The kinetics of the sintering process is well seen from the first derivative of porosity changes, what is shown in Fig. 4.

Intensive shrinkage is observed up to 100 min of sintering. The most intensive shrinkage is observed for the sample with 3 layers since it has the highest porosity. To check if this sintering time is long enough to obtain good adherence of the silica film to the glass substrate, the simply scratch test using the standard Vickers diamond pyramid and constant load of 10 mN was performed. The results are shown in Fig. 5.

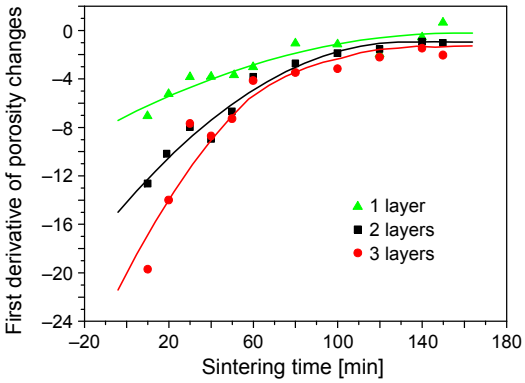

Fig. 4. First derivative of porosity changes with time.

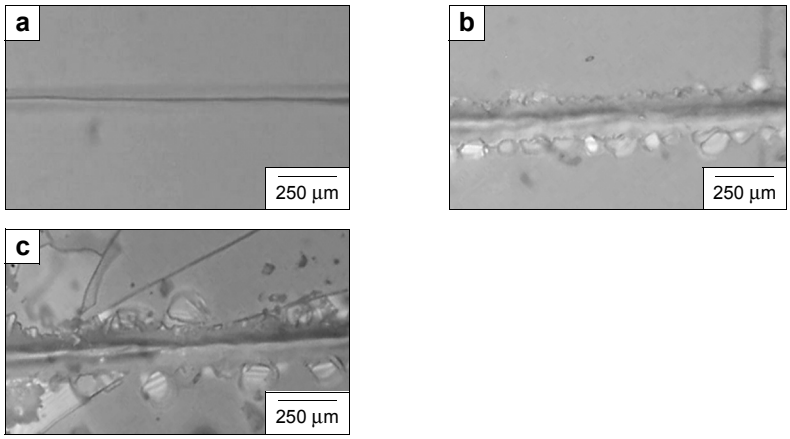

Fig. 5. Scratch test of the samples with 1 (**a**) 2 (**b**) and 3 layers (**c**), synthesized at 400°C during 100 min.

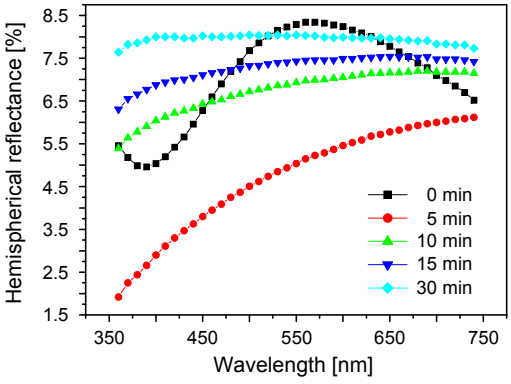

Fig. 6. Changes in the reflectance spectra with boiling time for 1 layer samples sintered at 400°C during 100 min. The numbers indicate the time of boiling.

The scratch test has shown that the adherence was not obtained in case of 2- and 3-layer samples. Relatively good adhesion is observed in case of 1-layer sample. In order to verify the corrosion resistance, the samples were tested by the immersion in distilled water at the temperature of 100°C. Changes in the reflectance spectra with the boiling time for the samples with 1 layer are presented in Fig. 6. The spectra show that after 5 min of boiling, the top layer is washed out leading to higher roughness and a thinner layer with better antireflection properties. Further boiling removes gradually the silica film and after 30 min the reflectance spectra are close to pure glass substrate spectra – compare Fig. 2**a**. SiO_2 layer was removed after 15 min of boiling from the samples with 2 and 3 layers. The conclusion is that the treatment at the sintering temperature of 400°C during 100 min is not enough to obtain a fully corrosion resistant SiO_2 film on a glass substrate.

3.2. Sintering at 500°C

Thickness and porosity changes with sintering time were shown in Fig. 7. In case of 3-layer sample, the porosity is reduced from 36% to about 18% after 300 min of sin-

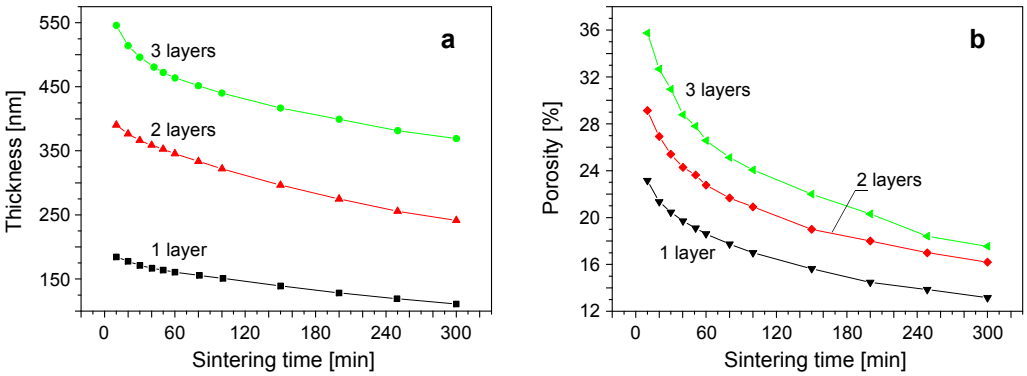

Fig. 7. Thickness changes (**a**) and porosity changes (**b**) with the time of sintering.

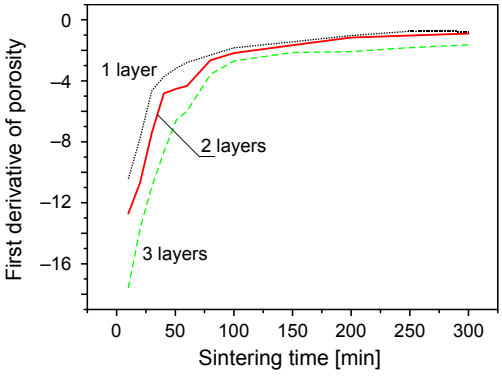

Fig. 8. First derivative of porosity changes with the sintering time.

tering. The porosity shrinkage of a 1-layer sample is much smaller – from 23% to 13% during the same sintering time.

The dynamics of sintering is seen in Fig. 8 where the first derivative of porosity changes with sintering time is shown. The most significant changes in porosity are observed up to 100 min of sintering. After that time the porosity does not change significantly.

The samples were tested for adherence properties as it was described before. The results have shown that in case of 1- and 2-layer samples good adhesion was obtained after 20 min while 3-layer samples need much longer sintering time – at least 40 min. The results of the scratch test for samples sintered during 20 min are shown in Fig. 9.

The boiling test has shown that proper corrosion resistance can be obtained after 30 min of sintering time for a sample with 1 layer. The changes in the reflectance spec-

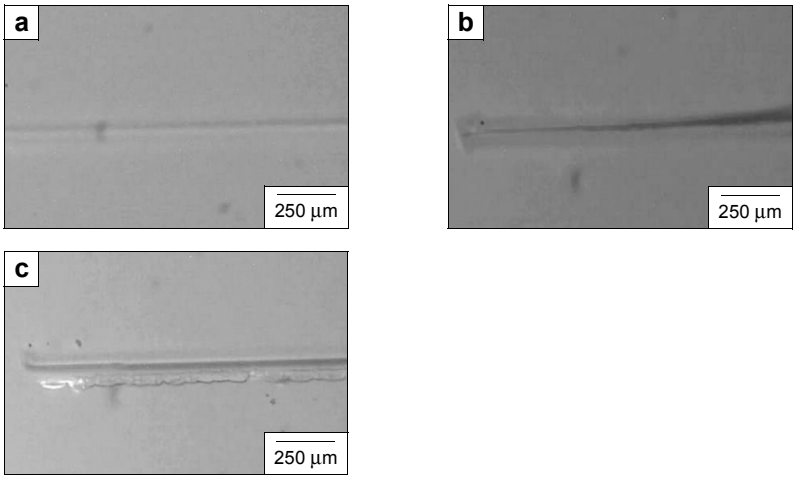

Fig. 9. Scratch test of the samples with 1 layer (**a**), 2 layers (**b**) and 3 layers (**c**) synthesized at 500°C during 20 min.

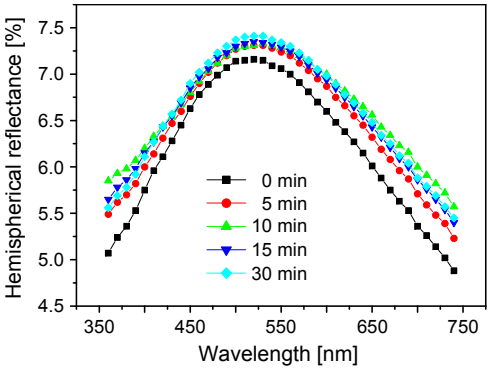

Fig. 10. Changes in the reflectance spectra with boiling time. A sample with 1 layer sintered at 500°C during 30 min.

tra are not significant even after 0.5 hour of boiling – Fig. 10. The changes in the spectra observed after first 2 min of boiling are most probably due to the removal of the top roughness of the layer.

In case of 2- and 3-layer samples much longer sintering time is needed to obtain chemical resistance. It has been found that the double layer samples have good chemical resistance against water corrosion after 100 min of sintering. The triple layer sample shows significant changes in reflectance spectra after that time of sintering, see Fig. 11. It is evident from Fig. 11 that the thickness of the sample decreases with the boiling time, what means that the SiO_2 layer is steadily removed. The most appropriate sintering temperature giving a good hot water resistant coating in case of 3-layer samples is 150°C.

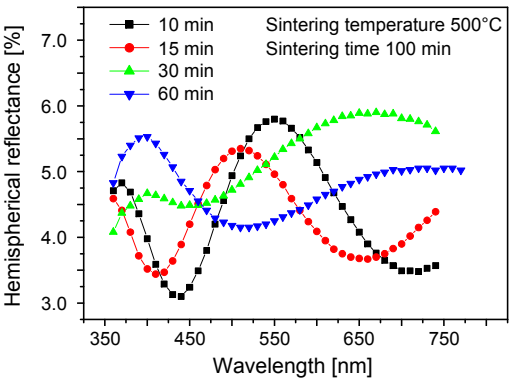

Fig. 11. Hemispherical reflectance spectra of the sample with 3 layers with the boiling time.

As the adhesion of SiO_2 layer to the glass substrate containing sodium is obtained by diffusion of sodium from the substrate to the layer, the sintering process at the layer-substrate interface is controlled by a sodium diffusion rate [19, 20]. Sodium diffusion accelerates the sintering of the layer and eliminates porosity. The reaction results in the formation of the Si bonds between SiO_2 from the layer and the components of the substrate.

4. Conclusions

The results of this study lead to the conclusions that the temperature of sintering is a key factor in obtaining a water resistance coating at water boiling conditions. The next important factor is sintering time, but in case of a thicker porous layer (or multilayers), densification leading to water resistance cannot be obtained at lower sintering temperatures in reasonable time. The samples with 1 and 2 layers can show good adhesion and water resistance after sintering at 450°C during 60 and 150 min, respectively. 3-layer samples need sintering temperature at least of 500°C and sintering time of

150 min. The application of sol–gel prepared coatings in a harsh environment is possible; however, time and temperature of sintering need to be carefully adjusted.

Acknowledgments – The research was financed by the National Ministry of Higher Education under grant 11.11.160.365/14.

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Received October 10, 2014
in revised form November 27, 2014