Preparation and characterization of SiO_2/TiO_2/methylcellulose hybrid thick films for optical waveguides

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SiO_2/TiO_2/methylcellulose composite materials processed by the sol-gel technique were studied for optical waveguide applications. With the help of methylcellulose, an organic binder, SiO_2/TiO_2/methylcellulose hybrid thick films were prepared by a single spin-coating processes. After annealing at 70 °C for an hour, 2.5-μm crack-free and dense organic–inorganic hybrid optical films with a refractive index of 1.537 were achieved. Optical losses of plane waveguide made up of those films and ordinary slide glass substrate are around 0.3 dB/cm at 650 nm. Scanning electronmicroscopy (SEM) and UV-visible spectroscopy (UV-VIS), have been used to characterize the thick films.

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Optical-quality films of a few μm thickness are a basic requirement for integrated optics[1−3]. Since such films are thick by normal coating standards, a number of specialized methods have been developed to form them. 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. It is a popular and widespread technique for preparing coating films in laboratories. But people in industry are not encouraged enough to employ this technique for mass production. One of the factors is the basic sol-gel process which suffers from a serious limitation when it comes to depositing thick films by a single spin-coating process, the maximum thickness of a layer resulting from a single deposition is 0.7 μm, thicker layers generally crack as a result of shrinkage at the drying stage[4].

Thick films can been built up by repetitive operation of process cycle in which a layer of sol-gel material is deposited by spin coating, then densified by rapid thermal annealing[5]. However, it has been found previously that such films also tend to fail by cracking, even when each individual layer is considerably less than 0.7-μm thick. Holmes *et al.* have proposed a new process for deposition of thick films of silica and titania-doped silica on silicon substrates[4]. They demonstrate that it is possible to fabricated crack-free thick films, only by the samples thermally annealed at the correct temperature. But this process is time-consuming and impracticable in industrial production. Further more, the channel waveguide is losses of ~2.4 dB/cm at 0.633-μm wavelength.

There is an attractive way to combine the properties of very different materials and produce molecular-scale composite materials via sol-gel processing. The materials thus prepared possibly have improved optical and mechanical properties. For example, the use of organically modified silane (ORMOSIL) precursors or polyvinylpyrrolidone (PVP) can produce very thick single coating layer[6−8]. Another alternative approach is to incorporate organic molecules into the essentially inorganic matrix using the same sol-gel technique[9]. When organic groups are integrated into the glass matrix, the shrinkage is low due to the bulky organic components.

In this paper, by adding methylcellulose (MC), an organic binder, a film with a thickness of 2.5 μm was fabricated using a single spin coating process. Composing organic-inorganic hybrid materials is a strong point of the sol-gel method and a profitable attempt without a high temperature. MC is flexible material with good optical properties. At the same time, a water solution of MC is a high viscosity additive so that less dosage than other binders such as polyvinylpyrrolidone[6] is demanded to modify the sol, which lessens the influence of additives on the construction of the materials.

Both slide glass and silicon used as substrates were cleaned ultrasonically in acetone, rinsed with deionized water and dried with pure nitrogen. The preparation of sol follows the scheme shown in Fig. 1. 10-ml

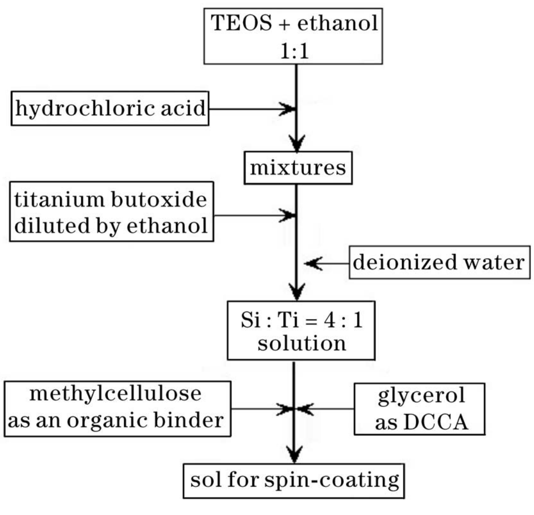

Fig. 1. Process for sol preparation.

tetraethoxysilane (TEOS) was mixed with 10-ml ethanol. After stirred for 30 min, 1.6-ml 0.1-mol/L hydrochloric acid was added to the solution and the mixture was stirred for 1 hour. 3.7-ml titanium butoxide diluted to 11.5 ml by ethanol was added to the foregoing sol and the mixture was stirred for 2 hours (Si:Ti = 4:1 by mol). Then 1.6-ml deionized water was added to the mixture and the stirring was continued for 1 h. The whole above procedures were conducted at room temperature (15 °C). However, if SiO_2/TiO_2 sol was produced by adding TiO_2 sol to SiO_2 sol, it is more possible that a heterogeneous network containing Ti-rich and Si-rich domains is formed in this work and it will bring negative influence to optical quality of films used for waveguides.

MC power was swollen in 85 °C water, then the mixture was cooled down to room temperature naturally with continuous violent stirring till a clear sol was gained. 18.5-g water solution containing MC (mw63000, 3% in water) as organic binder and some glycerol as drying controlling chemical agent (DCCA) were added to the SiO_2/TiO_2 sol respectively. Then the mixture was stirred for 75 min, then filtered by nylon strainers with 350 meshes and continued to stir for 45 min again. The final sol was dispensed onto glide glass or silicon wafer through a 0.22-μm filter with a syringe and the sol-gel film was spun onto the substrate at 900 rpm for 40 s with a single process. To the spin-coating process, the initial 20 s was under a saturated ethanol atmosphere by covering a big beaker whose inner wall was daubed over by ethanol and the final 20 s was in air atmosphere. The thinner films were prepared at 2000 rpm, while other conditions were controlled to be the same.

After the samples spun at 900 and 2000 rpm were dried at room temperature for 24 hours and at 70 °C for one hour, film900 and film2000 were gained respectively. The Film900 tended to dehisce and was difficult to resist a temperature of 200 °C. The film2000 on slide glass was annealed from 200 to 600 °C and film2000 on silicon was annealed from 200 to 800 °C for one hour.

A 650-nm laser beam was coupled into a waveguide made up of film900 with slide glass substrate by a prism[10]. Measurements are made by loading the sample against the prism and rotating the laser light until coupling. At coupling angle, the minimum signal of photo detector occur. The angle is measured and the rotation continued until the next coupling mode is observed. The thickness and refractive index of the film are calculated from the measured coupling angles. The evaluated refractive index of a composite film is about 1.537. The waveguide refractive index be easily tailored by adding titania to a silica matrix.

Multimode waveguide attenuation is measured by a charge coupled device (CCD) system[11]. As an optical mode propagates in the waveguide, the light is scattered and a characteristic light track appears on the waveguide surface. It is assumed that the scattered light is proportional to the guided mode intensity. By taking a digital picture of the track for guided mode, the light intensity variation along the track is obtained. Figure 2 shows the total intensity of light scattered from the waveguide, plotted against the position along the waveguide. The curve was fitted to the exponential decay function

$$I(x) = C + I_0 e^{-\alpha x}, \quad (1)$$

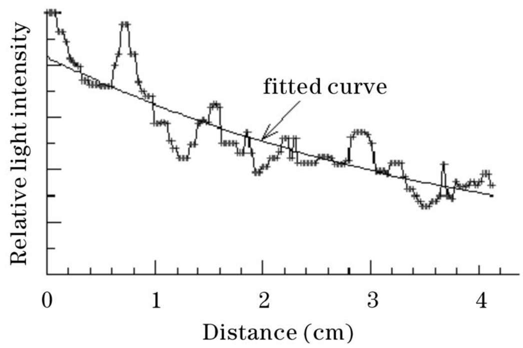

Fig. 2. Total scattered light intensity from the waveguide as a function of position.

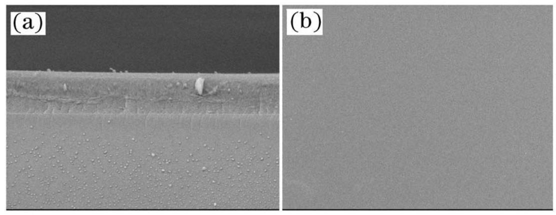

Fig. 3. SEM micrograph of films. (a) cross-section of film900; (b) surface of film900 on slide glass substrate.

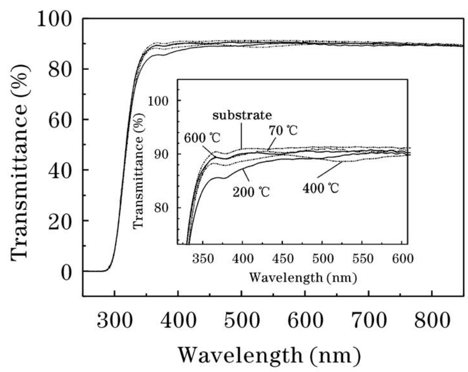

Fig. 4. Optical transmittance spectra of thinner sample compared with glass substrate.

where C correspondeds to background, I_0 is the light intensity at x_0, and α is the attenuation coefficient. From the slope of line the attenuation was found to be $\sim$ 0.3 dB/cm. So a good waveguide with ordinary slide glass as substrates had been gained expediently in lab by chemic method.

Scanning electron microscopy (SEM) micrographs of samples are shown in Fig. 3. Figure 3(a) shows a SEM cross-sectional appearance of film900 on slide glass substrate. The film with thickness of about 2.5 μm is dense and porous-free. Figure 3(b) shows the surface picture of the film900 on slide glass substrate. The surface of the film is crack-free, complanate and compact. Films with those characters are likely to be used for optical waveguides.

The Film900 tended to dehisce and was difficult to resist a temperature of 200 °C. But a crack-free film about 600 nm was gained after a film2000 with thickness of 1.1 μm was annealed at 600 °C, and easy to investigate transmission properties. Figure 4 shows the optical transmittance spectra at the same position of a film2000 on a glass substrate with different annealing temperatures. It is found that all samples hand high transmittance at different temperatures, so high quality hybrid optical films have been achieved. From Fig. 4, results of the samples annealed at 200 and 400 °C were worse. It is concluded that the surface of the film became coarse when the film was annealed at medium temperature[8].

In conclusion, thick and crack-free sol-gel SiO_2/TiO_2/MC films were successfully fabricated with a single spin-coating process. The refractive index of the films is about 1.537 after the films were dried at only 70 °C without high-temperature annealing. About 0.3-dB/cm propagation loss of the planar waveguide film has been obtained based on the scattered-light measurement method at 650 nm. The results indicate that this technique is widely applicable to other hybrid films and inorganic films, which require considerable thickness and high optical quality.

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References

1. C. M. Whang and S. S. Lim, Bull. Korean Chem. Soc. **21,** 1181 (200).
2. R. M. Almeida, J. Non-Cryst. Solids **259,** 176 (1999).
3. H. C. Wang, X. J. Yi, S. H. Chen, G. Huang, and X. W. Li, Chin. J. Lasers (in Chinese) **30,** 1107 (2003).
4. A. S. Holmes, R. R. A. Syms, M. Li, and M. Green, Appl. Opt. **32,** 4916 (1993).
5. Z. J. Hou, Q. M. Tao, L. Y. Liu, L .Xu, W. C. Wang, and F. M. Li, Chin. J. Lasers (in Chinese) **26,** 253 (1999).
6. W. Que, Z. Sun, Y. Zhou, Y. L. Lam, Y. C. Chan, and C. H. Kam, Thin Solid Films **359,** 177 (2000).
7. H. Kozuka, M. Kajimura, T. Hirano, and K. Katayana, J. Sol-Gel Sci. Technol. **19,** 205 (2000).
8. W. Que, Y. Zhou, Y. L. Chan, and C. H. Kam, Appl. Phys. A **73,** 171 (2001).
9. S. Motakef, J. M. Boulton, and D. R. Uhlmann, Opt. Lett. **19,** 1125 (1994).
10. J. Shi, Z. Q. Cao, J. Zhu, and Q. S. Shen, Appl. Phys. Lett. **84,** 3253 (2004).
11. G. Bu, D. Ciplys, M. Shur, R. Gaska, R. Rimeika, A. Khan, and J. Yang, in *Proc. IEEE Lester Eastman Conference on High Performance Devices 2002* 248 (2002).