Effect of Solvent Content on the Properties of Nanostructure Silica Thin Film by Sol-Gel

A. Shokuhfar, E. Eghdam[*], M. Alzamani

Mechanical Department (Advanced Materials and Nanotechnology Research Lab), K.N. Toosi University of Technology, Tehran, 19697 64499, Iran

Abstract   It is known that silica sol-gel coatings microstructure depend on the components of the sol. In order to develop different microstructures of the silica coatings and comparing their optical properties, a variety of silica sols were prepared which were consist of TEOS, water, catalyst and changing the solvent content, at room temperature. Prepared glass surfaces were coated with silica sol using a dipping technique, with constant withdrawing rate. Prepared coatings were investigated by field-emission scanning electron microscopy (FE-SEM) and UV–Vis. spectroscopy. Transmittance spectra showed that silica coatings featured a distinct increase of substrate transmittance at all wavelengths (400-1100 nm). The result indicated that by increasing the solvent content, the porosity of coating increased and the coating was more densified therefore the silica coating transmittance increased by 3-4% points. FE-SEM showed that the nanostructure silica coating grain size were estimated ~20-40 nm.

Keywords   Solvent content, Silica, Transmittance, Sol-gel, Dip-coating

1. Introduction

SiO$_2$ thin films have been widely used for optical coatings as anti-reflective and protective layers[1-3] and also for different microelectronic structures, as diffusion barriers and/or insulating layers with additional planarization ability[4-7]. Recently, the physico-chemical properties of SiO$_2$ thin films have being applied in various methods to improve photovoltaic devices, as encapsulant coatings and/or to isolate electrical contacts in the cell[8-10].

To prevent disturbances of external light and increase the transmittance of incident light, antireflective technologies are widely applied in optical components, solar cells, displays, automotive glass, thermochromic windows, etc[11].

The sol-gel process is one of the most important techniques to coat glasses, ceramics and metals with amorphous thin films. There is great technological interest in the preparation of colored and multilayered dielectric films by sol-gel [12]. Researches and applications for the coating from sol have recently been reviewed by Schroeder[13], Dislich and Hussman[14], Dislich[15], Sakka[16] and Orgaz et al.[17].

Sol-gel technology can produce vitreous and ceramic coatings with various compositions over different substrates with low cost. Sol-gel SiO$_2$ coatings are obtained by spining, dipping or spraying a solution prepared by dissolving aprecursor alkoxide in alcohol, catalyzed in an acid and hydrolyzed with water. After the deposition process, densification of the layers is obtained by heating at moderate temperatures (300-500℃) in furnace or inert atmosphere. The resulting sol-gel SiO$_2$ coatings have shown excellent mechanical and chemical stability, with optical and electrical properties that can be controlled by the sol preparation parameters[2,4,6].

In order to shift the reflectance value to minimum, a fine control of the coating thickness and refractive index is required[18,19]. Nearly zero-reflectance can be reached if "Eq.(1)" was established

$$n_c = (n_0 n_s)^{1/2} \tag{1}$$

Where n$_c$, n$_o$ and n$_s$ are refractive indices of the coating, incident medium and substrate, respectively. According to Eq. 1 in the air atmosphere, considering refractive indices of interesting glazing materials for solar energy applications as 1.47–1.57, sol–gel anti-reflective coatings must present index values within the range of 1.21–1.25, which is lower than that of any known solid material. Nonetheless, as the refractive index of a material is related to its density, by increasing the porosity, its value can be dramatically reduced. The relationship between refractive index and porosity is depicted by the "Eq.(2)"

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

Where n$_{pc}$, n$_{dc}$ and P are the refractive indices of porous and densified coatings, and the porosity percentage, respectively[20].

* Corresponding author:
ebrahim.eghdam@yahoo.com(E. Eghdam)

2. Experimental

2.1. Sample preparation

All chemicals were used as received without further puri-fication. The anti-reflective films were deposited on 2 mm thick automotive glass slides (100×40 mm^2) by dip-coating method. Withdrawal rate was adjusted to 1 cm/min. Anti-reflective sols were prepared by mixing absolute ethanol (EtOH, Merck, min 96 vol. %), distilled water and tetraethyl orthosilicate (TEOS, Acros Organics, 98%) ac-cording to the flow chart presented in Figure 1. The etha-nol/TEOS molar ratios were 10, 15, 20 and 25 and the wa-ter/TEOS molar ratio was 2 in order to fit the thickness of the coatings to the maximum transmittance.

To prepare the suspensions, TEOS was mixed with one-half of ethanol using a magnetic stirrer for 15 min. In a separate vessel, the remained ethanol was dissolved into distilled water and then the distilled water-ethanol mixture was added to TEOS-ethanol suspension drop by drop. When the mixture was homogeneous, HCl (Scharlau, 37%) was added drop by drop until the pH of the solution decrease to the value of 2. The anti-reflective sols were aged for 24 h before proceeding to coat. All the coatings were dried in air at room temperature for 24 h and subsequently were heated up to 500℃ with the rate of 10℃/minfor 30 min.

2.2. Sample characterization

UV–Vis transmittance measurements on coating were performed using a Perkin Elmer UV/Vis Spectrophotometer, Lambda 25 tescan model vega-Ii. The size of SiO$_2$ particles in coatings and surface morphology were investigated using a S-4160 Field Emission Scanning Electron Microscopy (FE-SEM) operating at 15 kV.

3. Results and Discussion

In general, many interdependent factors can play a prominent role in the final physical properties of sol-gel coatings: (i) sol-gel solution (ingredients, sequence of mix-ing, concentration and ratio of components, temperature, pH); (ii) applying technique (dip, spin, spray, laminar flow); (iii) substrate (glasses, plastics, metals, ceramics) and its surface preparation; (iv) coating (porosity, residual OH, structure, roughness, thickness). Dip-coating is the most popular method in which the colloids are evaporation induced and self-assembled on the substrate as it slowly withdrawn from the colloidal suspension. In this study several different silica sols were prepared to find the optimal deposition conditions on the microscope glass substrates for anti-reflective be-havior.

The thickness of the porous SiO$_2$ and therefore, the wavelength of the maximum transmittance, were finely tuned by controlling solvent ratio in the sol preparation stage .In Figure 2, substrate transmittance spectra (bare sample) and coated samples with nanostructure SiO$_2$ (as-received) with different ratio of precursor dilution factor

(D = [EtOH]/[TEOS]) is illustrated, which all were coated at the rate of 1cm/min. As one can deduce, SiO$_2$ nanostructure coating on the glass substrate, increase the transmittance percentage in the UV-Vis test. Considering figure 2, trans-mittance spectra at wavelength of 550 nm is maximum and around 2.3 % of increment in the transmittance relative to the bare sample achieves when using D=10 (AR-10 sample) in the solution. By increasing the D ratio from 10 to 15, the maximum value and its transmittance percentage shift to the wavelength of 500 nm and 92.9 % respectively (AR-15 sample). In this case, before and after the maximum point in the specified wavelength, transmittance spectra increase and decreased, respectively.

By increasing the D ratio from 15 to 20 (AR-15 to AR-20) the maximum transmittance didn't amplitude the amount of spectra, whereas the maximum transmittance is preserve ap-proximately at the 500 nm. According to Figure 2, increasing the D ratio more than 20 reduced the maximum value, obvi-ously.Of course, one can observe that the sample which was coated in the sol with D=25 shown lower transmittance com-pared to the sample which was coated in the sol with lower D ratio.
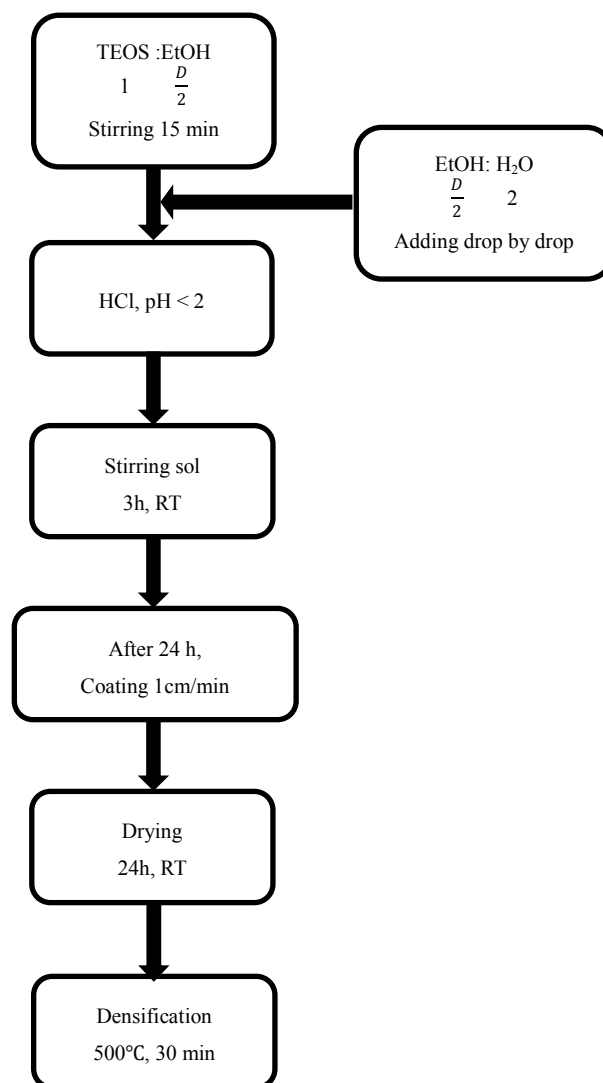

Figure 1. Flow chart of sol-gel processing for SiO2 films (The D factor indicate EtOH ratio molar)
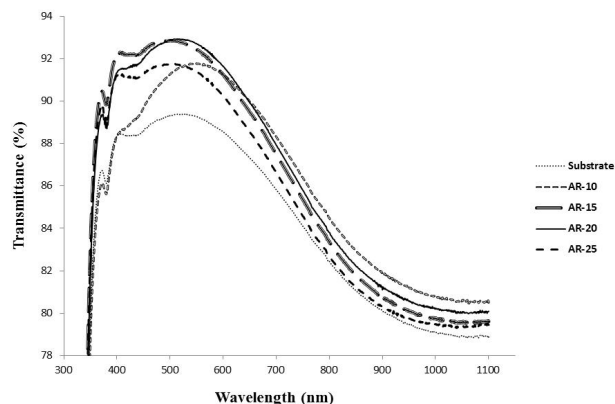
Figure 2.   Optical transmittance spectra of coatings with different D factor

Figure 2 also demonstrates that D ratio of 20 is a sufficient and optimum amount when using ethanol as solvent in the sol of glass, because it provides around 3.96 % increment in the transmittance rate relative to the bare sample.

By increasing solvent content, sol became dilute, so this factor increases the total porosity after coating and densification phase. The more porosity on the coating, the less optical reflective index and consequently transmittance increased. It should be noted that porosity increment due to solvent content increasing may influence coating lifetime.

From these optical transmittance spectra (as shown in figure 2), average transmittance values have been calculated in two different intervals: visible (400-800 nm) and infrared (800-1100 nm), in order to quantify and evaluate the influence of SiO_2 sol dilution on each spectral region. The average transmittance ratios (T_1/T_0) of the SiO_2 coated samples (T_1) and the uncoated glass substrate (T_0) are represented in Figure 3, both in the visible and infrared ranges, as a function of the precursor dilution (D) at the withdrawal velocity of $v = $ 1 cm/min.

At withdrawal velocity of v=1 cm/min, visible transmittance enhancement varies from 2.4 to 3.2% as the D ratio increase from 10 to 20. Futhermore, increasing D ratio decrease the transmittance ratio due to sol diluteness because of increasing solvent and prosity.

As it can anticipated, in the infrared optical range, the transmittace ratio decreases relatively. Similar to visible, the D=20 point is the best condition in the infrared rang. It has been proven that sol-gel SiO_2 covers the substrate surface like a paste, smoothing its irregularities, thus resulting in a heterogeneous SiO_2 thickness, higher over the valleys than over the protuberances of the substrate surface. In the present study the sol-gel coverage on the substrate increases as the D factor increases up to 20. The observed increase in the visible range transmittance can be attributed to the SiO_2 layer continuity on the glass substrate.

The micrograph of the surface of the SiO_2 nanostructure film, as shown in figure 4 (a-c), contains submicron pores. Size of SiO_2 grains can be estimated to be in the range of 20-40 nm.

As is clear, the more D factor, the more porosity and the less reflective index and the more optical transmittance.

With increasing D, the sol concentration became more dilute so that by evaporation of solvent, the coating thickness and weight per cm^2 lessen and therefore this process can lead to more porous coating. These results are compatible with what mentioned in Figure 2 & 3.
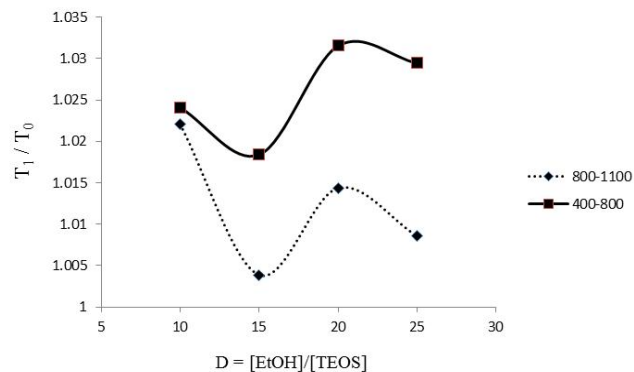

Figure 3.   Transmittance ratio (verage of T_1/T_0) of the SiO_2-coated samples, T_1, vs. the glass substrate, T_0 , as a function of the precursor dilution, D
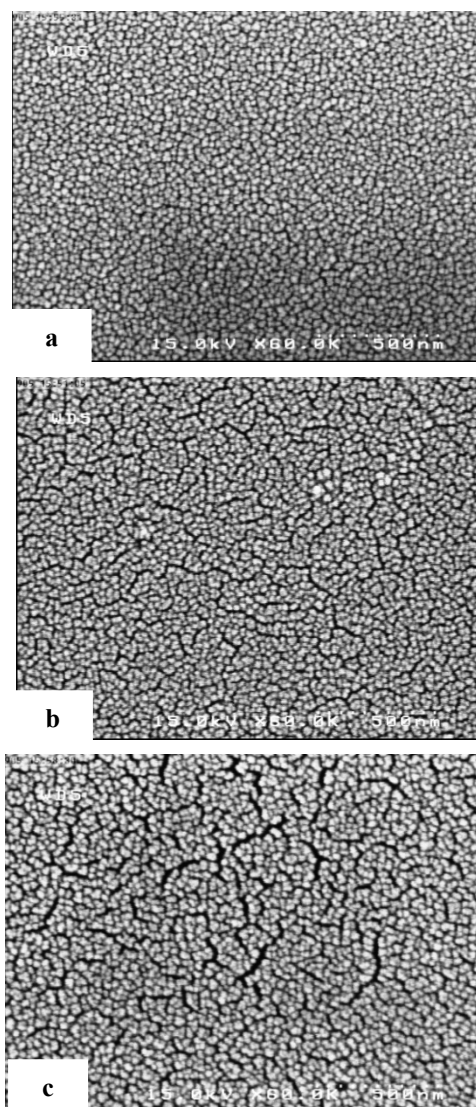

Figure 4.   FE-SEM micrograph of surface SiO_2 films, (a) D=10, (b) D=15, (c) D=20

4. Conclusions

Uniform nanostructure SiO_2 film was applied on glass substrate in this study with the least defects. The optical effects of microstructure of SiO_2 sol-gel coatings on the glass substrate were investigated. This research proved that with increasing D, the porosity and light transmittance increased. With increasing amount of D, the optimum thickness decreases therefore the reflective index decreases and light transmittance increases. The best anti-reflective behavior showed the coatings obtained from D=20 and the highest absolute transmittance (92.94%) was achieved at approximately 500 nm wavelength therefore sol-gel SiO_2 coatings on glass substrate can provide about 4 and 1.2% optical transmittance enhancement in the visible infrared range respectively.

ACKNOWLEDGEMENTS

REFERENCES

[1] Chen, D., 2001, Anti-reflection (AR) coatings made by sol-gel processes: A review., Sol. Energy Mater. Sol. Cells 68, 313 .

[2] Nostell, P., Roos, A., Karlsson, B., 1999, Optical and mechanical properties of sol-gel antireflective films for solar energy applications., Thin Solid Films, 351, 170.

[3] Gombert, A., Glaubitt, W., Rose, K., 1998, Glazing with very high solar transmittance., Solar Energy, 62, 177.

[4] Alam, M.J., Cameron, D.C., 2001, Characterization of transparent conductive ITO thin films deposited on titanium dioxide film by a sol–gel process., Surface Coating Technology 142-144, 776.

[5] Abe, K., Sanada, Y., Morimoto, T., 2001, Anti-Reflective Coatings for CRTs by Sol-Gel Process., Sol-Gel Sci. Technol., 22, 151-153.

[6] Wu, W.F., Chiou, B.S., 1997, Mechanical and optical properties of ITO films with anti-reflective and anti-wear coatings., Appl. Surf. Sci., 115, 96.

[7] Samuneva, B., Kabaivanova, L., Chernev, G., Djambaski, Kashchieva, E., et al. 2008, Sol-gel synthesis and structure of silica hybrid materials., Sol-Gel Sci. Technol., 48, 73-74.

[8] Morales, A., Dur´an, A., 1997, Sol-Gel Protection of Front Surface Silver and Aluminum Mirrors., Sol-Gel Sci. Technol., 8, 451.

[9] Yashan, G.R., Ermenko, A.M., Smirnova, N.P., Suzer, S., Ertas, G., et al., 2008, Morphology and Optical Properties of Thin Silica Films Contained Bimetallic Ag/Au Nanoparticles., Theoretical and Experimental Chemistry, 44, 356-357.

[10] Evans, P., English, T., Hammond, D., Pemble, M.E., Sheel, D.W., 2007, The role of SiO_2 barrier layers in determining the structure andphotocatalytic activity of TiO_2 films deposited on stainless steel., Applied Catalysis A: General, 321, 141.

[11] Jo, M.H., Hong, J.K., 1997, Application of SiO_2 aerogel film with low dielectric constant to intermetaldielectrics., Thin Solid Films, 308-309, 490.

[12] Schumacher, J.O., Hebling, C., Warta, W., 1997, Analysis and design of a thin film silicon solar cell on an insulating substrate., Proceedings of the 14th European photovoltaic Solar Energy Conference, Barcelona/Spain, 1467-1469.

[13] Tuttle, J.R., Berens, T.A., Keane, J., et al., 1996, Investigations into alternative substrate, absorber and buffer layer processing for Cu(In,Ga)Se$_2$-based solar cells., 25th IEEE Photovoltaic Specialists Conference, Washington, DC, USA, 797-798.

[14] S.Hegedus, S., Albright, S., et al., 1997, Substrates, contacts and monolithic integration.,Prog. Photovoltaics, 5, 365.

[15] O¨zsan, M.E., Johnson, D.R., et al., 1994,Characterisation of CdS/CdTe Thin Film Solar Cells., 12th European Photovoltaic Solar Energy Conference, 1604-1605.

[16] Liu, B.T., Yeh, W.D., 2010, Colloids and Surfaces A: Physicochemical and Engineering Aspects Antireflective surface fabricated from colloidal silica nanoparticles, 365, 145-149.

[17] Mohallem, N.D.S., Aaegerter, M.A., 1988, Multilayer SiO_2 and TiO_2 coatings on glasses by the sol-gel process., Non-Crystalline Solids, 100, 526-530.

[18] Brinker, C.J., Scherer, G.W., 1990, Sol-Gel Science., Academic Press, New York.

[19] Guill´en, C., Morales, A., Herrero, J., 2000, Performance of sol-gel SiO_2 coatings onto glass/SnO$_2$superstrates., Surface and Coatings Technology, 132, 31-35.