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Thick Silicate Glass Film for Waveguide

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ABSTRACT

The formation of a borosilicate glass film of 10-20 μm in thickness on a silicon substrate via an interfacial polymerization technique has been studied as the first step for the preparation of a planer waveguide for optical communication. A gel film prepared from the partially hydrolyzed TMOS mixed with boron alkoxides could be densified into a glass film of 16 μm in thickness having a smooth surface by the heat treatment up to 1000°C. A good reproducibility in the yield was obtained by completing the hydrolysis and condensation of the whole ingredient in the 5ml of precursor solution spread over water containing triethylamine as a catalyst within a cylindrical container of about 80mm inside diameter. The use of saturated aqueous solution of boric acid in stead of distilled water was necessary to hinder the re-dissolution of boron from the formed gel film.

Keywords: Thick Glass Film, Sol-Gel Interfacial Polymerization, Borosilicate

1. INTRODUCTION

There is a growing interest in the fabrication of a planer waveguide to develop an optical communication system without electrical signal to optical signal (E/O) or optical signal to electrical signal (O/E) conversion [1]. The techniques developed to date for the fabrication of such a planer waveguide include ion-exchange in a glass substrate [2], RF-sputtering [3], spin-coating of polymer material [4], thermal diffusion in a ferroelectric crystal such as $LiNbO_3$ [5], flame hydrolysis deposition of silicate glass [6], etc..

Among these techniques, flame hydrolysis deposition is advantageous over others in forming a glass layer of 10-20 μm in thickness having a similar refractive index to an optical fiber, which is important in connecting the waveguide to a single-mode fiber with low optical loss. This technique developed by the research group of NTT begins with the deposition of boron-doped and titania-doped silica soots on a silicon substrate to form the clad and core glasses of 20 μm and 8 μm in thickness, respectively , and is now getting widely applied [7]. But there still is a demand for a new method which is much more suitable than flame hydrolysis deposition in the doping of active rear-earth element such as Er, Nd in the core of the waveguide for the purpose of pumping the intensity of optical signal.

A method which is considered to be potentially advantageous over flame hydrolysis deposition in the formation of a doped thick silicate glass film is sol-gel interfacial polymerization [8]. The sol-gel interfacial polymerization developed by the present author begins with the hydrolysis and polycondensation of precursor alkoxides or their derivatives to form a gel film at the interface of two immiscible liquids, the upper organic phase and the lower inorganic phase, without direct contact with the substrate surface. The careful drainage of the two liquids causes a gentle placement of the gel film onto a substrate surface

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without forming chemical bonds between the materials. A silicate glass film of 10- 20 μm in thickness can be formed on a flat substrate by the subsequent densification of the gel film.

Although it is still at the stage of investigating the influences of various reaction parameters on the formation of silica gel film using a partially hydrolyzed silicon alkoxide, E-40, [9,10] the method can be extended , in principle , to binary, ternary silicate systems of desired composition by preparing the organic phase with alkoxides of various elements, which is not possible or hardly attainable by flame hydrolysis deposition or other sol-gel based techniques such as electro-phoretic deposition [11], coating of surface modified silica particles [12].

In applying an interfacial polymerization method to the fabrication of an optical waveguide, it is necessary to modify the process based on E-40 in various aspects. Since the glass film is formed on a silicon substrate, which is not only suitable to obtain a very flat surface, but has a potential to the development to an active waveguide in future, the precursor for the gel film is required to satisfy the conditions of 1) a low densification temperature below the melting point of silicon, 1200 °C, 2) the close thermal expansion coefficient to that of silicon, i.e., 4 ppm/oC, etc., in addition to the good reproducibility of composition and the thickness of eventual glass film.

To obtain a glass film with a good reproducibility of composition, it is necessary to use a precursor solution containing Si-O-Me bonds in advance rather than simply mix various alkoxides in an organic solvent to form the upper organic phase. As the Si-O-Me bond is sometimes unstable to the re-hydrolysis by the attack of water of high pH, some modification on the lower inorganic phase such as the use of a buffer solution in stead of distilled water may also be necessary.

In the present study, conditions for the formation of a gel film of binary borosilicate system to be used for a clad glass on a silicon substrate have been investigated by using TMOS and boronethoxide as starting materials , as the first step of the fabrication of a planer waveguide.

2. EXPERIMENT

2.1 Gel film formation

2.1.1 Preparation of precursor solution.

The experiment was carried out on a glass film of approximate composition $17B_2O_3$-$83SiO_2$ (mol%) . The thermal expansion coefficient and transition temperature of this glass are expected to be about 2ppm/°C and 500°C, respectively, by the extrapolation of the data [13]. The glass of the higher boron content than this composition was not tried because of the anticipated reduction in the chemical durability.

A precursor solution was prepared by a two step process. First, a stock solution containing nearly the similar amount of boron and silicon was prepared. A 10ml of TMOS was partially hydrolyzed with 1.2 ml of aqueous HNO_3 solution of pH=3, i.e., TMOS/H_2O=1/1 in mole, under vigorous stirring for 10 min. Then, a 10 ml of boronethoxide was added to the silicate solution and stirred for 2h in order to enhance the formation of oligomers containing Si-O-B bonds. Next, a 1 ml of the stock solution was mixed with 1 ml of TMOS for 5 min., then 10 ml of hexane was added to the mixture and stirred for another 10 min to be used as the precursor solution. 10 ml of thus prepared precursor solution contains about 800 mg of oxide ingredient.

2.1.2 Formation of gel film

The gel film formation was carried out by basically the similar way to the previous study [8-10] using a teflon reaction container

of 88 mm inside diameter and an exchangeable acrylate ring of 78 mm inside diameter. The modifications made were; 1) the reduction of the amount of precursor solution from 50ml to 4ml, in order to allow the reaction of the whole ingredient within a given time, 2) the use of triethylamine in stead of ammonia to have the better reproducibility of pH, 3) the use of an aqueous solution saturated with boric acid in stead of distilled water in order to hinder the re-hydrolysis of the formed B-O bonds in a gel film, 4) the introduction of a small amount of triethylamine, e.g., 0, 0.15, 0.2, 0.3, and 0.45 ml per 4 ml of precursor solution, in the upper organic phase to facilitate the reaction, and 5) the soaking of the formed gel film in hexane or acetone after being placed on a silicon wafer, in order to extract water remaining in the micropores of the gel film .

The thickness of the organic phase spread over the aqueous solution is approximately 1mm. The amount of oxide ingredient in 4 ml of the precursor solution is approximately 320 mg, and therefore, the thickness of the final glass film is expected to be about 24 μm assuming the density of the glass to be $2.2g/cm^3$ and the yield of reaction is 100%.

A 5 ml of triethylamine was dissolved in a 50 ml of an aqueous solution saturated with boric acid and mixed for 15 min. The pH of the solution thus prepared was 10.3. Immediately after the mixing for 15 min., the solution was poured in a teflon reaction container, followed by the pouring of 4 ml of the precursor solution on the inorganic phase through an equipment having about 50 pine holes on a disc of 70 mm diameter. This immediate introduction of the precursor solution was important to have a good reproducibility due to the time dependent change in the pH of the aqueous solution.

After 1h of reaction , the formed gel film was once placed on a silicon substrate of 75 diameter, which, in turn, had been placed in advance near the bottom of the container, by draining the liquid phases from the bottom of the container. The gel film was then soaked in 50ml of hexane or acetone at room temperature for 1 day within a tightly covered container in order to extract water which partly replaced for hexane during the reaction and were remaining in the micropores of the gel film.

2.1.3 Drying and heat treatment of gel film

The gel film soaked in hexane was taken out of the container and stored in a tightly sealed plastic wafer holder of 80 mm inside diameter and 2 mm high and left at room temperature for 1 day to allow very slow evaporation of hexane , in order to hider the crack formation due to capillary force, then exposed to ambient laboratory atmosphere, followed by drying in an oven at 60°C and 120 °C , respectively, for 1 day.

The dried gel film was heated in an oven at a rate of 0.5°C/min up to 300°C and held there for 4h in order to complete the endothermic reaction which, probably, is attributed to the release of water, then heated to 1000°C at a rate of 1°C/min to be densified into glass film during holding for 2h.

2.2 Measurement of gel film properties.

The examination of the effects of reaction parameters on the appearance and crack formation was made by the observation with a naked eye. The chemical composition of the dried gel film was determined by an Induction Coupled Plasma, ICP, (SEIKO DENSHI, Co., SPS1500VR) method on the solution obtained by leaching boron out of the gel film dried at 120°C in a hydrochloric acid of pH=1.0 at room temperature for 7days. The measurement of the weight of dried gel film to determine the yield of reaction was made on the samples dried up to 120°C.

An infrared absorption spectroscopy, IR, was carried out on the dried gel film by a KBr pellet method to confirm the effect of the replacement of aqueous boric acid solution for distilled water. Differential thermal analysis, DTA, was made in combination with thermo-gravimetry, TG, at a heating rate of 10°C/min up to 500°C on 10-20 mg of gel film dried at

120°C using RIGAKU TG8120. The thickness of the film was measured using a Surface Texture Measuring Instrument , SURFCOM1400A of TOKYO SEIMITSU Co. at the scanning rate of 0.06mm/sec and the magnification of 10×10^3 . The surface roughness was observed using an atomic force microscope, AFM, of SHIMAZU SPM-9500 on a sample of 1cm x 1cm square at the scanning rate of 2Hz over the areas of 1mm x 1mm and 10 mm x 10 mm .

3. RESULTS AND DISCUSSION

3.1. Appearance and properties of gel film.

The formation of gel film became appreciable 10-20min after the pouring of the precursor on the aqueous boric acid solution. The gel film which was initially transparent turned to translucent with time. The translucency was much more pronounced the solution of higher pH was used. The diameter of the gel film almost remained unchanged during the reaction. Some of the films cracked when separated from the wall of acrylate ring.

The appearance and the degree of crack formation of the dried gel film were dependent on the amount of triethylamine introduced in the upper organic phase, although the weight of the dried gel film was almost independent of the composition of the upper phase and about 85% of the ingredient, except for Sample No.1 and No.4 which were lower estimated because of the loss of the material.

A gel film formed from the precursor without containing triethylamine had a very smooth surface but slightly wavy and had a few cracks along which the film turned up. A gel film from the organic phase containing 0.15ml of triethylamine had also a smooth surface and remained unfractured, although it slightly separated from the substrate at its periphery as shown in Fig. 1. The gel films prepared from the organic phases containing the higher amount of triethylamine than 0.15 ml had rough surface and all fractured during drying. The roughness of the surface and the number of cracks increased with the increasing amount of triethylamine content. Thus, the optimum amount of triethylamine to be added in the upper phase is in the vicinity of 0.15 ml per 4 ml of precursor solution. The dependence of the crack formation on the amount of triethylamine is summarized in Table 1 along with the weight of gel film after drying at 120°C.

Fig.2 shows the TG-DTA curves for the dried gel film. It is known from the figure that the reduction in weight of about 25%, i.e., 3 mg per 12.0 mg, occurs during heating up to 500°C, probably due to the release of water and other organic solvent remaining in the micro pores. This reduction in weight is also expected during the heat treatment for densification. Therefore, the net yield of the reaction will be about 65% of the introduced ingredient in the upper phase, suggesting that the thickness of the finally obtained glass film will be 15 - 16 μm.

Table 1. The weight and the appearance of dried gel film prepared from the organic phase of various tryethylamine contents.

Sample No.	Precursor (ml)	Triethylamine (ml)	Weight (mg)	Apparent Yield (%)	Surface	Crack
1	4.0	0	220*)	69	Smooth	2-3
2	4.0	0.15	270	84	Smooth	0
3	4.0	0.2	255	80	Smooth	7-8
4	4.0	0.3	275	86	Rough	20-30
5	4.0	0.45	220*)	69	Rough	Many

*) ; Lower estimated due to the loss of material.

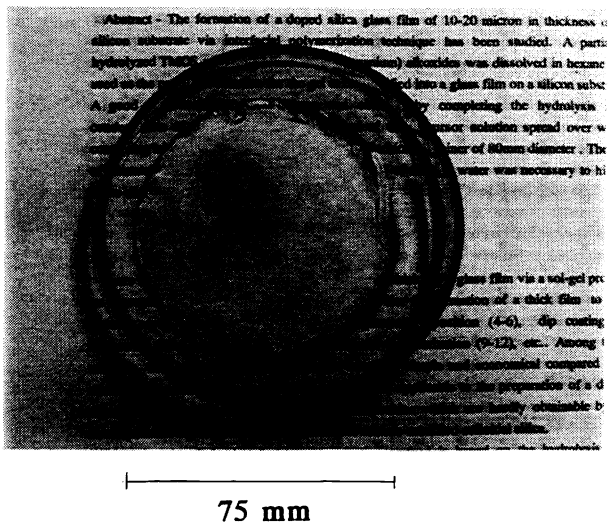

Fig. 1. Appearance of dried gel film prepared from the organic phase containing 0.15 ml of triethylamine per 4.0 ml of precursor solution.

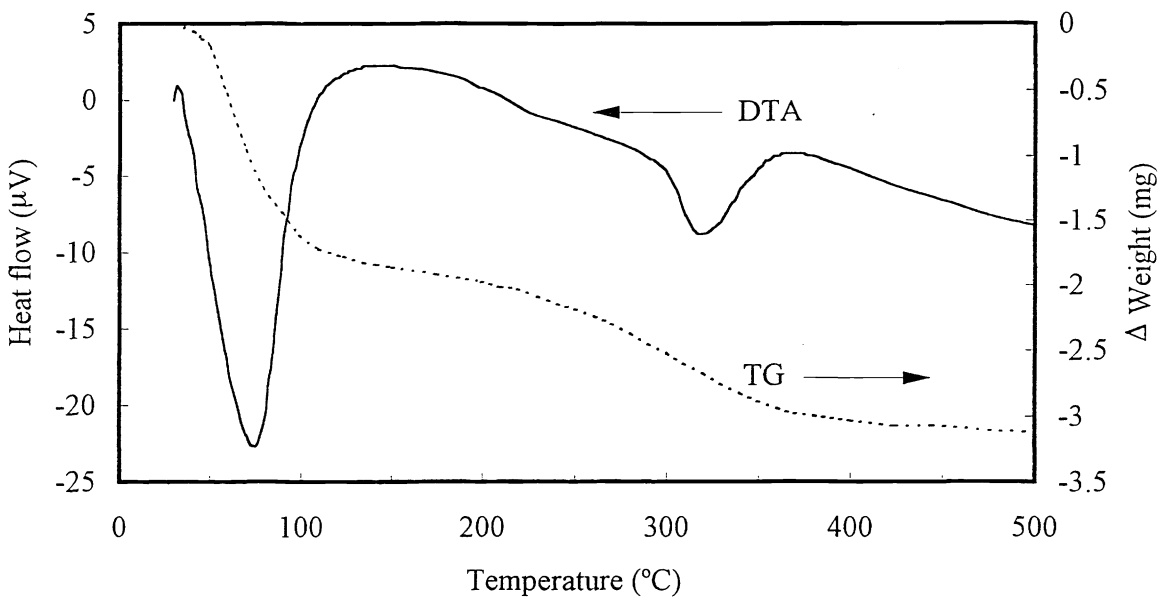

Fig. 2. TG/DTA curves of the gel film dried at 120°C , (Sample ; 12 mg).

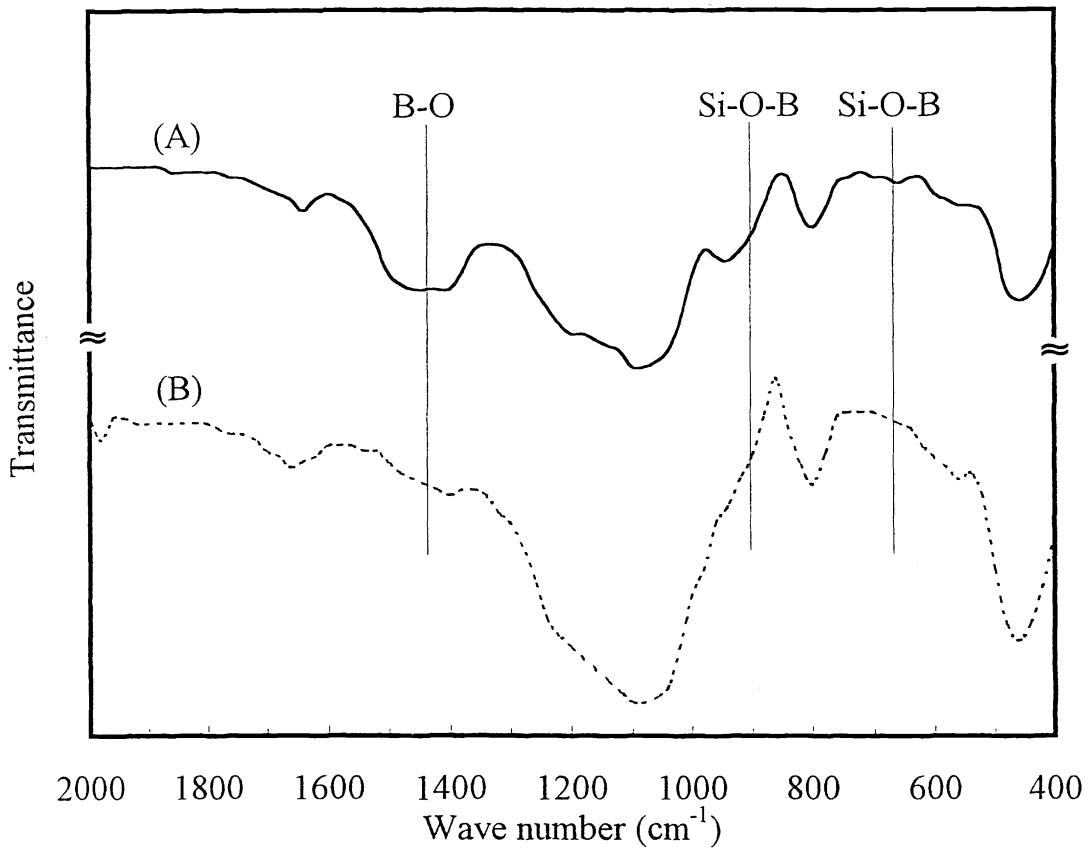

Fig. 3. IR Spectra of dried gel film.
A; Prepared using aqueous boric acid solution, B; Prepared using distilled water.

IR spectra of the gel films obtained with and without using a boric acids saturated buffer solution are shown in Fig.3. There is an absorption peak assigned to B-O bond in the vicinity of 1450cm^{-1} in the spectrum for the film obtained by using aqueous boric acid solution whereas no such a peak is seen in the spectrum for the latter sample, showing that B-O bond is re-hydrolyzed if the aqueous phase does not contain boron. The amount of boron content determined by ICP measurement was 30 mg in terms of B_2O_3 per 100 mg of dried gel. This value corresponds to the glass of $18B_2O_3$-$82SiO_2$ (mol%) if the weight loss during the heat treatment for densification is only due to the removal of residual organics and water, suggesting that the glass of desired composition was obtainable by using aqueous boric acid solution in the lower inorganic phase.

3.2. Properties of glass film.

The gel film subjected to the heat treatment up to 1000°C for densification turned to a glass film. But the film was turned up from periphery toward center, and adhered to the silicon substrate only at the small area near the center. This is perhaps due to too quick heating in the temperature range around 300°C where the endothermic reaction took place.

Fig. 4 shows the result for the measurement of thickness at the available area. The thickness of about 15 μm agrees well with the estimation from the weight of gel film and TG-DTA measurement. This value should be increased to the thickness necessary to form a clad layer, i.e., 20 μm by increasing the amount of precursor solution by 30-40%.

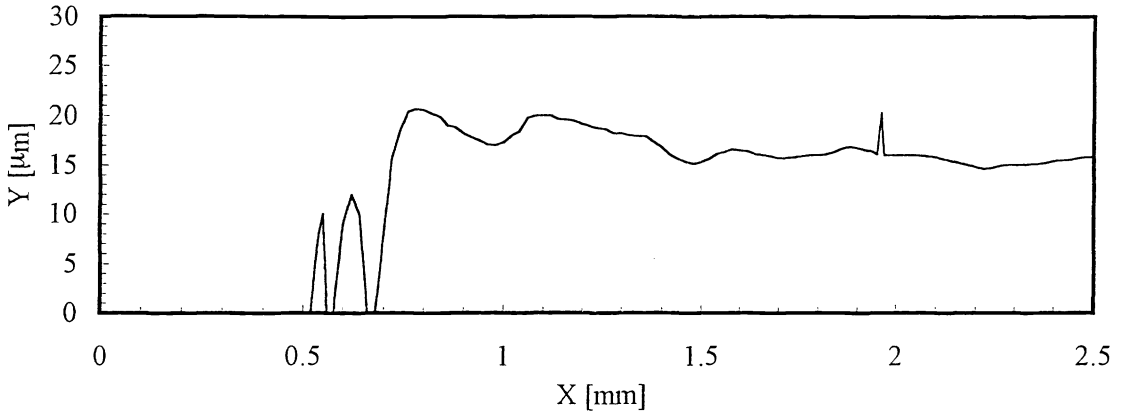

Fig. 4. The thickness of the glass film obtained by the heat treatment of gel film up to 1000°C

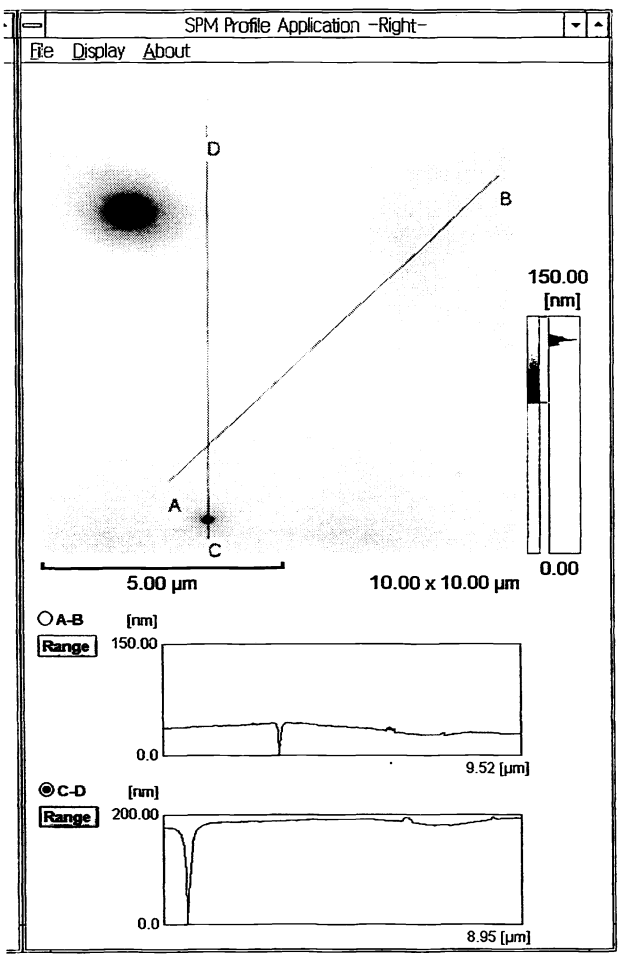

Fig. 5. The surface morphology of the glass film observed by AFM.

The issue that must be overcome is the uniformity of film thickness which is far from satisfactory, although the main reason may be the limited area of sample available to the measurement . The surface morphology of the glass film observed by an AFM is shown in Fig. 5. There are several pits and bosses in the film. It is not clear at this moment whether these defects are attributed to the processing conditions such as incomplete densification or just accidental. In any cases, the temperature for densification should be increased up to near 1200°C to minimize these defects and improve the uniformity of film thickness.

4. SUMMARY

A thick borosilicate glass film was formed on a silicon substrate via an interfacial polymerization technique using a partially hydrolyzed TMOS mixed with boron alkoxide as starting materials. A good reproducibility in thickness was expected by completing the hydrolysis and condensation of the whole ingredient in 4ml of the precursor solution spread within a cylindrical container of 80mm diameter over water containing triethylamine as a catalyst. The establishment of the heat cycle for the densification of a gel film into a glass film is the primary subject to the next step. Although the study is still at the stage of the formation of a glass film for clad layer of a waveguide, the application of the technique to the formation of a Er, or Nd doped glass of Al_2O_3-GeO_2-SiO_2, or Al_2O_3-TiO_2-SiO_2 system for core glass will be possible.

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