CALCINATION TEMPERATURE EFFECTS ON OPTICAL PROPERTIES OF NANO-POROUS SILICA THIN FILMS

MOHAMMADREZA MOJAB, #AKBAR ESHAGHI

Faculty of Materials Science and Engineering, Maleke Ashtar University of Technology, Esfahan, Iran

#E-mail: Eshaghi.akbar@gmail.com

Submitted February 22, 2015; accepted June 15, 2015

Keywords: Nano-porous, Thin film, Optical properties, Silica

Silica nano-porous thin films at various calcination temperatures were deposited on glass substrates with a layer by layer method. The structure, morphology, surface composition, transmittance and reflectance of the films were investigated by X-ray diffraction, field emission scanning electron microscopy, attenuated total reflectance fourier transform infrared spectroscopy and UV-VIS-NIR spectrophotometer, respectively. The results indicated that the transmittance of the films is increased by increasing the calcinations temperatures to 300°C and at higher temperature, it is decreased. The deposition of silica nano-porous film on the glass at the optimum calcination temperature (300°C) decreased refractive index of the glass at a wavelength of 550 nm from 1.5 to 1.37.

INTRODUCTION

Transparent materials have attracted much attention for use in optical applications [1-3]. However, the uses of transparent materials are limited because of their high surface reflection. Hence, anti-reflective coatings can be very useful to improve the performance of these materials by enhancing light transmittance. The anti-reflection principle is basis on the destructive interference between light reflected from the air-film and the film-substrate interfaces [4]. A thin film with an appropriate refractive index can be utilized as an anti-reflective coating for glass providing that: (1) the thickness of the film should be $\lambda/4n_c$, where λ is the wavelength of the incident light, and (2) The refractive index of the film is $n_c = (n_a n_s)^{1/2}$ where n_c, n_a and n_s are the refractive indices of the film, air and substrate, respectively. For glass, the refractive index of the anti-reflective film, according to condition (2) should be ~1.22. However, optical films with such a low refractive index are scarce or costly to produce. As a substitution, nano-porous optical materials such as silica nano-porous coating can be selected as anti-reflective coatings, since the insertion of the nano-pores can decrease the refractive index of the coatings and fulfill the anti-reflective requirements [5-8, 9]. The layer-by- layer method (LBL) is a desirable technology for the fabrication of silica nano-porous coatings [10]. It was found that the properties of silica nano-porous coatings are strongly dependent upon preparation conditions such as the pH of solution, thin film thickness, and calcination temperature. Within the literatures, few studies have reported the influence of calcination temperature on the characteristics of silica nano-porous thin films. In this study, the effect of calcination temperatures on the optical properties of the silica nano-porous thin films deposited on the glass substrates was investigated.

EXPERIMENTAL

Materials: polycation poly(diallyldimethylammonium chloride (PDDA, 20 wt. %, Mw) ca. 100 000-200 000), poly(acrylic acid (PAA *M*w ca. 100 000), and sodium silicate solution (reagent grade) were all purchased from Sigma-Aldrich. Distilled water was used throughout the experiment; soda-lime glass slides with a thickness of 1.0 mm were utilized as substrates.

Preparation of PDDA and Sodium Silicate Com-plexes: an aqueous solution of PDDA (2.0 mg·ml^{-1}) was added dropwise to aqueous sodium silicate (68.8 mg·ml^{-1}) under stirring. The final volume ratio of PDDA to sodium silicate solutions was 60:15. The pH value of the aqueous PDDA-silicate complex solution was adjusted to 4.0 by using 1 M HCl.

Fabrication of nanoporous thin film: The glass slides were first immersed in a (2 mg·ml^{-1}) PDDA solution for 10 min to give the substrate a positive charge, then rinsed with water, and dried. Then multi-layer films of PAA/PDDA-silicate were immobilized onto the glass substrates according to the following general steps:

a) The glass substrates were immersed in a solution of PAA (1.0 mg·ml^{-1}, pH 4.0) for 5 min, followed by rinsing with water, and drying.

b) The substrates were immersed in a solution of PDDA-silicate complexes for 20 min, followed by rinsing with water, and drying with a heater.

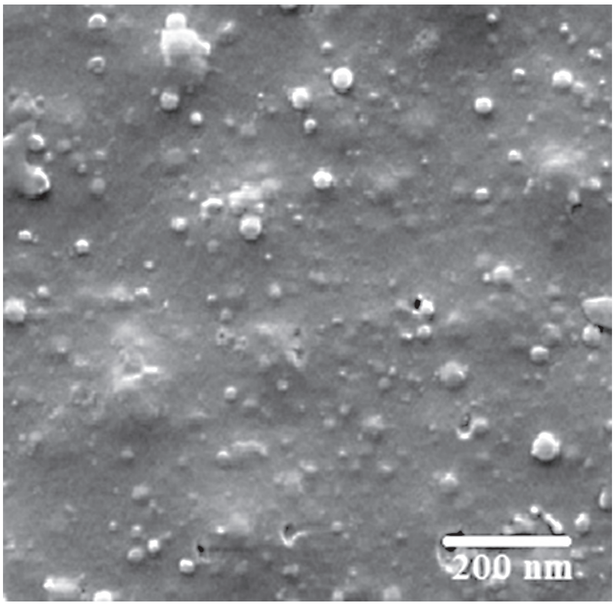
Steps (a) and (b) were repeated until the desired number of deposition cycles was reached. Multi-layer films of the PAA/PDDA-silicate with *12*-cycle deposition is noted as $(PAA/PDDA\text{-}silicate)_{12}$. Finally, the coated slides were calcinated at various temperatures (200, 300, 400 and 500°C) for 4 hours.

Characterization: The surface characteristics and morphology of the thin films were determined using an attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR; Bruker Germany, Tensor 27) and field emission scanning electron microscopy (FE-SEM, Hitachi S4160, Cold Field Emission, Voltage 20KV). The transmittance and reflectance spectra of the thin films were obtained using a UV-VIS-NIR spectrophotometer (Shimadzu UV-3100).

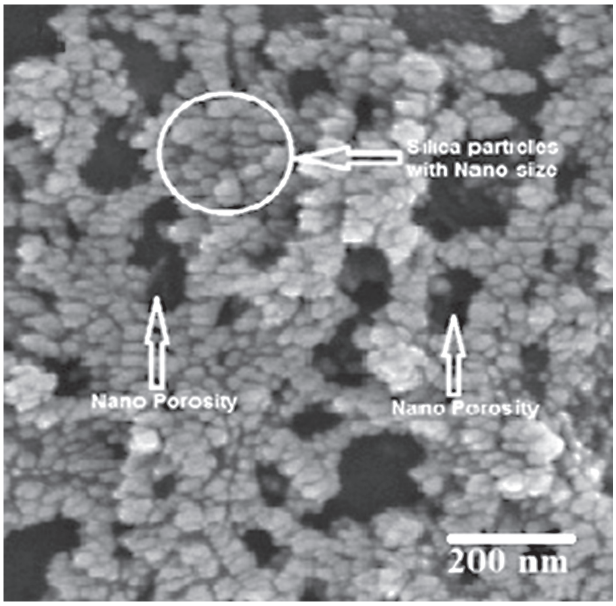
RESULTS AND DISCUSSION

The surface characteristics of the film calcinated at 300°C were studied by ATR-FTIR (figure is not shown here). The adsorption band at about 850 and 1070 cm^{-1} is assigned to the stretching vibration of the Si–O–Si band which indicates the existence of amorphous silica [11].

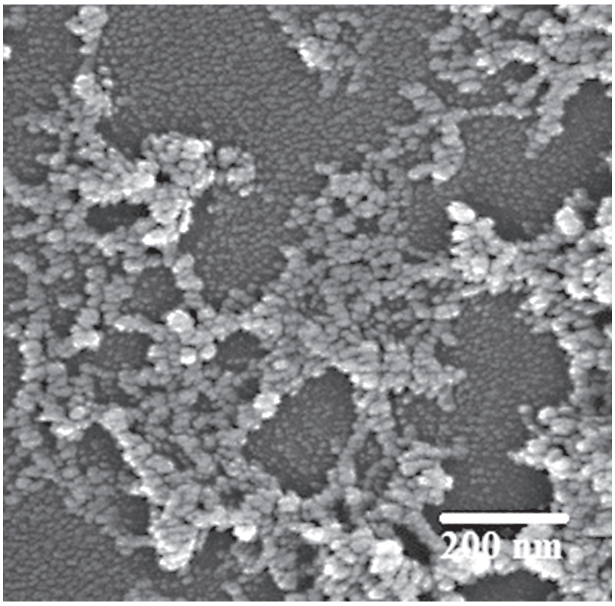
Figure 1 shows FE-SEM images of the silica nanoporous thin films calcinated at various temperatures.



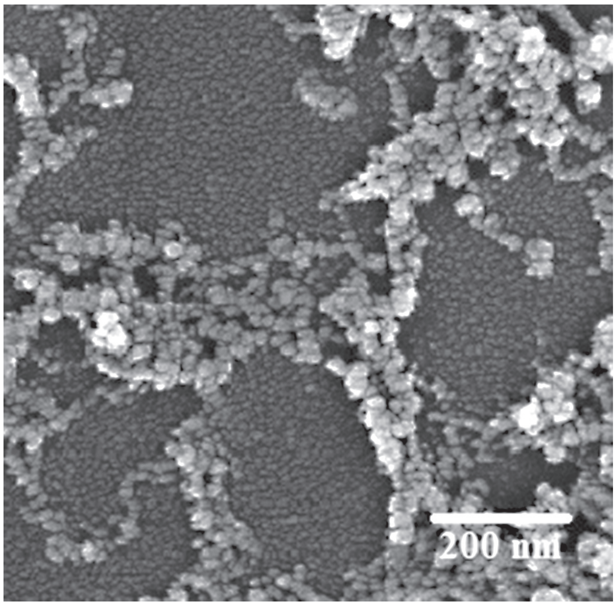
a) 200 °C



b) 300 °C



c) 400 °C



d) 500 °C

Figure 1. FE-SEM images of the thin films calcinated: a) 200, b) 300, c) 400 and d) 500°C.

It can be seen that the porous structure was not formed in the thin film calcinated at 200°C. At this temperature, the organic components did not burn completely, and Si-O bonding was incomplete. Therefore, the nano-porous structure was not form. Figure 1 shows that a nano-porous structure formed in the silica thin film calcinated at 300°C. Nano- pores with sizes between 30 and 80 nm are clearly observed in the thin film calcinated at this temperature. These nano-pores were formed during the burning of PDDA and PAA organic components in the calcination process. Accordant to the FE-SEM images, it may be seen that the pore sizes and silica nano-particles in the thin films increased with an increase in the calcination temperature. When the calcination temperature approached the transtion temperature of the soda lime glass substrate, the morphology of the thin film changed and porous structure vanished. These conditions affect the optical properties of the thin film which is discussed in the following.

Figures 2 and 3 display the transmittance and reflectance spectra of the glass and glass coated silica nano-porous thin films calcinated at various temperatures. Figure 2 indicates that the transmittance of the coatings is increased by increasing the calcinations temperatures to 300°C, but at higher temperatures, is decreased. Figure 3 shows that the reflectance of the coatings is decreased by increasing the calcination temperatures to 300°C, but at higher temperatures, is increased. In other words, silica nanoporous thin film calcinated at 300°C

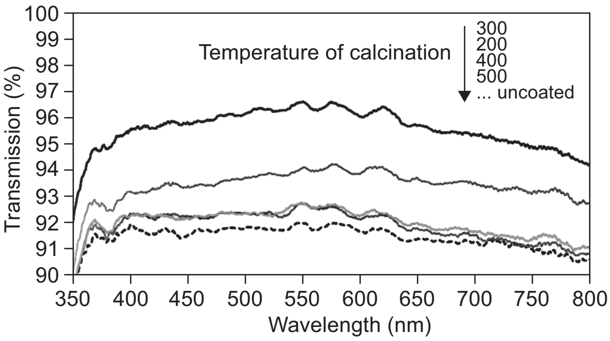


Figure 2. Transmittance spectra of the films at different Calcination temperatures.

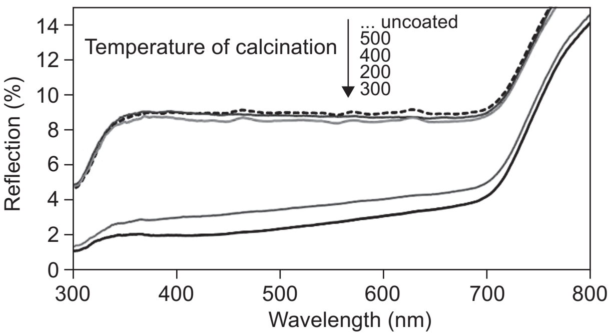


Figure 3. Reflectance spectra of the films at different calcination temperatures.

can act as an anti-reflective thin film for glass substrate. It is clear that the transmittance of glass coated silica nano-porous thin film decreases when the temperature increases. This phenomenon can be attributed to the low transition temperature of glass substrate. By increasing the calcination temperature, the temperatures come close to the transition temperature of the glass substrate, and this leads to softening of the glass. This phenomenon can change the surface morphology of the coatings and cause a change in the pore structure and the arrangement of silica nanoparticles in the thin film (see Figure 1). In other words, by changing the surface morphology, pore sizes in the thin film increase and possibly vanish during calcination which leads to light scattering [9]. In addition silica thin film calcinated at 200°C revealed lower transmittance than films calcinated at 300°C. At this temperature, the organic components did not burn completely and nano-porous structures were not formed. Thus, this film has a dense structure and could not increase the transmittance in comparison to the nano-porous thin film obtained at 300°C. Overally, the nano-porous thin film has a lower refractive index than a dense one. This is one of the key factors which affect the transmittance of the thin film calcinated at various temperatures. Therefore, the effect of calcination temperatures on the refracrive indexes of the glass coated silica nano-porous thin films can be explained as follows:

It is well known that the reflection can reach zero in glass coated with a thin film with a thickness of $d_c = \lambda/4n_c$, when the refractive index of the thin film satisfies the Equation $n_c = (n_a n_s)^{1/2}$. Therein, the refractive index of the air and glass can be approximated as 1 and 1.5, respectively. Thus, the refractive index of the thin film, n_c, can be measured as 1.23. That is the common theory used to describe glass substrate deposited with thin film. Therefore, we cannot use these relations to discuss nano-porous materials. For nano-porous materials, Li [12-13] proposed a new method to calculate the refractive indexes. According to the Li method, we can consider the nano-porous coating and glass substrate as a whole bulk film with a determined thickness of d_{bulk} and the refractive index of n_{bulk}. When d_c is close to $\lambda/4n_c$, this thin film can approach the minimum reflection level and the following equation can be utilized:

$$n_{bulk} = n_c^{\,2}/n_s \tag{1}$$

and as formerly known, $R = (n_{bulk} - 1)^2/(n_{bulk} + 1)^2$, where R is the reflectance of bulk film.

Therefore, the glass substrate with the anti-reflective thin film should satisfy the following equations:

$$R_s = \frac{(n_s - 1)^2}{(n_s + 1)^2} \quad \text{and } R = \frac{[n_c^2/(n_s - 1)]^2}{[n_c^2/(n_s + 1)]^2} \tag{2}$$

The minimum reflectance can be extracted from the reflectance curve in Figure 3. The coated glass has a minimum reflection of 2.34 % at 550 nm. The reflection extracted from the curve, is attributed to both glass surfaces with silica nano-porous thin film. So the R_{min} for single surface is 1.17. According to equation 3, the n_{bulk} was calculated to be 1.24. The transmittance of the bare glass substrate is 91.8 % at a wavelength of 550 nm, and the single surface reflectance of the bare glass substrate at this wavelength was similarly calculated to be 8.9 % /2 = 4.45 %. Thus, n_s was calculated to be 1.53 from the equation 4. Therefore, n_c was calculated to be 1.37 at a wavelength of 550 nm according to Equation 2. The refractive indexes of the silica thin films calcinated at various temperatures were calculated and are indicated in Table 1. Table 1 shows that the refractive index increases with an increase in the calcination temperature. Thus, a decrease in the transmittance of the nano-porous coating with calcination temperature increasing can be attributed to a higher refractive index which causes light to be reflected [14].

Table 1. Refractive indexes of thin films calcinated at different temperatures.

	Temperature (°C)				bare glass parameters
	200	300	400	500	
n_c	1.45	1.37	1.52	1.52	1.53
λ (nm)	550	550	550	550	550
R_{min} (%)	1.98	1.17	4.38	4.20	4.45

CONCLUSIONS

The effect of calcination temperatures on the optical properties of silica nano-porous thin films deposited on glass substrates was investigated. The results indicated:

- Calcination temperature first increased transmittance of the glass coated silica nanoporous thin film and then decreased it as the calcination temperature was increased.
- The maximum transmittance and minimum reflectance was obtained in the silica nano-porous thin film calcinated at 300°C.
- Silica nano-porous thin film calcinated at 300°C can be use as an antireflective coating for glass substrates.

REFERENCES

1. Lee Y.L., Ruby D.S., Peters D.W., McKenzie B.B., Hsu J.W.P.: Nano Lett. *8*, 1501 (2008).
2. Walheim S., Schffer E., Mlynek J., Steiner U.: Science *283*, 520 (1999).
3. Yu P., Chang C.H., Chiu C.H., Yang C.S., Yu J.C., Kuo H.C., Hsu S.H., Chang Y.C.: Adv. Mater. *21*, 1618 (2009).
4. Macleod H.A.: *Thin-Film Optical Filters*, Elsevier, New York, 1969.
5. Cho J., Hong J., Char K., Caruso F.: J. Am. Chem. Soc. *128*, 9935 (2006) .
6. Gemici Z., Schwachulla P.I., Williamson E.H., Rubner M.F., Cohen R.E.: Nano Lett. *9*, 1064 (2009).
7. Zhang L., Li Y., Sun J., Shen J.: Langmuir, *24*, 10851 (2008).
8. Eshaghi A., Eshaghi A.: Appl. Surf. Sci. *258*, 2464 (2012).
9. Budunoglu H., Yildirim A., Bayindir M.: J. Mater. Chem. *22*, 9671(2012).
10. Dubas S.T., Kumlangdudsana P., Potiyaraj P.: Colloid. Surface. A *289*, 105 (2006).
11. Eshaghi A., Aghaei A. A., Zabolian H.: Ceramics – Silikaty *57*, 210 (2013).
12. Li X., He J.: ACS Appl. Mater. Interfaces. *4*, 2204 (2012).
13. Eshaghi A., Mojab M.: J. Non-Cryst. Solids. *405*, 148 (2014).
14. Wicht G., Ferrini R., Schuttel S., Zuppiroli L.: Macromol. Mater. Eng. *295*, 628 (2010).