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Study of refractive index and thickness of TiO_2/ormosil planar waveguide

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Hybrid titania/ormosil waveguide films have been prepared by sol-gel method at low thermal treatment temperature of 150°C. The influence of processing parameters including the molar ratios of $Ti(OBu)_4$/ glycidoxypropyltrimethoxysilane (GLYMO) and $H_2O/Ti(OBu)_4$ (expressed as R), especially aging of sol, on the refractive index and thickness of film was investigated. The optical properties of films were measured with Scanning Electron Microscope and m-line spectroscopy. The results indicate that the film thickness increases with the aging time of sol, but the variation of refractive index as a function of aging time of sol depends on the relative ratio of GLYMO to Ti-alkoxide. The relation between film thickness and corresponding sol viscosity is linear as the volume of GLYMO is 80% within the range of measured data.

Keywords: sol-gel process, aging, optical property, TiO_2/ormosil planar waveguide
PACC: 4280L, 7865T, 8140T

1. Introduction

Planar waveguides have recently attracted much attention due to their promising applications in integrated optics.[1−5] The formation of waveguide requires the guiding layer to have refractive index higher than the substrate and cladding. The number of guiding mode depends on the thickness and refractive index of the guiding layer. Notwithstanding that pure inorganic films with low optical losses made by sol-gel technique combine good mechanical and thermal stability, crack-free and thicker ($d > 1\mu$m) coatings are difficult to achieve using only inorganic precursors, because high heat treatment temperature is necessary to burn out organic components in films to effect film densification.[6−9] Organically modified siliane (Ormosil) materials derived from the sol-gel process possess organic properties. Inorganic ingredient is mainly responsible for adjusting refractive index and maintaining the hardness of films. Decreased network connectivity originating from organic component leads to an enhanced relaxation rate and to lower densification temperature. Thus crack-free and thicker films can be easily deposited in a single step by spin-coating or dip-coating method, and preparation of multimode waveguides become possible.[10,11] In recent years, investigations on inorganic–organic hybrid planar waveguides prepared via sol-gel route are increasing due to their outstanding advantages compared with other methods. Many articles stressed the selection of alkoxide, solvent, catalyst and organic precursors, which really affect the optical properties of waveguide films through modifying the microstructure such as porosity, cluster size and surface roughness.[12−15] Atkins *et al* reported the effect of an ormosil system comprising methyl- and phenyl- substituted silica on the film optical properties, with methyl and phenyl playing opposite roles in adjusting the refractive index.[16] However, little research work has been carried out on the effect of processing parameters on the film properties, especially the aging of sol. Aging refers to the time spent between the synthesis and subsequent dip-coating or spin-coating of sol. 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/ glycidoxypropyltrimethoxysilane (GLYMO) ormosil solutions were researched. 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.

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2. Experiment

The ormosil sols were prepared using titanium butoxide ($Ti(OBu)_4$,98%) and 3-glycidoxypropyltrimethoxysilane (GLYMO,98.8%) as starting precursors. The detailed procedure of sol synthesis is described as follows: GLYMO was dissolved in ethanol, and prehydrolized with distilled water. In a separate container, $Ti(OBu)_4$ was mixed with acetylacetone (Acac) in the molar ratio of $Ti(OBu)_4$: Acac=1:1. Then the solutions were mixed together based on the desired $Ti(OBu)_4$ content. In the last step, different amounts of water were added to them according to the final molar ratio of H_2O:$Ti(OBu)_4$ in sols. The mixture was stirred for 2h. In this experiment, two groups of sols were prepared as described in Table 1.

Table 1. Composition of ormosil sols.

Sol		R (H_2O/Ti molar ratio)	$Ti(OC_4H_9)_4$ /(%mol)	GLYMO /(%mol)
Group 1	T1	8	60	40
	T2		40	60
	T3		20	80
Group 2	W1	4	20	80
	W2	8		
	W3	12		
	W4	16		

All the films were obtained by dip-coating at 1cm/min speed of withdrawing. Soda-lime-silica glass slides and silicon wafers were used as substrates after ultrasonically cleaned with acetone, distilled water and ethanol. The viscosities of sols were measured at once after coating of films, the prepared sols were stored in darkness and aged for 18 days altogether. The coated films were fired at 150°C for 2h, all the films were single layer with thickness varying from 0.307μm to 16.11μm. The film thickness was measured with scanning electron microscope (JSM-6360LV). The refractive index of the film was determined by dark m-line spectroscopy,[17] the incident light wavelength being λ=632.8nm. The viscosity of sol was measured with a rotation viscometer (NJD-1).

3. Results and discussion

3.1. Thickness

Figure 1 shows the dependence of film thickness and viscosity upon the aging time of the sol: (a), (b) for different volume percentages of GLYMO in group 1; (c), (d) for different molar ratios of H_2O :$Ti(OBu)_4$=R in group 2. It can be seen that the film thickness generally increases with the increase of sol aging time because the longer the aging period, the higher the viscosity of sols. This indicates that condensation reactions occur to a larger extent after long sol aging time. Larger volume 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. For the sol with R=4 in group 2, there is no obvious viscosity change with the increase of sol aging time. Because of too small a total amount of water (only a quarter of stoichiometry) in this case, the initial hydrolysis rate is larger than the condensation rate. As the hydrolysis reaction proceeds, water is rapidly consumed. The condensation reactions are insufficient. This can be proved by the rough and non-uniform surface of films. So the viscosity of this sol is very low. Until two weeks later, the quality of films 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 thick film are obtained in this sol. With further increase of water content in $R > 8$ sols, large amount of water is considered to speed up hydrolysis, which is followed by slowing down of the condensation extent, so the viscosity drops as R rises, and the film thickness decreases with increasing R.

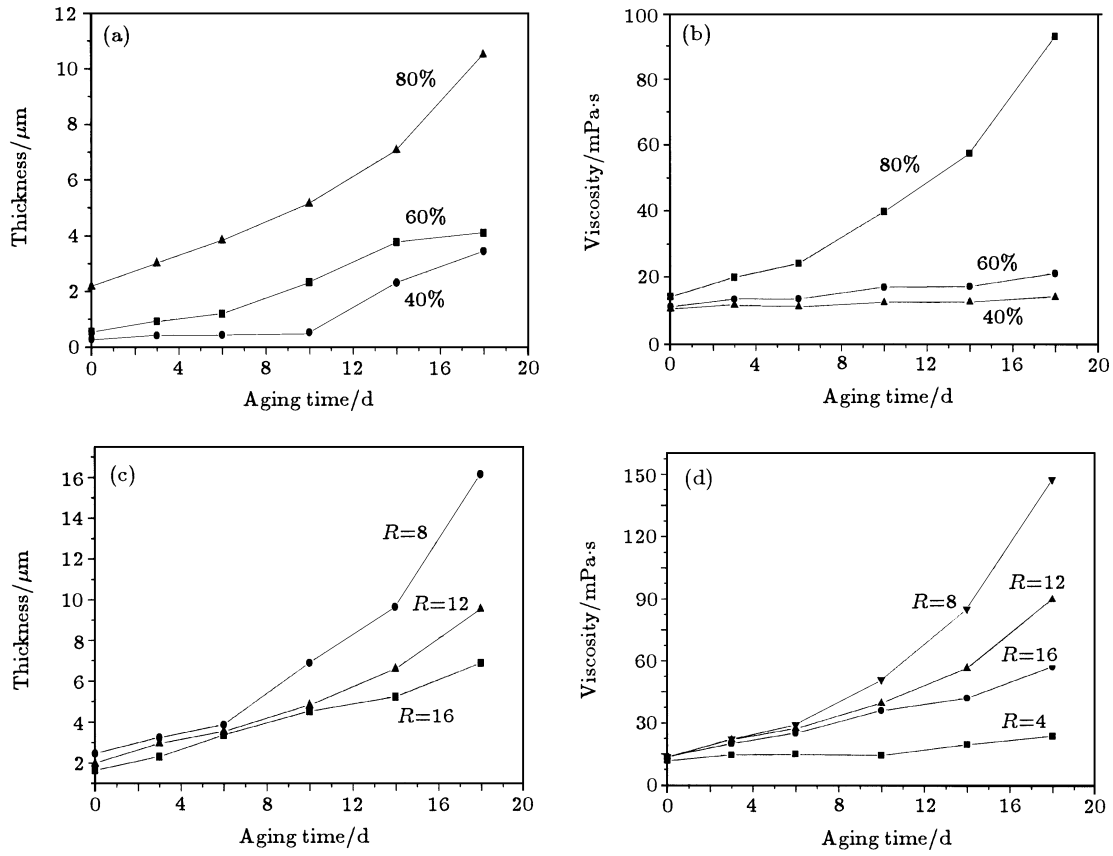


Fig.1. Dependence of film thickness and viscosity on the aging time of sol with (a) and (b) different volume percentages of GLYMO (c) and (d) different molar ratios of H_2O:Ti.

The relation between film thickness and corresponding sol viscosity is also investigated. The thickness of films containing different amounts of water or GLYMO as a function of viscosity of sols is shown in Fig.2. As can be seen, the relation between film thickness and corresponding viscosity is linear within the range of measured data in Fig.2 (a), and similar slopes of lines were found for all the samples despite the difference in water content. This result seems to disagree with previous reports, which asserted that the expression between film thickness and viscosity of sol is $d \propto \eta^{1/2}$ [18] or $d \propto \eta^{2/3}$.[19] It is clear that the relation between d and η is not linear but curvilinear. However, it should be noted that these two relations are derived from a premise that the regime is of low capillary number ($N_{Ca} = \eta U/\sigma$). In fact, when the viscosity of sol increases to some extent, deviation from this assumption will occur. In our experiment,

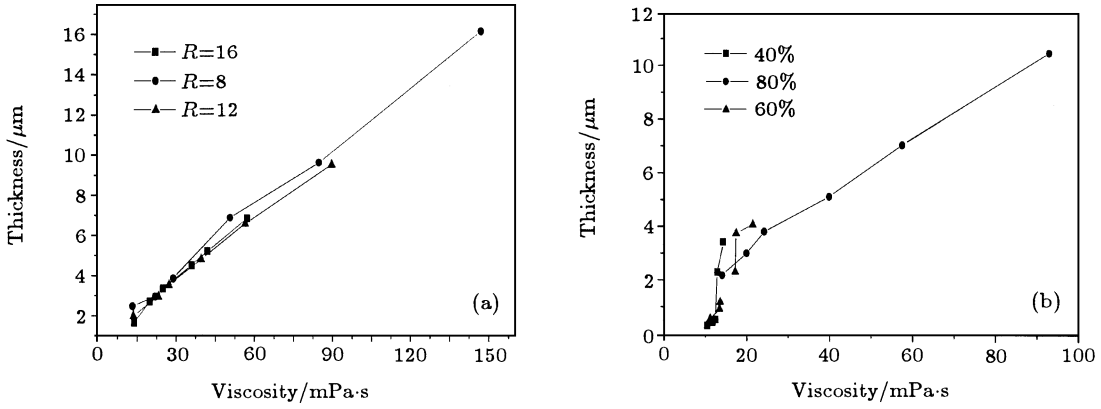


Fig.2. Thickness of the film as a function of the viscosity of the sol with (a) different amounts of water and (b) different GLYMO contents.

large amounts of organic precursor were added to the solution to obtain thicker film, so the viscosity is large and the low capillary number regime is no longer valid. Therefore, instead of 1/2 or 2/3, the exponent of η is 1 in the viscosity range from 13.4 to 147.5mPa·s. For the samples with lower GLYMO content (40%, 60%) in Fig.2 (b), the exponent of η is not 1, 2/3 or 1/2, and their increase rates with the viscosity in the film thickness are faster than those of samples with higher GLYMO content (80%); the notable variation of surface tension and density of sol may be important reasons.

3.2. Refractive index

The refractive index of films as a function of aging time is shown in Fig.3. As expected, the refractive index of films with lower GLYMO content is higher than those with higher GLYMO content due to more TiO_2 content per volume in Fig.3 (a). Two contrary tendencies were observed. Within the aging time of 18 days, the refractive index of films containing 40%, 60% by volume of GLYMO increase slowly, but as the GLYMO content increases to 80%, the refractive index decreases gradually with sol aging time so that the refractive index becomes lower than the substrate after 6 days sol aging time 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 change of refractive index with sol aging time in sols with different water amounts. 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.[12,20] And aging also reduces the refractive index at all three water contents due to the existence of 80% volume of GLYMO in sols.

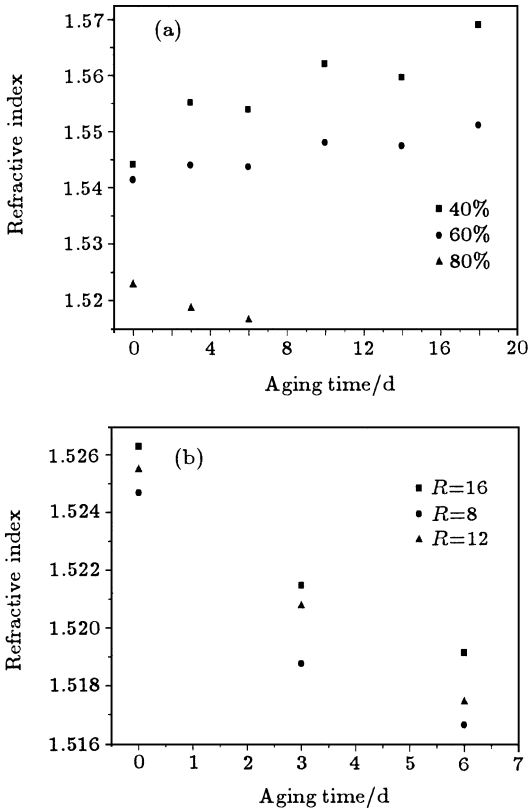


Fig.3. Refractive index of the film as a function of the aging time of the sol with (a) different GLYMO contents (b) different amounts of water.

4. Conclusions

Hybrid inorganic–organic waveguide films have been synthesized by the sol-gel dip-coating method from $Ti(OBu)_4$ and GLYMO precursors and low thermal treatment process. Within the designed aging period, the thicknesses of the coated films increase as the aging time of sols increases and the film from sol with R=8 has largest thickness. The relationship between film thickness and corresponding sol viscosity is linear as the volume of GLYMO is 80% within the aging time of 18 days. The variation of refractive index as a function of aging time of sol depends on the relative ratio of GLYMO to Ti-alkoxide.

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