

Preparation and characterizations of $\text{SiO}_2/\text{TiO}_2/\gamma$ -glycidoxypropyltrimethoxysilane composite materials for optical waveguides

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Abstract. $\text{SiO}_2/\text{TiO}_2/\gamma$ -glycidoxypropyltrimethoxysilane composite materials processed by the sol-gel technique were studied for optical waveguide applications. Waveguide films with thickness more than $1.7\ \mu\text{m}$ were prepared on a silicon substrate by a single-coating process and low-temperature heat treatment from these high-titanium-content composite materials. Scanning electron microscopy (SEM), atomic force microscopy (AFM), thermal gravimetric analysis (TGA), UV-visible spectroscopy (UV-VIS), Fourier-transform infrared spectroscopy (FT-IR), and X-ray photoelectron spectroscopy (XPS) have been used to characterize the waveguide films. TGA curves showed that organic compounds in the composite materials would decompose in the temperature range from $200\ ^\circ\text{C}$ to $480\ ^\circ\text{C}$. SEM, AFM and UV-VIS results showed that a dense, porous-free, and high transparency in the visible range waveguide film could be obtained at a low heat-treatment temperature. It was also noted that the carbon content in the film with higher titanium content heated at high temperature was evidenced by XPS. The waveguide propagation loss properties of the composite material films were also investigated and showed a dependence on the titanium molar fraction.

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Optical-quality films of a few μm thickness are a basic requirement for integrated-photonic devices that are fabricated on silicon substrates. Since such films are thick by normal coating standards, a number of specialized methods have been developed to form them. Among different synthesis methods, the sol-gel processing is one approach because of the high optical quality of materials produced and freedom to impregnate them with a variety of additives to modify their optical characteristics. Purely inorganic sol-gel derived material is a research area that people have been exploring for a long time [1–6] and sol-gel materials such as SiO_2 and TiO_2 have been investigated for optical applications [7, 8]. However, a single purely inorganic sol-gel layer

cannot generally be made thicker than $0.2\ \mu\text{m}$ by a single-coating process and the heat-treatment temperature is generally quite high. In order to overcome this problem, some researchers have used organically modified alkoxysilanes and tetraalkoxysilanes to produce organically modified silicates (ORMOSIL). For example, Motakef et al. [9] synthesized a composite material of poly(dimethylsiloxane)- SiO_2 - TiO_2 and achieved an optical propagation loss of $0.15\ \text{dB/cm}$ at $633\ \text{nm}$ in a slab waveguide with a thickness of $1.55\ \mu\text{m}$. Recently, Sorek et al. [10–12] and Zevin et al. [13] reported that a dense sol-gel composite film could be obtained without baking from titania/ORMOSIL or zirconia/ORMOSIL. However, the properties and optical waveguide applications of $\text{SiO}_2/\text{TiO}_2/\gamma$ -glycidoxypropyltrimethoxysilane (GLYMO, $[(\text{OCH}_2\text{CH})\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2]\text{Si}(\text{OCH}_3)_3$) composite films produced by the sol-gel process have not been well investigated. In this work, high optical quality $\text{SiO}_2/\text{TiO}_2/\gamma$ -glycidoxypropyltrimethoxysilane composite materials processed by the sol-gel technique were prepared. The waveguide films fabricated by the composite materials were characterized using SEM, AFM, TGA, UV-VIS spectroscopy, FT-IR spectroscopy, and XPS in order to study their optical and microstructural properties. In addition, the propagation loss properties of the composite material waveguide films were also investigated based on the scattered-light measurement method.

1 Experimental

1.1 Solution preparation and composite thin film formation

γ -glycidoxypropyltrimethoxysilane (GLYMO) from Alfa AESAR was used as organic silicon (ORMOSIL) source, tetrapropyl orthotitanate $(\text{TiOC}_3\text{H}_7)_4$ from ACROS was used as titania (TiO_2) source, tetraethoxysilane (TEOS) used as silica (SiO_2) source was obtained from Fisher Scientific. Other chemicals were hydrochloric acid (37 wt% in water) from Aldrich and acetylacetone ($\text{CH}_3\text{COCH}_2\text{COCH}_3$) from Fluka.

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In the preparation of the solution, for a solution A, 1 mole of TEOS was mixed with 4 moles of ethanol and 4 moles de-ionized water, and after being stirred for 30 min, 0.1 mole hydrochloric acid was added into the solution. Then the solution was stirred again for 60 min. For solution B, 1 mole of GLYMO was mixed with 4 moles of ethanol and 4 moles of de-ionized water, and the solution was stirred for about 30 min. For solution C, tetrapropyl orthotitanate was added to acetylacetone at a molar ratio of 1 : 4 under a nitrogen environment and the solution was agitated until homogenization was reached. Three solutions (s. A, B, and C) were then mixed to have different molar ratios of SiO_2 to TiO_2 , namely depending on the desired titanium content in the final sol-gel film. However, the molar ratio of GLYMO to SiO_2 was fixed to be 1 : 1. Accordingly, in our case, the studied molar ratios of GLYMO : SiO_2 : TiO_2 were 0.40 : 0.40 : 0.20, 0.35 : 0.35 : 0.30, 0.30 : 0.30 : 0.40, and 0.25 : 0.25 : 0.5, respectively. The final mixture solution was stirred for 25 h at room temperature. It should be noted that cleaning of the substrate is important for proper adhesion of the films. We used both silicon (Si) and microscope slide glass as substrates and they were ultrasonically cleaned in acetone and ethanol, respectively, rinsed with de-ionized water and dried with pure nitrogen. One layer of the sol-gel film was spun onto the substrate at 4000 rpm for 35 s. The coated films were then baked for 20 min at different temperatures of 100, 200, 300, 400, and 500 °C or higher.

1.2 Thin film characterization

X-ray diffractometry (XRD), SEM, AFM, TGA, UV-VIS spectroscopy, FT-IR spectroscopy, and XPS were used to characterize the films (or powders). XRD was carried out for the films using a Rigaku Rint 2000 Series X-ray diffractometer equipped with a thin-film attachment unit. The X-ray radiation source used was $\text{Cu } K_\alpha$, operated at 40 kV, 35 mA and the scanning speed was 4 °/min at a step of 0.02°. The thickness of the waveguide film was measured by a spectroscopic phase-modulated ellipsometer. The morphology of the films was examined under a SEM (JSM-5600 LV) and an AFM (Digital Instrument, Nanoscope IIIa) using the tapping mode. TGA was done on the composite powder obtained from solution at a heating rate of 2 °C/min by a Perkin Elmer 7 Series. The UV-visible transmission spectra were obtained from the composite films deposited on microscope glass slides in the range of 250–800 nm by a Perkin Elmer Lambda 16 UV/VIS Spectrometer with a resolution of ± 0.3 nm. The FT-IR spectra of the composite waveguide films were measured with a FT-IR (Perkin Elmer 2000, with a resolution of $\pm 1 \text{ cm}^{-1}$) spectrometer in the range of 4000–400 cm^{-1} . XPS result was obtained using $\text{Al } K_\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) as X-ray source, operating at 10 kV and 25 mA. The pass energy of the photodetector was kept at 20 eV. The operating vacuum pressure was at 10^{-9} mbar. The analysis area was about 1 mm in diameter.

XRD results of the films baked at different temperatures and with different titanium contents showed no crystalline phase and were amorphous. It was found that a dense, porous-free and transparent film could be obtained after a heat treatment at a temperature of 100 °C. Evidently, this result is in agreement with that reported by [10]. A film thickness

of more than 1.7 μm could be easily reached on a Si substrate by a single-spin coating process. It was also noted that the carbon phase in the film with higher titanium content and heated at 500 °C was evidenced by XPS. When such a film was deposited on a glass slide or a silica-on-silicon substrate, light waveguiding was easily demonstrated. About 1.3 dB/cm propagation loss was noted based on scattered-light measurement method at 633 nm.

2 Results and discussion

2.1 SEM and AFM

Figure 1 shows the SEM micrographes of the cross-sectional morphologies of the composite films with different titanium content and baked at 100 °C, which was spin-coated on pure Si substrate by a single coating process. It can be observed from the pictures that the films are dense and porous-free, and the thickness is about 1.5 μm , which is nearly in

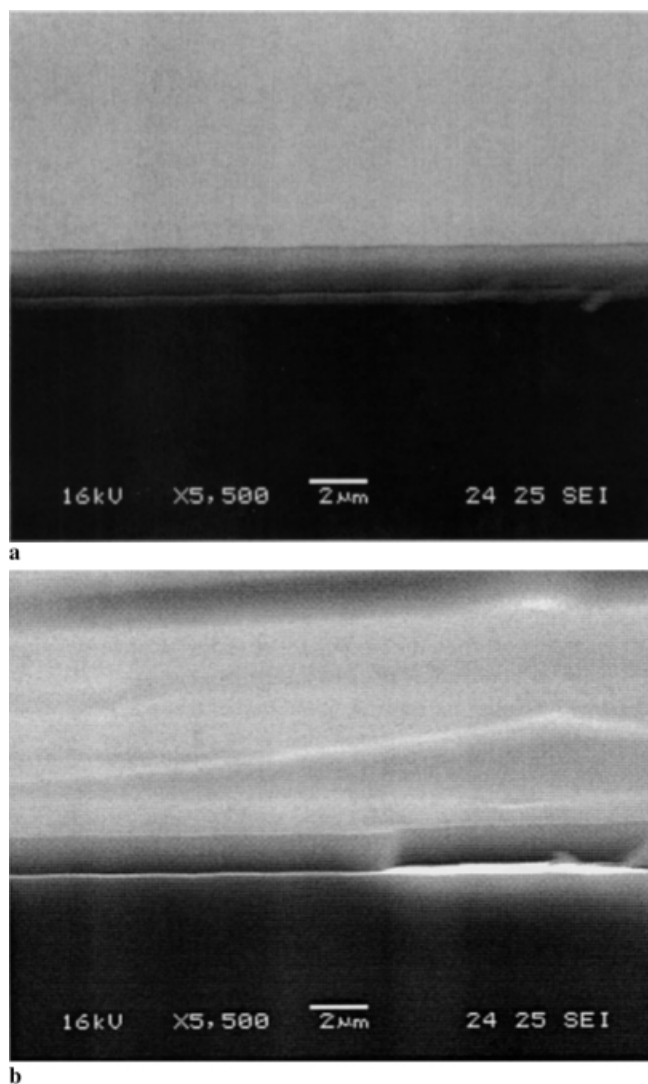


Fig. 1a,b. SEM cross-section appearances of the composite waveguide films with different titanium molar fraction and baked at 100 °C: **a** 0.2 molar titanium content, **b** 0.5 molar titanium content

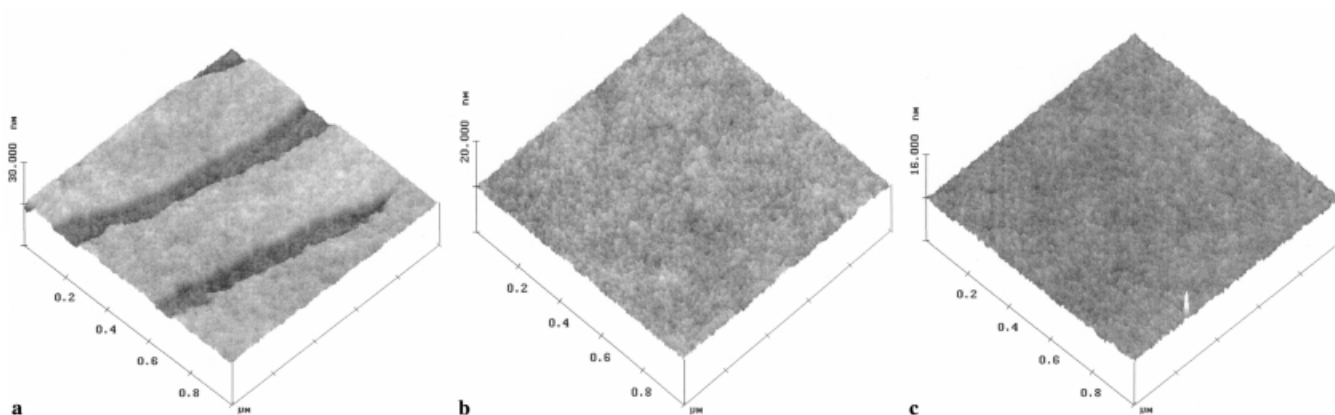


Fig. 2a–c. AFM images of the composite waveguide films baked at different temperatures: **a** 80 °C; **b** 300 °C; **c** 500 °C

agreement with that obtained by ellipsometer. It is obvious from SEM results that the film shows an amorphous structure and confirms further the XRD results. It should be mentioned that for the films with other titanium content their cross-sectional morphologies also appear dense and porous-free.

Figure 2 shows the AFM images of the films baked at different temperatures, for which the molar ratio of GLYMO : SiO₂ : TiO₂ was fixed at 0.4 : 0.4 : 0.2. It can be seen from Fig. 2a that the film baked at about 80 °C has a relatively high surface roughness, but a porous-free morphology. The high roughness may be related to the organic solvents that remain in the film. When baked at 500 °C (Fig. 2c), a dense, smooth and uniform morphology with relatively small surface roughness can be obtained. However, the film baked at 300 °C (Fig. 2b) shows a relatively porous surface as compared to that of Fig. 2c. This porosity observed in the 300 °C baked film could be a direct result of the large weight loss that occurs during heat treatment at this temperature. These results of Fig. 2 indicate that when the organic groups are integrated in the inorganic system, the shrinkage of the composite material is low because the bulky organic components fill the pores between the inorganic oxide chains. The composite materials can thus be made to reach its final density at a relatively low temperature. For example, the result in Fig. 2a actually shows that a porous-free film can be obtained at the baking temperature of 80 °C. Figure 2c indicates that when the organic compounds have been completely combusted and decomposed at the baking temperature of 500 °C, the observed film becomes a purely inorganic coating. When the baking temperature is in the middle as is shown in Fig. 2b, the organic compounds are partially combusted or decomposed, and therefore, pores could be observed. To understand this better, TGA was used to examine the thermal properties of the composite materials during the heating process.

2.2 TGA

In order to examine the thermal process of the composite materials, the thermal analysis was done for the powder of the composite material obtained from a solution poured into a petri dish by drying at room temperature for about 10 days. Samples of 30–40 mg crushed powder are put into an Au

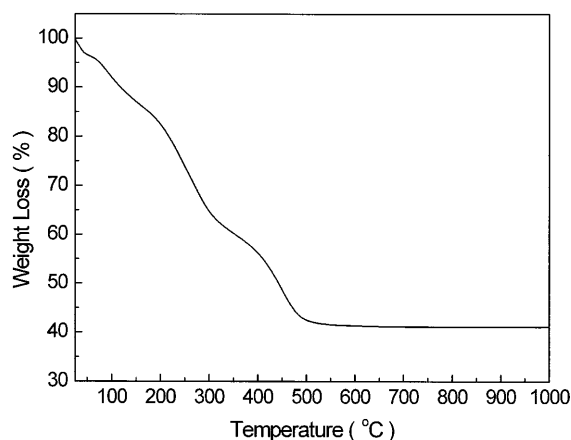


Fig. 3. TGA curve of the gel obtained from the solution with 0.2 molar titanium content

crucible for TGA. The heating rate is 2 °C/min in a flowing air. The recorded temperature range is from room temperature to 1000 °C. Figure 3 shows the TGA curve of the gel powder. The weight loss occurs at three stages, namely, below 200 °C, between 200 and 310 °C, and from 310 to 480 °C. Below 200 °C, therefore, the weight loss is considered to be due to the evaporation of water and the volatilization and the thermal decomposition of the remnant of organic solvents. Between 200 and 310 °C, the weight loss is attributed to the carbonization or the combustion (oxidation) of organic compounds, that is to say, this weight reduction is due to the loss of carbon, hydrogen, and oxygen. Between 310 and 480 °C, the weight losses are probably ascribed to the further combustion of organic compounds. As there is no major weight loss afterwards, it can be considered that, for the powdered sample, the organic groups have been completely burnt off. Evidently, these results can be used to explain the appearance of the holes in Fig. 2b that the film was heated at 300 °C. Accordingly, it can be concluded that it is necessary for the heat treatment temperature to be below 200 °C to obtain a dense porous-free composite film. It should be mentioned that it is known that the microstructure of powders can be quite different from that of a film, this analysis can, nevertheless, serve as a guide to what might similarly happen to the films.

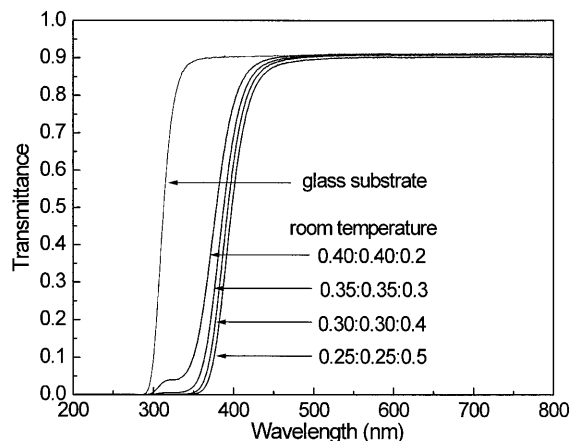


Fig. 4. Dependence of optical transmittance of the films dried at room temperature on titanium content

2.3 UV-VIS transmission properties

Figure 4 shows the optical transmittance spectra of the films with different Ti molar fractions. Note that these films were coated once. The films in Fig. 4 were processed at room temperature. It can be seen from Fig. 4 that the transmittance of the films becomes lower if the Ti content increases. There is a strong absorption from 300 nm to 360 nm; obviously, this absorption is ascribed to that of organic solvents. The low Ti content precursor, therefore, is expected to produce more transparent waveguide films than those prepared from higher Ti content precursors. We suspect that the decrease in transmittance with the increase of Ti content may result from an acetylacetonate complex formed during preparation of the precursor [14]. Figure 5 shows the optical transmittance spectra of the films baked at different temperatures; here, the molar ratio of GLYMO : SiO₂ : TiO₂ is 0.40 : 0.40 : 0.2. It can be seen that the films obtained at room temperature and baked at 100 and 200 °C have high transmittance, except for the absorption from organic solvents between 300 nm and 360 nm. Evidently, the absorption of organic solvents disappears gradually with the increase of baking temperature. However, the films baked at 300 and 400 °C have a significantly larger absorption up to 700 nm, and noticeable dis-

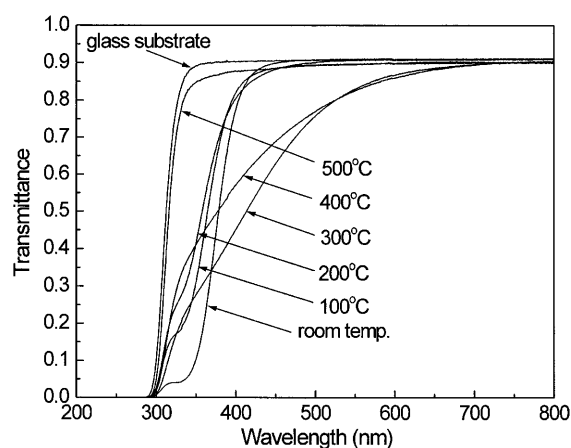


Fig. 5. Optical transmittance spectra of the films baked at different temperatures (molar ratio of GLYMO : SiO₂ : TiO₂ was fixed 0.40 : 0.40 : 0.2)

coloration is observed. However, the film baked at 500 °C has a much higher transmittance than those baked at 300 and 400 °C; no discoloration was observed, and the absorption of organic solvents has disappeared completely. Based on the result obtained by TGA as mentioned before, this behavior could be explained as follows. The films baked at 300 and 400 °C were porous due to the incomplete decomposition of the organic compounds. As a result, in addition to the absorption because of the remaining acetylacetonate complex, a relatively large degree of scattering of incident light could also occur by the pores caused from the incomplete decomposition of the organic compounds. When the baking temperature was increased to 500 °C, the organic compounds were completely decomposed and a purely inorganic dense film was obtained. As a result, both the absorption and the scattering caused by the relatively large pores are substantially suppressed. It could be concluded that heat treatment between 100 and 200 °C is necessary to attain a dense, low absorption, and high transparency in the visible-range sol-gel SiO₂/TiO₂/GLYMO waveguide thin films by the present process.

2.4 FT-IR spectra

Figure 6 shows FT-IR spectra of the films heated at different temperatures. The main band at a frequency of 1100 cm⁻¹ is assigned to Si—O—R stretching vibrations of ethoxy groups directly bonded to silicon [15]. This band decreases in intensity with increasing heat treatment temperature, and there is a shift of the Si—O—R band from 1100 cm⁻¹ toward 1048 cm⁻¹, which is indicative of a densification of the silicon-oxide skeleton. The shoulder at ≈ 1200 cm⁻¹ (for the films heated at 300 °C or above) is attributed to the transverse optical mode of the out-of-phase mode of the asymmetric stretching vibration by Kamitsos et al. [16, 17] and disputed by Almeida et al. [18, 19] as due to the longitudinal optical component of the high-frequency vibration of SiO₂. The short-wave shoulder of the Si—O band at 1080 cm⁻¹ becomes more pronounced with higher heat treatment temperature which may be connected with C=C stretching at 1627 cm⁻¹. The band at a frequency of 934 cm⁻¹ appears as an intense peak that is still present in every sample even at 800 °C.

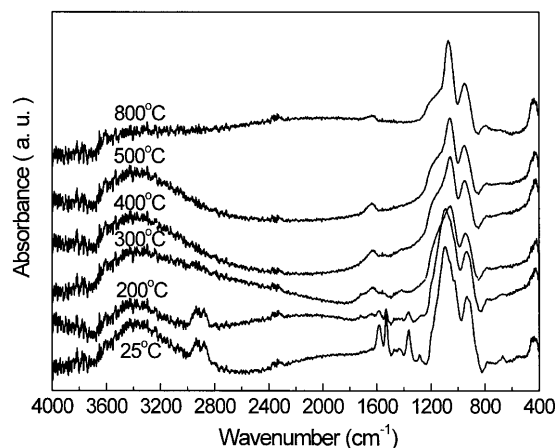


Fig. 6. FT-IR absorption spectra of the films baked at different temperatures (molar ratio of GLYMO : SiO₂ : TiO₂ was fixed 0.40 : 0.40 : 0.2)

This band is attributed to the stretching vibration of Si–OH or SiO⁻ groups [18] superimposed to Si–O–Ti stretching [20–22]. The low-frequency band between 410 cm⁻¹ and 460 cm⁻¹ is attributed to rocking motions of the oxygen atoms perpendicular to the Si–O–Si plane [23, 24]. We can obtain from Fig. 6 that for the films heated at 100 °C, there are peaks at 1281 cm⁻¹, 1358 cm⁻¹, 1528 cm⁻¹, and 1583 cm⁻¹. These peaks should be attributed to organic solvents. When the heat treatment temperature is increased to 200 °C, these peaks become quite weak and even vanish. We can also observe that the broad peak centered at 2892 cm⁻¹, which corresponds to –CH₂– symmetric stretching vibration, vanishes after heat treatment at 300 °C or above. We attribute these to the burning reaction in the densification process. Furthermore, a broad band between 3100 cm⁻¹ and 3700 cm⁻¹, observed in the samples heated below 500 °C but not at 800 °C, is attributed to O–H stretching [23]. This also shows that the films heated below 500 °C contain a lot of hydroxyl or water molecules and a rise in the heat treatment temperature leads to a decrease of hydroxyl and even vanish.

2.5 XPS

The chemical composition and bonding states of the films were investigated by XPS. As shown in Fig. 7a, O 1s and 2s; Ti 2s, 2p, 3s and 3p; C 1s; Si 2s and 2p peaks can be clearly seen in the film with a 0.5 molar titanium content and a heat treatment at 500 °C in air. It is noted that C–C bonding appeared at 284.64 eV, as shown in Fig. 7b. The peaks at about

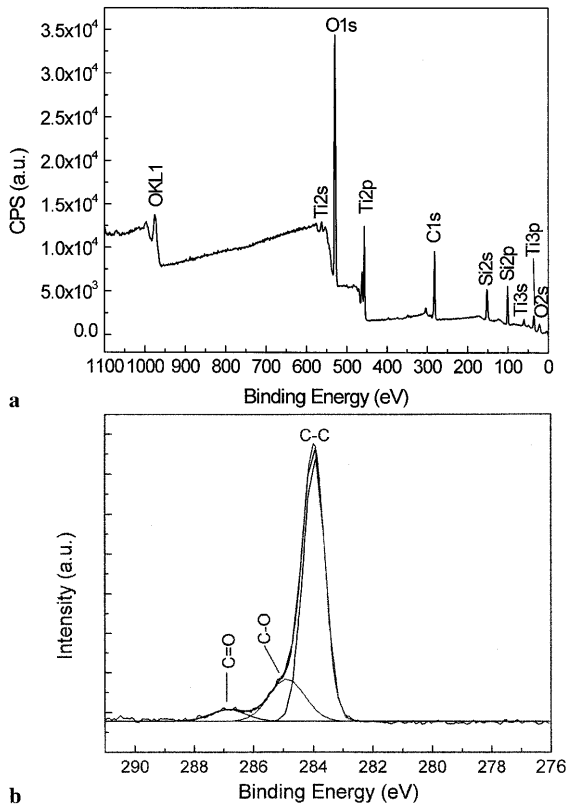


Fig. 7. XPS spectrum of the waveguide film with 0.5 molar titanium content and baked at 500 °C

288.40 and 286.13 eV are from C=O and C–O, respectively. The C 1s peak position is 284.15 eV for graphite (*sp*² C) and 285.50 eV for diamond (*sp*³ C). The C 1s peak position of our film is 284.64 eV, which is close to that of graphite. This indicates that the film mainly contains *sp*² carbon phases. The up-shift to high energy implies that a tiny amount of *sp*³ carbon phase may possibly exist in the film [25]. In fact, for high titanium content films, they look slightly brown after a high-temperature treatment and the existence of carbon in the films was also confirmed by Raman scattering [26]. It is obvious that the carbon phase will affect the waveguide propagation properties of the films greatly.

3 Waveguide properties and applications of the composite material films

In order to further characterize the waveguide properties of the films, such a film was deposited on a silica-on-silicon substrate to fabricate waveguides and observe propagation loss of light waveguiding. A loss of the planar waveguides with different titanium contents was evaluated by scattered-light measurement [27, 28]. The scattered-light power measurement was made every 2 mm apart. A total of five or more separate points were taken with our setup and the method has a measurement error of about ±0.1 dB/cm. The mean loss was typically 1.3 dB/cm at 633 nm for the waveguide film with a thickness of about 6.0 μm, which was fabricated from the solution with 0.2 molar titanium content and baked at 100 °C. It was also noted that the loss increases as the titanium content rises; typically exhibited losses were ≈ 10 dB/cm. Figure 8 shows the dependence of propagation loss of the waveguide films on titanium molar content. It is obvious that the loss of waveguides prepared under the present process conditions is relatively larger as compared to those reported previously for SiO₂–TiO₂ planar waveguides were substantially lower. Actually, the low-loss waveguide films contained several defects, possibly dust, which visibly scattered light to a greater extent than the surrounding sol-gel medium. Loss measured through sections of a film containing these defects should be higher. It is also possible, for a guided wave propagating in a planar medium,

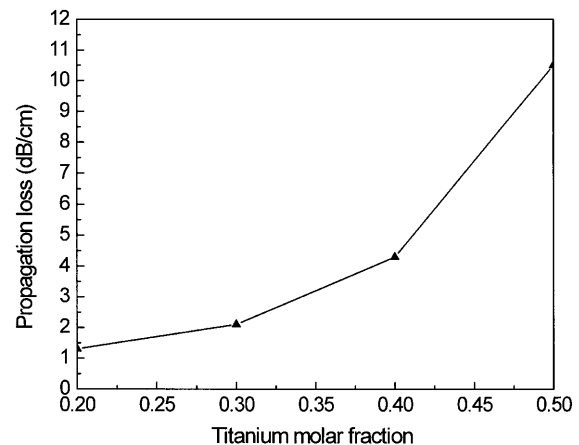


Fig. 8. Dependence of optical propagation loss of the waveguide films on titanium content

that local refractive-index fluctuations in the volume of the guide and deviations from a perfectly plane geometry at the waveguide-cladding boundaries contributed to the losses. In addition, high surface roughness of the film and nonuniform hydrolysis and condensation of the binary alkoxide mixture that was discussed in the UV-VIS sections undoubtedly resulted in a big scattering loss. The homogeneity of a sol-gel glass synthesized from a mixture of two or more alkoxide precursors is affected by the relative rates of homocondensation and heterocondensation. Silicon alkoxides hydrolyze relatively slowly, and acid or base catalysis is frequently used to accelerate the reaction. However, titanium alkoxides hydrolyze at a much faster rate, as a result, acetylacetonate was employed to reduce the reaction rate through the formation of an acetylacetonate complex in our experiment. This complex has been proven to have a strong absorption in the visible region [14]. The influence of the complex seems to be more evident with the increase of titanium content as a stronger absorption is observed (UV-VIS results). In addition in mixtures of titanium and silicon alkoxides, it is still possible that a heterogeneous network containing Ti-rich and Si-rich domains is formed in this system [32], which could cause severe scattering loss. For the contribution of surface roughness to loss, the theoretical treatment detailed by Unger [33] also shows that scattering of a guided wave in a planar waveguide film at the waveguide-substrate boundary is proportional to the product of the variance of surface roughness and its correlation length. It was noted by AFM in our films that with an increasing in the titanium content, the surface becomes rougher, especially, some micro holes and grooves can be observed in the film with 0.5 molar titanium. Generally, the organic content of the film can be pyrolyzed and the carbon content will be oxidized at heat treatment in ambient condition. However, the carbon content in high titanium content film (0.5 molar) is detected by XPS measurement. Obviously, these micro holes and grooves of the film surface as well as the impurities such as carbon phase inside the film undoubtedly affect the loss of the waveguide greatly. It should be mentioned that since the precise loss measurement system was not available in our laboratory, the precise loss of the waveguide could also not be obtained.

4 Conclusions

Sol-gel-derived $\text{SiO}_2/\text{TiO}_2/\text{GLYMO}$ composite material films have been studied in the optical slab-waveguide configuration. A waveguide thin film with thickness of more than $1.7 \mu\text{m}$ has been prepared by sol-gel spin-coating technique and low-temperature heat treatment. FT-IR, UV-VIS and XPS results showed that the waveguide films with high titanium content cause a strong absorption and severe scattering losses because of TiO_2 particles or the formation of the amorphous carbon phase inside the film and micro holes and grooves of the film surface. The waveguide films baked

between 200°C and 400°C have a significantly larger absorption and a noticeable discoloration. Therefore, the low titanium content precursor and the heat-treatment temperature between 100°C and 200°C are expected to produce dense, porous-free, low-absorption, high-transparent composite waveguide films based on SEM, AFM and UV-VIS results. About 1.3 dB/cm propagation loss of the planar waveguide film with low titanium content has been obtained based on the scattered-light measurement method at 633 nm in wavelength.

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