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Effect of Processing Parameters on the Optical Properties of TiO_2/Ormosil Planar Waveguide

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Abstract. Hybrid TiO_2/ormosil waveguiding films have been prepared by the sol-gel method at low thermal treatment temperature of 150°C. The influence of processing parameters including the molar ratios of titanium butoxide ($Ti(OBu)_4$)/3-glycidoxypropyltrimethoxysilane (GLYMO) and $H_2O/Ti(OBu)_4$ (expressed as R), especially aging of sol on the optical properties was investigated. The optical properties of films were measured with scanning electron microscope (SEM), UV/VIS/NIR spectrophotometer (UV-Vis), m-line and the scattering-detection method. The results indicate that the film thickness increases with the increase of sol aging time, but the variation of refractive index as a function of sol aging time depends on the relative ratios of GLYMO to $Ti(OBu)_4$. Higher transmittance and lower attenuation of the planar waveguide can be obtained in the sol with lower $Ti(OBu)_4$ contents and shorter aging time.

Keywords: sol–gel, ormosil, planar waveguide, optical properties

1. Introduction

Planar waveguides have recently received much attention due to their promising applications in integrated optics [1–5]. The formation of waveguide requires the guiding layer having refractive index higher than the substrate and cladding. The number of guiding mode depends on the thickness and refractive index of guiding layer. Low optical loss is an important parameter of waveguide. Notwithstanding that purely inorganic films made by the sol–gel technique have good mechanical properties and thermal stability, crack-free and thick ($d > 1\ \mu$m) coatings are difficult to achieve. High heat-treatment temperature is necessary to burn out organic components in films and make films more densified [6–9]. Organically modified silane (Ormosil) materials overcome those defects. Thick films with high optical quality can be easily obtained [10–14]. In recent years, Wenxiu Que et al. [15] reported the effects of heat-treatment temperature and relative ratios of starting precursors on the microstructures and optical properties of the films. However, influences of sol–gel processing parameters such as addition of water content, especially sol aging time on the optical properties including attenuation of waveguiding film were not well discussed. Aging refers to the time spent between the synthesis of sol and subsequent dip-coating or spin-coating. Different aging time of sol will bring different optical properties to the films derived from the sol. In this work, two groups of TiO_2/GLYMO ormosil sols were prepared. One group includes three sols with different Ti contents; the other group consists of four sols but with different amounts of water. Different aging time of sol was used to investigate the effect of aging time on the properties of final films.

2. Experimental

The starting solution for film deposition was obtained by mixing titanium butoxide ($Ti(OBu)_4$,98%) and

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Table 1. Composition of ormosil sols.

Sol		*R* (H_2O/Ti molar ratio)	$Ti(OC_4H_9)_4$ (%mol)	GLYMO (%mol)
Group T	1	8	60	40
	2	8	40	60
	3	8	20	80
Group W	4	4	20	80
	5	8	20	80
	6	12	20	80
	7	16	20	80

3-glycidoxypropyltrimethoxysilane (GLYMO,98.8%), together with ethanol and acetylacetone (Acac) as stabilizers. Hydrolysis of the solution was promoted by the addition of distilled water. In this experiment, two groups of sols were prepared as described in Table 1. The films prepared from sols aged for 3 days will be indicated as TA or WA, 6 days as TB or WB. All the films were obtained by dip-coating at a withdrawal speed of 1 cm/min. Soda-lime-silica glass slides were used as substrates after ultrasonically cleaning with acetone, distilled water and ethanol. The prepared sols were stored in the darkness and aged for 18 days altogether. The coated films were fired at 150°C for 2 h. All the films were single layer and the thickness varied from 0.307 μm to 16.11 μm.

The film thickness was measured with scanning electron microscope (JSM-6360LV). As shown in Fig. 1, the thickness was obtained by measuring the width of film cross-section. The thickness accuracy is ± 0.01 μm. The UV-VIS transmittance spectrum of film deposited on soda-lime-silica glass slide in the range of 250–700 nm was examined by a 900UV/VIS/NIR spectrophotometer (Perkin-Elmer-Labmda). The refractive index of film was measured with dark m-line method [16]. The incident light wavelength is $\lambda = 632.8$ nm, and the measurement error is ± 0.001. The prepared waveguiding films support one or two guiding mode. The viscosity of sol was measured with rotation viscometer (NJD-1). The scattering-detection method [17] was used for measuring optical loss of the film. The laser light ($\lambda = 632.8$ nm, He-Ne laser) was launched into the waveguide by a prism and the polarization of the laser beam was parallel to the plane of the waveguide (TE mode). The scattered light was collected in a direction perpendicular to the plane of the film with a CCD camera and the loss was measured through an exponential fit of the decaying scattered intensity, assuming a homogeneous distribution of the scattering centers in the film. The measurement error is ± 0.002 dB/cm.

3. Results and Discussion

3.1. Thickness

Figure 2 shows the dependence of film thickness and sol viscosity upon the aging time of the sol. It can be

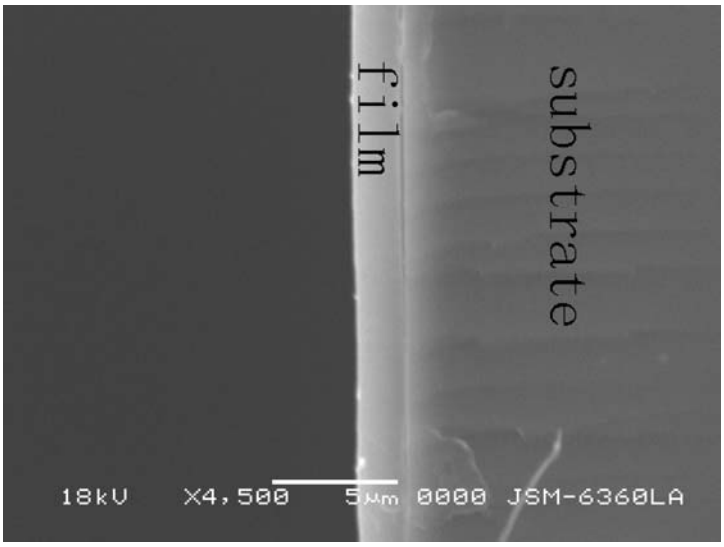

Figure 1. SEM micrograph of the film cross-section.

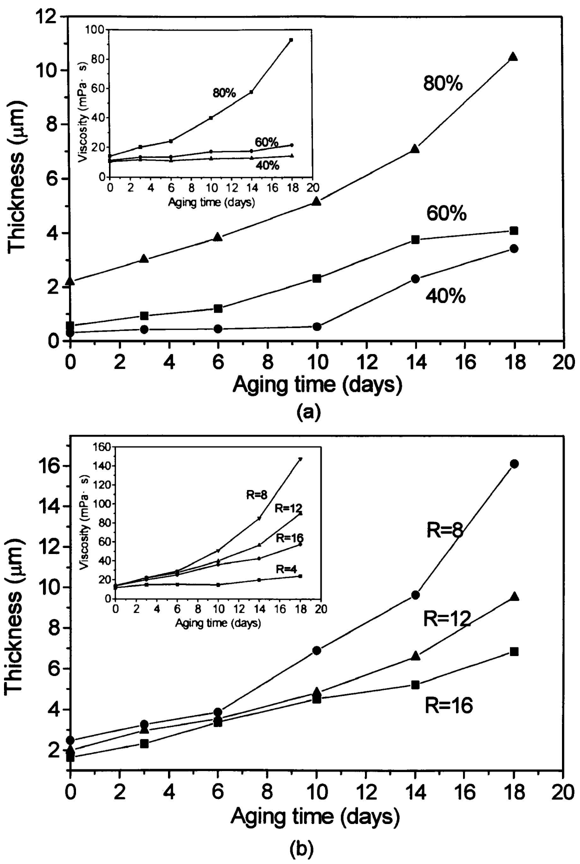

Figure 2. Dependence of the film thickness and sol viscosity on the aging time of sol with (a) different molar percentages of GLYMO (b) different molar ratios of H_2O:Ti (expressed as R).

seen that the film thickness increases with the increase of sol aging time, because the longer the aging period is, the higher the viscosity of sol is. This result indicates that condensation reactions occur to a larger extent after long sol aging time. Larger molar percentage of GLYMO leads to thicker films, which is also ascribed to the higher viscosity of the sol resulting from the longer molecular chain of organic material. In Fig. 2(b), for the sol with $R = 4$, there is no obvious viscosity change with the increase of sol aging time. Because of too small total amount of water (only a quarter of stoichiometry) in this case, the initial hydrolysis rate is larger than condensation rate. As the hydrolysis reactions proceed, water is rapidly consumed. The condensation reactions are insufficient. This can be proved by the rough and non-uniform surface of film. So the viscosity of this sol is very low. Until two weeks later, the quality of film prepared with this sol cannot be improved. This fact indicates that the sufficient condensation reactions need more time when the amount of water is too small. For the sol with $R = 8$ (half of stoichiometry), water content is proper to promote both hydrolysis and condensation. Largest viscosity and thickest film are obtained in this sol. With the further increase of water content in sols ($R > 8$), large amount of water is considered to speed up hydrolysis, which followed by slowing down the condensation extent, so the viscosity drops as R rises, and the film thickness decreases with R increases.

3.2. Refractive Index

Refractive index of film as a function of aging time is shown in Fig. 3. As expected, the refractive indices of films with lower GLYMO contents are higher than those with higher GLYMO contents due to more TiO_2 content per volume in Fig. 3(a). Two contrary tendencies were observed. Within the aging time of 18

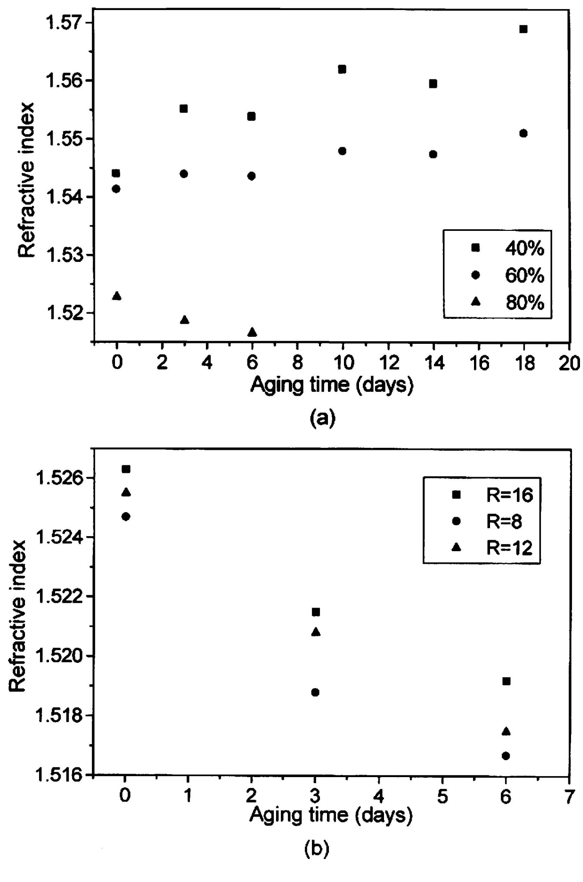

Figure 3. Refractive index of the film as a function of the aging time of sol with (a) different molar percentages of GLYMO (b) different molar ratios of H_2O:Ti (expressed as R).

days, the refractive indices of films containing 40%, 60% GLYMO increase slowly. As the GLYMO content increases to 80%, however, the refractive indices decrease gradually with the increase of sol aging time. The film index becomes lower than that of the substrate after 6 days sol aging and cannot be measured by *m*-line method. These facts suggest that the variation of film index resulting from sol aging strongly depends on the relative molar percentage of GLYMO to Ti-alkoxide. It can be deduced that there exists an optimum GLYMO:Ti$(OBu)_4$ ratio to obtain both proper film thickness and refractive index. Figure 3(b) shows the refractive index changing with the aging time of sols. Different amounts of water were added to the sols. Obviously, the refractive index increases with increasing amount of water at the same aging time, probably because additional water changes the polarity of solvent, making it more polar [18, 19]. Aging also reduces the refractive indices at all three water contents due to the existence of 80% GLYMO in the sols. The further investigation on the variation of refractive index is still under way.

3.3. *UV-Vis Transmittance*

The UV-Vis transmittance spectra of the films, prepared from sols with various amounts of GLYMO (Group T) and sols aged for 3 days, are shown in Fig. 4(a). The inset is enlarged spectra between 250 and 400 nm. The films are transparent at the wavelength longer than about 330 nm, and exhibit sharp absorption edges. The maximum transmittance exceeds 90%, which indicates that the films have no intrinsic absorption [20]. The weak transmittance fluctuation in the range from 400 to 700 nm is due to the interferences in the thin film (TA1 and TA2) owing to the reflection at the air-film and film-substrate interfaces, and the fluctuation is more evident in the thinner film. Meanwhile, the higher proportion of Ti$(OBu)_4$ content in the initial sol is responsible for the reduction of film transmittance, which is in agreement with Ref. [15]. This result can be attributed to the absorption of acetylacetate complex formed during the preparation of the sols. The high hydrolysis rate of Ti$(OBu)_4$, causes precipitation of TiO_2 particles in the resultant material and increases scattering loss of waveguiding film, so the acetylacetone was selected to reduce the reaction rate through the formation of chelate complex. However, this complex has been proved to have a strong absorption band in the visible region [21]. The function of the complex will be

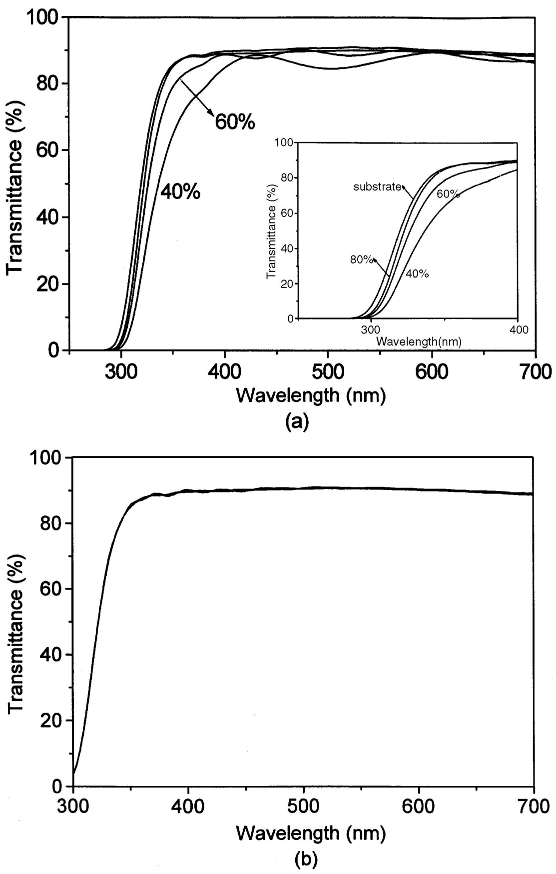

Figure 4. UV-Vis transmittance spectra of the films prepared from sols with (a) different molar percentages of GLYMO (b) different molar ratios of H_2O:Ti.

more evident with the increase of Ti content and thus lower transmittance was observed. Figure 4(b) shows the UV-Vis transmittance spectra of the films prepared from sols with different amounts of water (Group W) and sols aged for 3 days. It is clearly observed that the transmittances of all the samples are similar in the range from 300 to 700 nm, suggesting that the variation of water amount does not affect the transmittances of films. Figure 5 shows the UV-Vis transmittance spectra of the films prepared from sol 3 in Group T and sol aged for different days. As can be seen, sol aging decreases the transmittances of the films, which is also ascribed to the stronger absorption of acetylacetate complex caused by the increase of film thickness.

3.4. *Optical Losses*

Optical losses of waveguiding films prepared from two groups of ormosil sols are given in Table 2. It can be

Table 2. Attenuation of the waveguiding films ($\lambda = 632.8$ nm). The films prepared from sols aged for 3 days are indicated as TA or WA, 6 days as TB or WB. The serial number is the same as in Table 1.

Sample	Attenuation (dB/cm)	Sample	Attenuation (dB/cm)
TA1	0.858	TB1	0.981
TA2	0.623	TB2	0.691
TA3	0.507	TB3	0.643
WA5	0.513	WB5	0.638
WA6	0.721	WB6	0.942
WA7	0.647	WB7	0.785

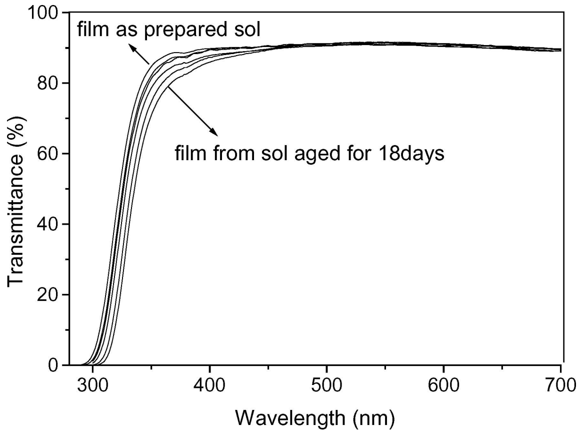

Figure 5. UV-Vis transmittance spectra of the films coated with the sols aged for different days.

seen from the data that the losses of all the samples are lower than 1 dB/cm, indicating a high level of chemical homogeneity in the hybrid waveguides. In general, the more the number of constituents of a film, the higher the probability of obtaining high optical loss, because attenuation is directly related to refractive index fluctuations within the network [12]. It also can be observed from Table 2 that the losses are related to $Ti(OBu)_4$ percentage in the sol since the attenuation increases with the increase of $Ti(OBu)_4$ content. In an earlier publication, the conclusion that as the ormosil content increases, the film becomes smoother has been drawn [22]. Therefore, this result is ascribed to the different surface roughness of films, directly affecting the amount of in- and out- of plane scattering levels of the waveguides. However, no trend is apparent in the attenuations of waveguiding films as a function of water content in the sols. Because the hydroxyl ions in films do not absorb at 632.8 nm, the absorption losses of hydroxyl ions have minimum contribution to the total measured losses. In addition, the longer the aging time of sol is, the higher the optical loss is. It is observed that the thickness fluctuation becomes greater with the prolonged aging time. This phenomenon is probably due to the higher viscosity of sol after long time aging, which causes more difficult relaxation and thus impedes the homogeneity of film thickness. Therefore, longer aging time is considered to be not beneficial to the reduction of optical loss of waveguiding film.

4. Conclusions

Hybrid inorganic-organic waveguiding films have been synthesized by the sol–gel method. Within the designed aging period, the thickness of 0.307–16.11 μm and the refractive index of 1.53–1.55 at 632.8 nm were obtained in the single layer films. The thickness of the coated films increases as the aging time of sol increased. The variation of refractive index as a function of aging time of sol depends on the relative ratios of GLYMO to $Ti(OBu)_4$. The addition of $Ti(OBu)_4$ and sol aging decrease the transmittance of the film. Optical losses at the wavelength of 632.8 nm were tested to be lower than 1 dB/cm in all the films. It was found that the film attenuation increases with the increase of $Ti(OBu)_4$ contents in the sols, but does not show any dependence on water content. Longer sol aging time causes higher loss of waveguiding film. In this work, waveguiding films prepared from sol 3 in Group T and sol aged for 3 days have the best optical qualities.

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