Preparation and Characterization of Sol-Gel Derived SiO$_2$-TiO$_2$-PDMS Composite Films

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Received August 14, 2001

Thin films of the SiO$_2$-TiO$_2$-PDMS composite material have been prepared by the sol-gel dip coating method. Acid catalyzed solutions of tetraethoxy silane (TEOS) and polydimethyl siloxane (PDMS) mixed with titanium isopropoxide Ti(O^{i}Pr) were used as precursors. The optical and structural properties of the organically modified 70SiO$_2$-30TiO$_2$ composite films have been investigated with Fourier Transform Infrared Spectroscopy (FT-IR), UV-Visible Spectroscopy (UV-Vis), Differential Thermal Analysis (DTA) and prism coupling technique. The films coated on the soda-lime-silicate glass exhibit 450-750 nm thickness, 1.56-1.68 refractive index and 88-94% transmittance depending on the experimental parameters such as amount of PDMS, thermal treatment and heating rate. The optical loss of prepared composite film was measured to be about 0.34 dB/cm.

Keywords : SiO$_2$-TiO$_2$-PDMS film, Sol-gel synthesis, Optical and structural properties, Inorganic-organic hybrid film.

Introduction

There is a tremendous demand for optical materials in integrated optics, laser materials, data storage or communication technologies. The prevailing tendency is to integrate several specific functions into the same type of material and, in general, organic-inorganic composites can provide the multifunctional properties. It has been reported[1-5] that an interesting range of multifunctional composites *via* sol-gel route can be achieved by tailoring the inorganic crosslinking and length, type of organic crosslinking, functional groups of organic molecules and processing variables. A notable advantage of the organically modified inorganic composites is the possibility of obtaining thick, crack-free coatings and bulk materials compared to pure inorganic system which suffer cracking during heat treatment.

Sol-gel process can prepare pure oxide films with a thickness of 0.3-0.5 μm. Stresses developed during drying causes cracking in thicker films and the use of organically modified inorganic composites may help avoid these problems allowing to obtain thick films.

Sol-gel derived silica-titania gel films provide considerable interest[6-8] since they enable fine control of refractive index and thickness for optical applications. For a planar waveguide application, the basic condition is that the guiding layer must have a refractive index higher than the substrate and cladding optical media. Single mode waveguide on fused silica (n=1.45) or soda lime substrates (n=1.51) requires a thickness of the guiding layer typically in the range of 0.2 to 5 μm, depending on the refractive index of the layer itself (in the range 1.65 to 1.512).

Recently, we reported the effect of processing variables on structural changes and optical properties of sol-gel derived 30TiO$_2$-70SiO$_2$ films.[6] In the present study, however, the 30TiO$_2$-70SiO$_2$ films have been modified by incorporating polydimethyl siloxane (PDMS) into it *via* the sol-gel process. PDMS was chosen as the organic component for the synthesis of hybrid films because the terminal SiOH groups can condense with the oxide precursors to produce Si-O-Si and Si-O-Ti bonds which are thermodynamically stable. Since PDMS is known for its superior relaxation properties, PDMS modified hybrid films not only provide thicker films but also cause little cracking problem during drying. Even though there are many reports on PDMS modified silica xerogel,[9-12] the effect of processing variables on optical properties of PDMS modified 70SiO$_2$-30TiO$_2$ films still remains quite unexplored.

In the present study, effects of experimental variables such as heating temperature, heating rate and the amount of PDMS on structural changes, refractive index and the thickness of organic-inorganic hybrid films coated on soda-lime-silicate glass were investigated. The refractive index and film thickness were obtained from the fringe pattern of the UV-Vis transmission spectra using Envelope method[13] and optical propagation loss was measured using Prism coupler.[14] Also we studied structural evolution of the composite powders which occurred during thermal treatment by use of FT-IR.

Experimental Section

The metal alkoxides used as inorganic precursors were silicon tetraethoxide and titanium isopropoxide Ti(O^{i}pr). Silanol-terminated PDMS with a molecular weight of 400-700 g/mole was commercially obtained from Aldrich. Ethanol was dried and used as solvent. Chemical reactivities of the precursors show significant differences.

$$R_{Ti(O^iPr)} \gg R_{TEOS} > R_{HO\text{-}PDMS\text{-}OH} .$$

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Moreover, the polymer is hydrophobic and in high molecular weight form. Therefore it separates from aqueous solutions. These difficulties were substantially overcome by using a stepwise batch polymerization process which yielded a stabilized clear sol solution. In the synthesis of solutions, TEOS, PDMS, ethanol and HCl were first mixed and partially hydrolyzed for 2 hours at 80 °C before addition of Ti(O^{i}Pr) diluted with ethanol. Molar ratio of SiO$_2$: TiO$_2$ was 0.7 : 0.3 and wt.% of PDMS to metal alkoxides was varied between 5 to 15%. Next, water was added until the final molar ratio (Rw) of water to alkoxides reached one. Figure 1 illustrates the experimental procedure for preparing PDMS modified SiO$_2$-TiO$_2$ hybrid films and powder.

The prepared solutions were filtered using a 0.2 μm filter to minimize particulate contamination.

Films were deposited on the cleaned Soda-Lime-Silicate substrate by dip coating with pulling velocity 7 cm/min and dried at 150 °C for 20 minutes after each deposition. After drying, the coated films were heat-treated at various temperatures with different heating rates. By use of the multideposition process, the films with the thickness in the range 0.45-0.75 μm were obtained.

In order to study the effect of the heating rate on the refractive index of the film, the dried films were heat-treated by both the fast and the slow heating processes. In the fast heating process the substrates were placed directly into the furnace preheated to the desired temperature and held for 30 minutes. In the slow heating process, however, the coated substrates were placed in the furnace and the temperature
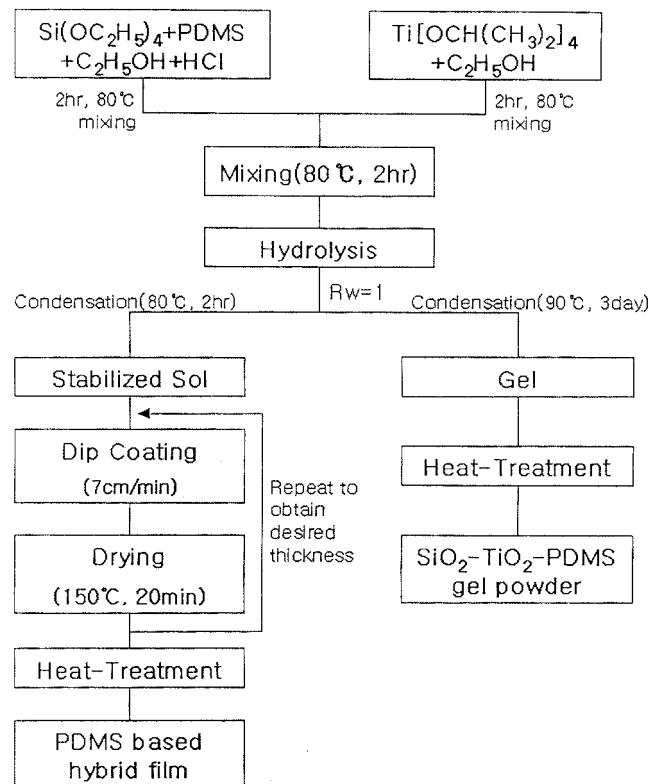
were raised slowly with the heating rate of 5 °C/min to the desired temperature and held for 30 minutes. The thermal analysis was carried out for the gel powder from the sols that had been poured into petri dishes and dried at 90 °C for 1 week.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out on powder at a heating rate of 5 °C/min using TA instrument SDT 1500 in flowing air. UV-VIS transmission spectra were taken from PDMS-SiO$_2$-TiO$_2$ hybrid films deposited on soda lime glass slides in the range of 300-800 nm using Shimedzu UV 2401. The FT-IR spectra in the range 400-4000 cm^{-1} with a resolution of 2 cm^{-1} were recorded using Bio-Rad FTS-155. Optical loss of the hybrid films was measured using prism-coupling technique to obtain a streak in the wave guide. These measurements were made using a helium-neon laser (λ = 632.8 nm) and the optical losses were obtained in dB/cm.

Results and Discussion

The DTA and TGA curves obtained from gel powders are reported in Figure 2. The significant weight loss below 200 °C is attributed to the evaporation of adsorbed water, the vaporization and the thermal decomposition of the organic solvent. The bound water in the pore with very small radius is difficult to remove and the endothermic peak around 150 °C is considered to be evaporation of adsorbed water. The two strong exothermic peaks at 215 and 307 °C are ascribed to the combustion of -C$_2$H$_5$ groups or related to the destruction of titanium alkoxy constituents. Another broad exothermic peak is present between 400 °C and 600 °C, which is attributed to the combustion of organic compounds such as -OC$_3$H$_7$ groups.

Figures 3, 4 and 5 illustrate the sequential FT-IR spectra of the samples at each step of the process comprising starting

Figure 1. Flow diagram for the preparation of SiO$_2$-TiO$_2$-PDMS thin film and powder.
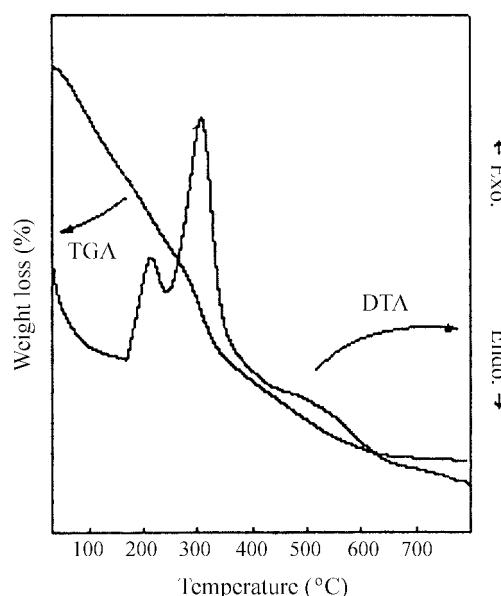
Figure 2. (a) TGA and (b) DTA of SiO$_2$-TiO$_2$-PDMS powder.
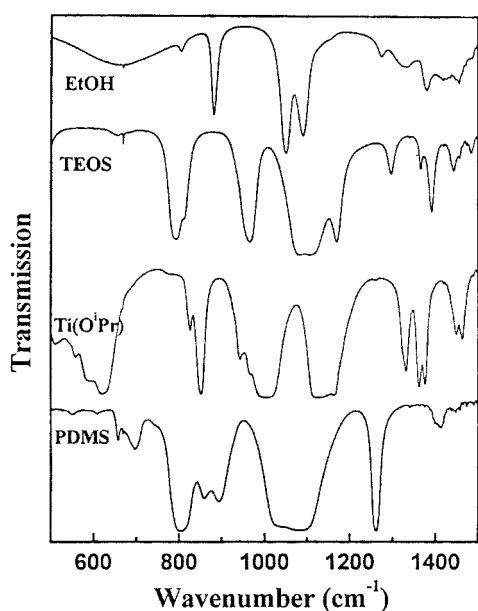
Figure 3. FT-IR spectra of starting materials.
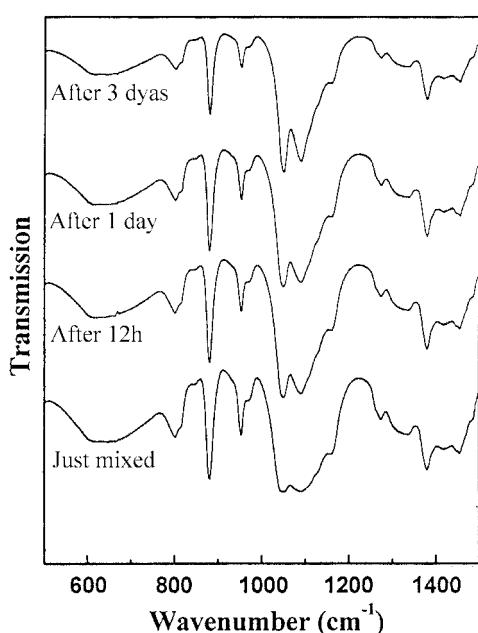
Figure 4. FT-IR spectra during the hydrolysis of SiO_2-TiO_2-PDMS sols.

Figure 5. FT-IR spectra of gel powders sintered at various temperatures.

materials (Figure 3), hydrolysis of sol solutions of PDMS modified metal alkoxides (Figure 4), and thermal treatment of hybrid gel powders (Figure 5).

Metal alkoxides of Si(IV) and Ti(IV) are reported[15] to show absorption bands attributed to ν (M-O) stretching modes around 800 and 620 cm^{-1}, respectively. Therefore IR peaks of TEOS and Ti(O^{i}Pr) at 790 and ~620 cm^{-1} in Figure 3 are assigned to ν(Si-O) and ν(Ti-O) stretching vibration. The peaks at 881, 1048 and 1086 cm^{-1} in the ethanol[16] have been assigned to CH_3 or CH_2 deformation, C-O symmetric stretching, and C-O asymmetric stretching vibration. The strong peaks of PDMS at 800 and 1264 cm^{-1} [17] are associated with the CH_3 deformation and CH_3 asymmetric bending vibration, respectively.

As the hydrolysis and condensation proceeded, the spectra in Figure 4 were significantly masked by the solvent ethanol, and the main change that may be observed are the reduction of the intensity of the peaks at 800 cm^{-1} and 950 cm^{-1}. Also very broad strong peak at about 1080 cm^{-1} which can be ascribed to composite of C-O stretching of TEOS and ethanol shifts to lower frequency and changes to distinctive sharp band. The intensities of the ethanol peaks at 880, 1048 and 1080 cm^{-1} start to decrease after 3 days of hydrolysis.

In a gel powder, prepared at 100 °C in Figure 5, the characteristic peaks of ethanol almost disappeared and the new band emerged at 440 cm^{-1}. As the thermal treatment temperature were increased from 100 °C to 500 °C, very broad bands with strong intensity around 920 and 1050 cm^{-1} shifted to 960 and 1065 cm^{-1}. The shift to higher frequency and the sharpening of the bands indicate shortening of bond distance Si-O and a reduction in mean Si-O-Si and Si-O-Ti bond angle and angular distribution. The low frequency peak near 450 cm^{-1} is assigned to Si-O-Si out of plane bending. The bands at 790 cm^{-1} and 1050 cm^{-1} are ascribed to Si-O-Si symmetric and antisymmetric stretching vibration.[6,18,19]

It is also often reported[6,18,19] that bands within the range 900-1000 cm^{-1} are composite features of Si-OH, Ti-OH and Si-O-Ti species. The strong band at the frequency of ~950 cm^{-1}, therefore, is assigned to stretching vibration of Si-OH superimposed to Si-O-Ti stretching. Also, the weak peak at 1250 cm^{-1} which was absent in the spectra of 70SiO$_2$-30TiO$_2$ reported by Whang[6] is clearly present even after thermal treatment at 500 °C. This band is related to CH_3 symmetric bending vibration of PDMS.

Optical Properties of PDMS hybrid films. It is noted
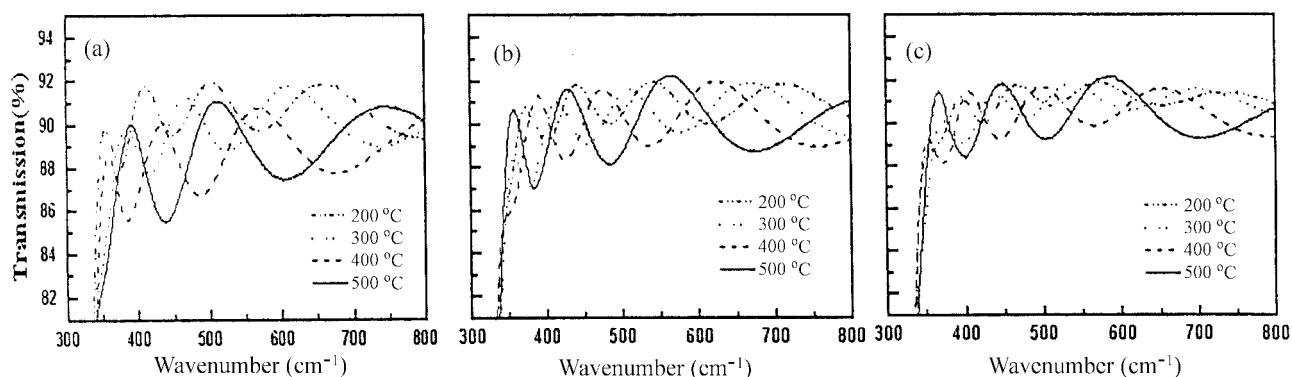
Figure 6. UV-VIS spectra of 70SiO₂-30TiO₂-(a) 5, (b) 10, (c) 15 wt.% PDMS thin films heat-treated at various temperatures with direct insertion method.
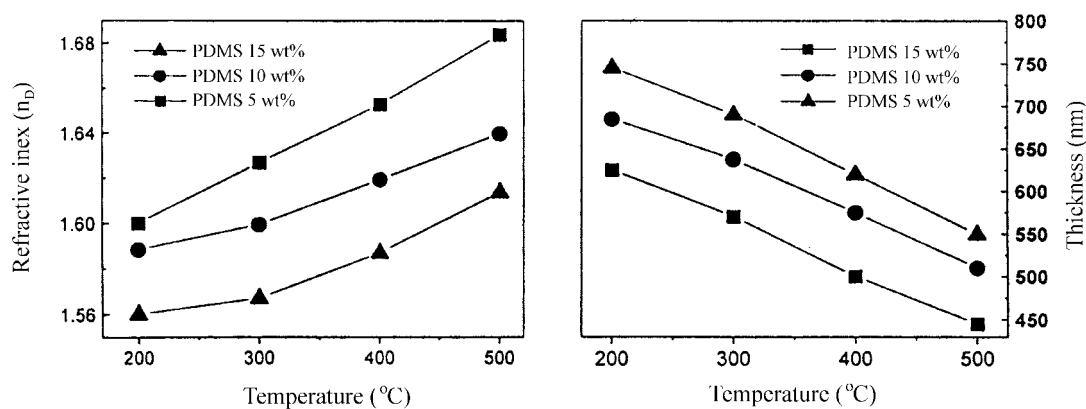
Figure 7. (a) Refractive Index and (b) Thickness of 70SiO₂ -30TiO₂ with different PDMS wt.% thin films heat-treated at various temperatures for 30 min.

that the films coated on soda-lime glass are transparent and colorless. The UV-VIS transmission spectra of the films with various amount of PDMS ranging from 5 to 15 wt.% and heated at different temperatures are shown in Figure 6 (a), (b) and (c), respectively. The films heat-treated at 200 °C and 300 °C for 30 minutes with direct insertion method have high transmission, except for the absorption from the organic solvents which disappears gradually with the increase in

heating temperature. Also it can be observed that the transmittance of the hybrid film with 5 wt.% of PDMS is lower than that of the film with 15 wt.% of PDMS.

The film thickness and refractive index of the film were calculated from the fringe pattern of the UV-Vis spectra employing Envelope method which had been described in our previous paper.[6] Figure 7(a) and (b) show the refractive index and the film thickness of the film as a function of
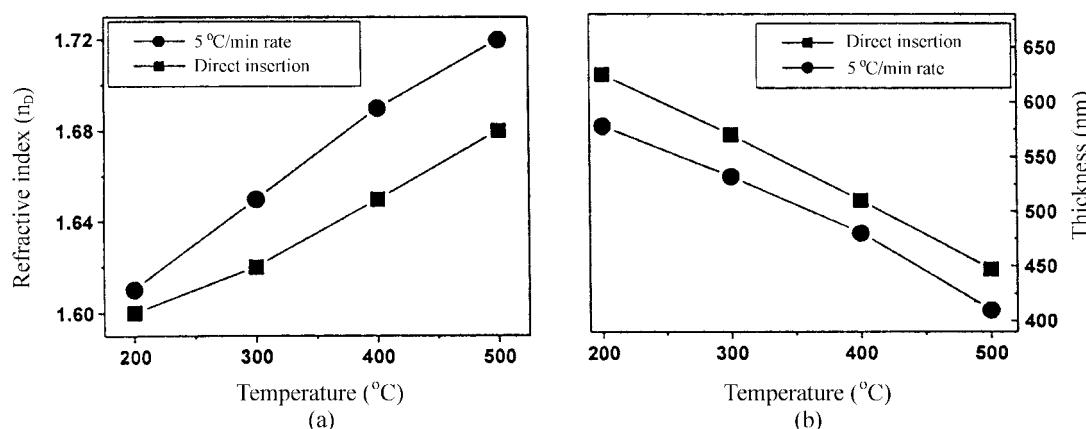
Figure 8. Refractive Index (a) and Film Thickness (b) of 70SiO₂-30TiO₂-5 wt.% PDMS thin films heat-treated at various temperatures for 30 min with different heating rate.

heating temperature with different amount of PDMS. For the $70SiO_2$-$30TiO_2$ with 5 wt.% PDMS film, the decrease in film thickness from 625 nm to 446 nm and increase in refractive index from 1.598 to 1.683 are observed as the heating temperature increased from 200 to 500 °C. Similar trends can be seen for the other two films with PDMS wt.% 10 and 15. The refractive index of SiO_2 films has been measured as 1.46 while that of TiO_2 films as 2.30. Since PDMS has a lower refractive index ($n_D = 1.405$) than SiO_2-TiO_2, incorporatin of a higher amount of PDMS should yield films with lower refractive index and that is exactly what we found in this figure.

Figure 8(a) and (b) show the effect of the heating rate on the refractive index and the thickness of the film. As shown in the figure, the refractive index of the film prepared by direct insertion method showed lower values than that of the film heat-treated by the slow heating process, 5 °C/min. On the other hand, the thickness of the film produced by the fast heating process was thicker than that of the film obtained by the slow heating process. The increase in refractive index from 1.685 to 1.725 and the decrease in film thickness from 447 to 410 nm were observed as the heating rate is varied from fast to slow (5 °C/min) at 500 °C. It is concluded that the slow heating process produces a thinner layer and higher refractive index due to a higher packing density of the film resulting from the gradual poly-cocondensation reaction between PDMS and metal alkoxides and slow decomposition of the organic components.

Optical losses measured in Strip Optical wave guides at $\lambda = 632.8$ nm are in the order of 0.34 dB/cm. These low losses are indicative of the high homogeneity and low surface roughness of the film.

Conclusion

PDMS modified $70SiO_2$-$30TiO_2$ composite films coated on commercial soda-lime silicate glass substrates have successfully been synthesized using sol-gel method. UV-Vis and DTA results indicate that the films baked between 200 and 400 °C exhibit a highly porous surface and the porosity is a direct result of large weight loss. The resulting composite films exhibit 88-94% transmittance, 1.56-1.68 refractive index and 450-750 nm thickness depending on the amount of PDMS, heating temperature and heating rate. The optical loss of the prepared film is measured to be 0.34 dB/cm indicating high homogeneity and low surface roughness of the film.

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