Transparent hydrophobic sol–gel silica coatings on glass

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Abstract: *Silica coatings have been prepared from sol-gel precursor solutions having a viscosity in the range of 2 to 20 mPa·s. The different values of viscosity were achieved by aging the solutions with various amount of water. A detailed analysis of transmittance and hydrophobic properties of coatings produced has been carried out. Two ways of addition of hydrophobic agent are considered.*

Keywords: *sol-gel technology, silica coatings, optical transmission, hydrophobic properties.*

INTRODUCTION

Silica films have been intensively investigated in recent years due to their unique properties: thermal and oxidative stabilities, chemical and corrosion resistance, low refractive index, antireflective properties, resistance to bacterial growth, etc. These films have numerous applications in high tech fields: aerospace, solar cell system, optics, microelectronics, automotive industries and engineering. The hydrophilic and hydrophobic silica based coatings can be produced by using some additives [1-5].

Several techniques have been applied to obtain coatings for commercial application. These include chemical vapor deposition, sputtering, deposition layer, plasma treatment, dip coating from a sol. For certain applications the sol-gel method is one of the most useful technologies to produce amorphous or crystalline oxide coating [2]. It has been demonstrated that sol-gel derived silica coatings exhibit comparable or even superior properties, such as homogeneity, purity, easy processing and ability to coat large and complex area substrate, compared to coatings prepared by other techniques. The sol-gel processing gives a very wide flexibility in preparation of materials and control composition and optical properties of them.

In this work we report on a sol-gel derived method for coating glass substrate with a thin film of silica by dip coating to produce transparent and hydrophobic properties.

EXPERIMENTAL

The coatings were prepared by the sol-gel method on 20x40 mm float glass substrates. The sol-gel precursor solutions were obtained mixing $Si(OC_2H_5)_4$ (TEOS), absolute ethanol as solvent and deionised water at 1:4:3 molar ratio. The hydrochloric acid was used as catalyst agent. The so-obtained sols were magnetically stirred for 15 min at room temperature before being used for the deposition of coatings. Prior to the deposition, the glass substrates were simply cleaned with ethanol and then dried in oven at 70^oC for one hour.

The coatings were deposited using the dip coating method, at a withdrawal speed of 5 cm/min. All coatings were dried at a temperature of 70^oC for 20 min under air conditions. Finally, these films were annealed at different temperatures from 200^oC to 450^oC for 20 min. and taken out from the oven after cooling at ambient temperature.

The fluoropolymer F-4MD grade (fluoroethylene-60% emulsifier OP-20) has been used as hydrophobic agents to improve the surface properties of silica coatings. Hydrophobic coating films were made by two different techniques. (1) Water solution of 20% F-4MD was diluted in silica sol followed by ultrasonic stirring for 10 min. Dipping procedure was similar to the one previously described. (2) Dipping the pre-coated substrate with layer of SiO_2 in water solution with 20% F-4MD followed by heat treatment at 200 ^oC.

The light transmission of the films was measured in the visible range using UV-VIS spectrophotometer (Specord M-400, Carl Zeiss). Wetting properties of the films were tested by measuring the static and dynamic water contact angles (WCA) using contact angle meter Easy Drop DSA 20E (KRUSS).

RESULTS AND DISCUSSION

The viscosity of sol is one of the most important characteristics that affects to the quality and thickness of the coatings. The rheological properties of solutions were investigated during the gelation process by method of capillary viscometry.

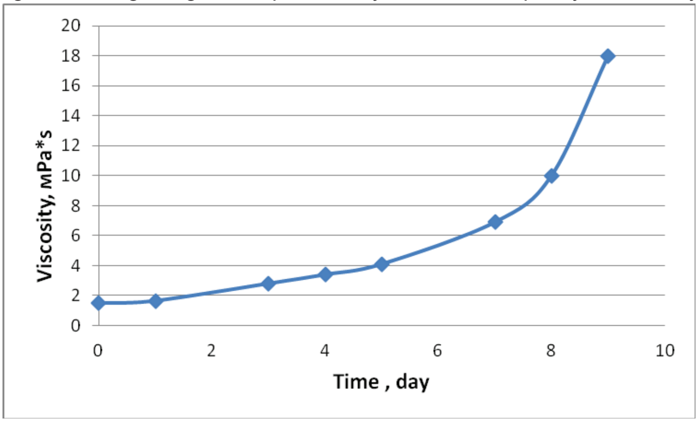

Figure 1 - Viscosity versus aging time for sol-gel precursor solution.

As shown in Fig. 1, the viscosity of the precursor solution continuously increases with the aging time. During the hydrolyzation – gelation process two different stages are clearly observed. These two stages can be characterized by the rate of change in the viscosity of the solution. The first stage corresponds to the initial steps of hydrolyzation of the solution, and it is characterized by a low rate of change in η. The second stage corresponds to the gelation/condensation process, characterized by a rate of change in η few times larger. It was determined that optimum viscosity of sol applied on the glass substrate ranges from 3 to 5 mPa * s. The coatings prepared from solutions with higher viscosity and heat treated at the same temperature have more thickness and can be cracked during the annealed treatment.

The temperature of heat treatment is another important parameter affected the properties of the coatings. Table 1 summarizes the transmittance of uncoated glass and samples with SiO_2 coatings annealed at various temperatures.

Table 1 - Light transmission of the samples (λ = 550 nm)

Property	Uncoated glass	Samples with SiO_2 coatings, annealed at different temperatures		
		T=300^{0}C	T=400^{0}C	T=450^{0}C
Transmittance T, %	89,20	89,28	90,95	92,12

The transmittance for all the coated glasses is clearly higher than that of the substrate. It was found that the increasing of heat temperatures from 300^{0}C to 450^{0}C improve of transmittance of 2,9 %.

The SiO_2 coatings are hydrophilic due to the presence of hydroxyl groups on the surface. One of the possible way to increase contact angle is to change surface chemistry by replacing the polar OH groups to non-polar due to the surface modification treatment with solution of fluoroethylene as hydrophobic agent [1]. Hydrophobic coating films were made by two different techniques. The contact angle measurement and transmittance of coatings obtained are shown in Fig 2.

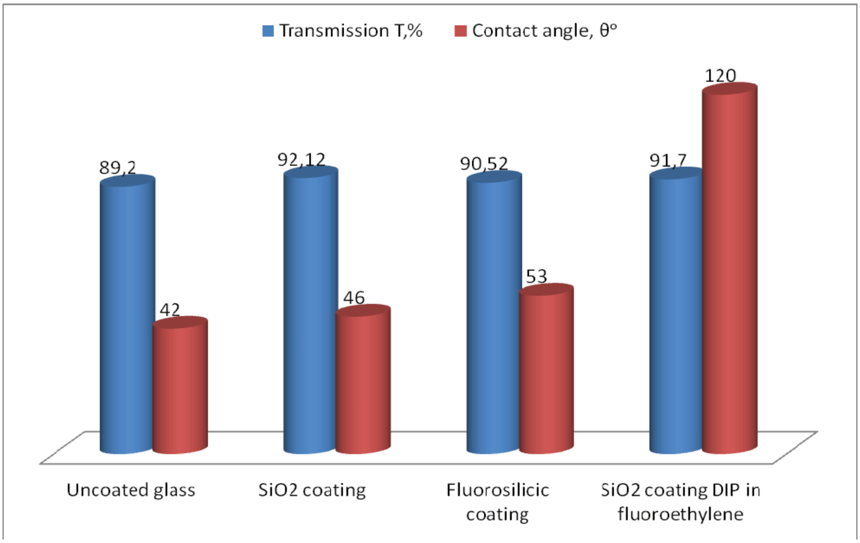

Figure 2 - Transmittance and water contact angle of coating produced by different techniques.

It is sometimes desirable for some applications that the glass remains transparent after being coated with hydrophobic silica. Figure 2 shows the effect of silica coating on the transmittance of glass after being coated with hydrophobic silica in the visible range. The transmittance of the uncoated glass substrate is also presented as comparison. It can be seen that additive of fluoroethylene does not affect transmission of glass, transmittances of all samples were larger than 90,5 – 91,5%. At the same time, diluting the precursor by adding fluoroethylene solution (techniques 1) slightly improved the hydrophobic properties of coatings. On the other hand, coating the SiO_2 film by fluoroethylene solution (techniques 2) allowed us to increase WCA significantly.

CONCLUSION

The present research is focused on the demonstration and comparison of the transmittance and hydrophobic properties of sol-gel silica coatings on float-glass substrate. The prepared sol was aged at 20 °C for 2-5 days and had viscosity from 3 to 5 mPa * s. The optimum heat treatment conditions were 450 °C for 20 min. The compositions which were modified with fluorine-containing additive show improved hydrophobic properties. The hydrophobic (WCA = 110-120°) and transparent (T ~ 92%) coatings have been successfully made.

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This paper has been reviewed