

Compositional analysis of SiO₂ optical film fabricated by flame hydrolysis deposition

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Flame Hydrolysis Deposition (FHD) is widely employed as a common process for fabricating passive integrated optical devices used in optical communications. It is used to deposit SiO₂ films by the hydrolysis of SiCl₄ in a high temperature H₂-O₂ flame. The planar waveguide circuit device fabricated by SiO₂/Si became an improved replacement for fiber devices since it can be mass produced by employing semiconductor fabrication technology. The waveguide device size, price, productivity, and reproducibility are better than those of fiber devices. Since many processing parameters of FHD are involved in forming multi-component amorphous silica films consisting of SiO₂-B₂O₃-P₂O₅-GeO₂, it has not been easy to predict the optical, mechanical, and thermal properties of deposited films from simple process parameters, such as the flow rate of source gases. Furthermore, the prediction of the final film composition becomes even more difficult after sintering at high temperature because of the evaporation of volatile dopants. The motivation of the present study was to clarify the quantitative relationship between simple processing parameters and chemical composition in sintered films. Quantitative compositional analysis of silica soot by Fourier Transformation Infrared spectroscopy (FTIR) and Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) was carried out under conditions of controlled dopant amount to obtain the quantitative composition. By measuring FTIR absorbance spectra, the compositional changes of B-O, Si-O and H₂O(OH) in silica films were analyzed. The concentrations of these dopants were also measured by ICP-AES, which were then compared with the FTIR result. The final quantitative relationship between simple processing parameters and composition was deduced from the comparison between the two results.

Key words: Optical device, FHD, PLC, silica film, FTIR.

Introduction

Flame Hydrolysis Deposition (FHD) is a common process for fabricating passive integrated optical devices used in optical communications. It is widely employed to deposit SiO₂ films utilizing the hydrolysis of SiCl₄, GeCl₄, POCl₃ and BCl₃ in a high temperature H₂-O₂ flame.

It is known that the precise control of deposition, and accurate compositional control is very difficult in this process. An additional process of densification of the porous soot into dense SiO₂ film is required in the FHD process. However, despite the difficulties of the FHD process, it is extensively employed to deposit thick SiO₂ amorphous films up to 30 μm thick since the deposition rate is fast and the material quality is already proven in Vapor-Phase Axial Deposition (VAD) or Outside Vapor Deposition (OVD) processes for optical fibers.

A waveguide formed by the FHD process consists of a core layer that guides the light and undercladding and overcladding layers that shield the core layer. For the fabrication of SiO₂ waveguides, the refractive index of

the core layer should be higher than that of both cladding layers. Some dopants such as B, P and Ge are added to control the refractive index and the processing temperature. In the FHD process, one of the important goals is to control the composition of each layer. The composition of the layer can be sensitively changed by the temperature of the source materials in the vaporization chamber, the flow rate of carrier gases, the temperature of the H₂-O₂ flame, the geometrical structure of the flame torch, the angle and distance between the torch and substrate, the structure of the ventilation system and the rate of ventilation to remove soot which is not deposited.

Among many processing parameters, the flow rate of the source gas is generally controlled to achieve the compositional variation. However, it is not easy to relate the experimental parameters to the thermal and optical properties of the optical waveguide, since other experimental parameters can easily influence a major parameter under control. Furthermore, a technique to conveniently analyze soot and film compositions has not been yet established because of B which is the most important dopant. Since B and P have a relatively high vapor pressure, the film composition varies before and after sintering.

There were two objectives in this research. One was to identify the structural peaks of silica and dopant B in

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FHD deposited silica soot and film and to measure quantitatively the variation of these peaks as a function of flow rate of source gases. The other was to obtain extinction coefficients, which show the relationship between the FTIR peak height and the absolute concentration.

Many compositional and structural studies on silica have been conducted by FTIR which is well-known as an excellent analytical tool for compositional and structural variations of hydroxyl in silica, and for physically absorbed H₂O [1, 2]. FTIR is a relatively simple and non-destructive method for compositional analysis. In addition, it is easy to prepare samples in the form of powders, thin films and bulk.

In the present research, the extinction coefficient of the B-O band could be obtained by determining the absorbance of the B-O band though the FTIR absorption spectra and the concentration of B from the ICP-AES analysis. Furthermore, the concentration changes in FHD deposited soot and film along with the various flow rates the dopant could be determined. In order to obtain quantitative dopant data, ICP-AES was employed in this research. By determining the relationships between the FTIR absorption spectra and the ICP-AES concentration, the extinction coefficient of B₂O₃ was consequently obtained.

Experiments

For analysis, samples were prepared of ground silica soot obtained by FHD and thick silica film that was densified in the sintering process. The flow rate of each source gas was as follows: SiCl₄ 90 sccm, POCl₃ 40 sccm, BCl₃ 5, 8, 10 and 13 sccm. In the fabrication process, process parameters other than the flow rate of the source gas were approximately fixed. Samples were made according to planar waveguide fabrication processes. An undercladding was deposited on the Si substrate by FHD in the form of a porous soot and finally sintered into an optical glass film. Pre-sintering intends to give some mechanical integrity to the soot particles. The pre-sintering was carried out at 800 to 1000°C. Solution doping was then carried out for 24 hours. After the solution doping, the porous layer was sintered into a dense silica glass film by heat treatment at 1300 to 1350°C [3-5].

For FTIR measurement of the soot, the prepared soot powder was mixed with KBr. The mixed sample was then ground into fine powder and uniaxially pressed at 34.5 MPa into a disc 1.2 cm in diameter and 0.4~0.45 mm thick. The film samples, which were about 5 µm in thick, were etched to 1~2 µm because film thickness over 2 µm exceeds detection ability of FTIR. A Nicolet Magna-IR 760 spectrometer was used for FTIR analysis, and the measurement conditions were: resolution 4 cm⁻¹, scan number 64, scan wavenumber 400~4000 cm⁻¹.

The FHD silica samples were treated with HF (10%) and H₂SO₄ (2.5%) etching solution. The etching rate of silica film was determined on the basis of the reference etching rate measured on silica glass [6]. The sample mass was measured within less than 1 percent error before and after the etching process.

The absolute chemical concentrations in the FHD soot and film samples were measured by ICP-AES. The FHD film samples were dissolved in 10% HF and 2.5% H₂SO₄ solution, and then maintained for 2~3 hours at 150°C. After adding deionized water into the dissolved solution of FHD film, the HF and H₂SO₄ in solution were completely evaporated and removed at 150°C. The ICP-AES analyses were done using a JOVIN YVONJY 138 Ultrace model.

Results and Discussion

a) Absorption spectra of FHD soot

The FTIR absorption spectra of FHD soots made with various flow rates of BCl₃ are shown in Fig. 1. An Si-O asymmetry stretching band is found at 1110.81~1108.88 cm⁻¹, Si-O symmetry stretching band at 815.75~813.82 cm⁻¹ and Si-O rocking band at 474.41~472.48 cm⁻¹ [7-11]. Table 1 gives the peak position data for the reference and the experimental FTIR data of the H₂O, SiO₂, B-O and B-O-Si bands. As summarized in Table.1, the structural Si-O asymmetric stretching band, the Si-O symmetric stretching band and the S-O rocking band of FHD soot are located at higher wavenumbers than in high purity silica for optical fibers. It is known that the position of the Si-O structural bands of silica could depend on the silica fabrication process and the amount of H₂O in the silica. The higher fictive temperature, which means that the silica soot is fabricated at a higher temperature, produces the peak shift to higher wavenumber [11, 12].

In Fig. 1, bands related to B are found at 1390.44 cm⁻¹ (B-O band), 916.13~914.1 cm⁻¹ (B-O-Si band) and 673.04 cm⁻¹ (B-O overtone band). Especially, the B-O stretching band (1390.44 cm⁻¹) is used to analyze

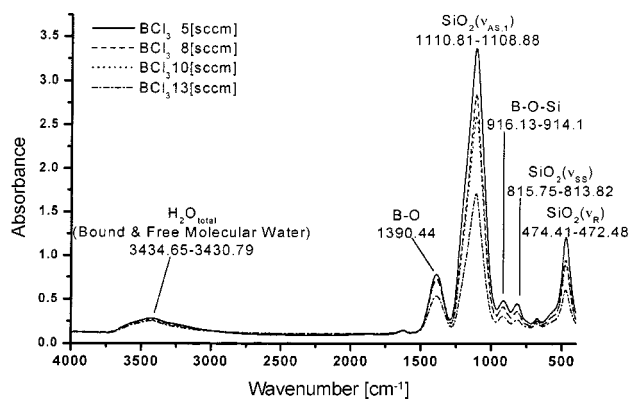


Fig. 1. FTIR absorption spectra of FHD soot at various BCl₃ flow rate.

Table 1. Comparison between Reference FTIR data and Result of experimental FTIR data [7-11]

Fundamental band	Silica glass [cm ⁻¹] ^[7-11]	Silica for optical fiber cladding [cm ⁻¹] ^[11]	FHD soot [cm ⁻¹]	FHD film [cm ⁻¹]
H ₂ O band	3410	3417.3	3434.65-3430.79	—
SiO ₂ (A,S*)band	1114-1060	1105.03	1110.81-1108.88	1097.31-1089.6
SiO ₂ (S,S**)band	850-800	794.54	815.75-813.82	808.04-802.25
SiO ₂ (R***)band	468-450	466.7	474.41-472.48	468.62-460.91
2ν _{ss} (SiO ₂), ν _{As,2} (SiO ₂)+ν _R (SiO ₂)*	1633	1627	—	—
ν _{As,1} (SiO ₂)+ν _R (SiO ₂)*	1873	1870	—	—
ν _{ss} (SiO ₂)+ν _{As,2} (SiO ₂)*	1990	1995	—	—
B-O band	—	—	1390.44	1390.44-1369.23
B-O-Si band	—	—	916.13-914.1	916.03
B-O Overtone band	—	—	673.04	—

. SiO₂(A,S) : Asymmetric Stretching band

*. SiO₂(S,S**)band : Symmetric Stretching band

*. SiO₂(R***)band : Rocking Motion band

composition of B [12]. Figure 1 also shows the results for the absorption spectra of OH groups with various flow rates of BCl₃. One of the H₂O bands is located at 3434.65~3430.79 cm⁻¹ [12, 13].

Boron in FHD silica soot is so hygroscopic that the water would adhere to the surface of soot particles during deposition or by handling in air after deposition. H₂O molecules were mostly removed during the heat treatment or sintering processes. However, the water molecules can react with silica network and change to chemically absorbed OH⁻, which accelerates crystallization during the soot sintering process [11]. Based on reports for the absorption of the P-O band in FHD soot, the P-O band peak could not be observed, since the position of this peak almost overlapped with the Si-O peak, due to the similar atomic weight of Si and P [14-16].

b) Absorption spectrum of FHD film

The film samples, which were about 5 μm in thick, were etched to 1~2 μm because film thickness over 2 μm exceeds detection ability of FTIR. Thus the Si substrate of the FHD film was etched to 1~2 μm

thickness in acid solution. The FTIR absorption spectra of FHD films at various flow rates of BCl₃ are shown in Fig. 2. In this figure, H₂O peaks above wavenumber 1500 cm⁻¹ could not be distinguished. However, B-O and Si-O stretching band spectra were found with high enough intensity to study the concentration relationship of B.

Comparing the soot with the film, Figs. 1 and 2, the absorbance of the B-O band (1390.44~1369.23 cm⁻¹) and the B-O-Si band (916.03 cm⁻¹) were largely reduced in the film, and the B-O overtone band could not be distinguished. In the film case, H₂O band peaks could not be distinguished in the 3450~3400 cm⁻¹ wavenumber range [12].

Figure 3 provides the absorption spectrum and the change of absorbance of the B-O stretching band at the various flow rates of BCl₃. Figure 3(a) is the B-O band absorption spectrum for soot and Fig. 3(b) is the B-O band absorption spectrum for film. It seems that absorbance of the B-O band decreases with the increasing flow rate of BCl₃. It is required to correct the absorbance of B-O stretching band to a reference peak, which is chosen to be the Si-O asymmetric band in this work, due to variation in the conditions of specimens such as the ratio of KBr, the thickness and the particle size.

After sintering, the film thickness was thinner than the soot for FTIR measurement. Hence, the total absorbance of the film became lower than that of soot.

In Fig. 4, the absorption spectrum of the Si-O asymmetric stretching band, which is used to correct absorbance of B-O stretching band, is shown with the various BCl₃ flow rates. Therefore, Fig. 3(c) provides the normalized B-O stretching band absorbance of soot and film to provide corrected absorbance of the B-O stretching band as a function of the variation parameters. In Fig. 3(c), the normalized absorbance of B-O stretching band has a tendency to increase linearly with the increasing flow rate of BCl₃.

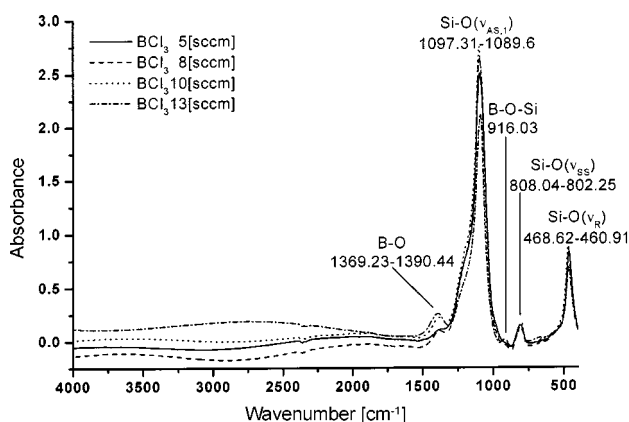


Fig. 2. FTIR absorption spectra of FHD film at various BCl₃ flow rate after eliminating Si wafer.

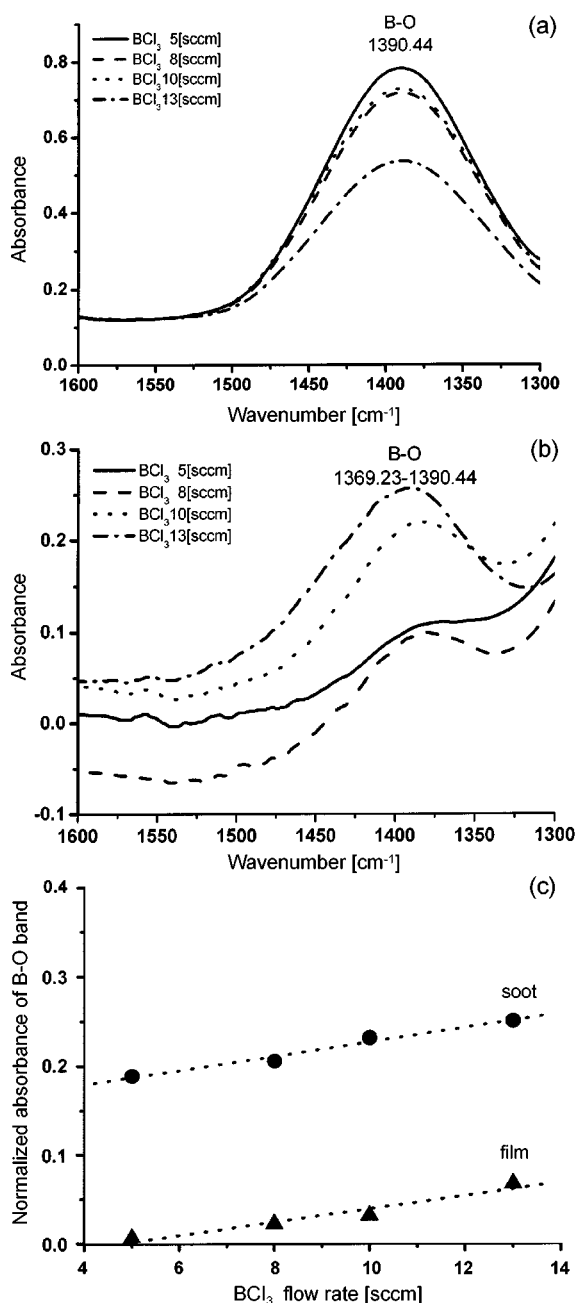


Fig. 3. Absorption spectrum and absorbance of B-O stretching band at the various BCl₃ flow rate. (a) B-O band absorption spectra of soot (b) B-O band absorption spectra of sintered film (c) Normalized B-O stretching band absorbance of soots and sintered films.

As mentioned earlier, it is required to correct the absorbance of the B-O stretching band to a reference peak, which is chosen as the Si-O asymmetric band in this work, due to variation in the conditions of specimens such as the ratio of KBr, the thickness and the particle size. Furthermore, it would be convenient that the absorbance of B-O peak is directly correlated with the B concentration. To meet this requirement in the calculation, the normalization of the B-O band absorbance was necessary in this study.

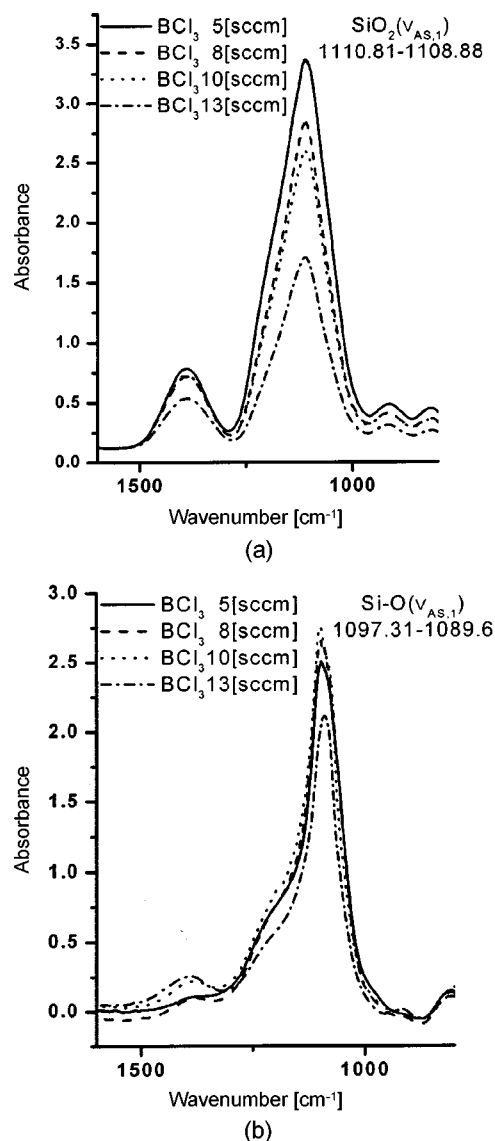


Fig. 4. Absorption spectra of Si-O Asymmetric stretching band at the various BCl₃ flow rate. (a) Si-O Asymmetric stretching band spectrum of soots (b) Si-O Asymmetric stretching band spectra of sintered films.

c) Relationship between FTIR and ICP-AES

When IR light passes through a sample, a specific bond vibration absorbs light of its resonant, or overtone, frequency in proportion to how many of these bonds are present. This relationship is given by the Beer-Lambert law [1, 2].

$$A = \varepsilon \cdot C \cdot L$$

Where A is the maximum absorbance of a peak (unit-less) and ε is the absorption coefficient (liter/mol·cm) for that peak. C is the concentration of the absorbing species (mol/L) and L is the light path length through the sample (cm). On the basis of the corrected absorbance of the B-O band, the Beer-Lambert law can be change into the following formula:

Table 2. Absorbance of B-O band, Si-O asymmetric stretching band and normalized B-O band absorbance in FHD film measured by Two-point base line method

BCl ₃ flow rate [sccm]	B-O Absorbance	Si-O Absorbance	B-O Absorbance /Si-O Absorbance
5	0.0177	2.4647	0.007181
8	0.0608	2.6405	0.023026
10	0.0874	2.6747	0.032677
13	0.1416	2.0747	0.068251

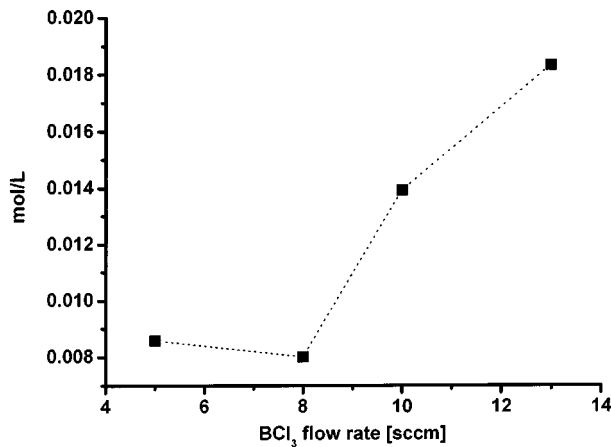


Fig. 5. Boron mole concentration of sintered films measured by ICP-AES as a function of BCl₃ flow rate. (Line is a guide for eye and has no scientific meaning.)

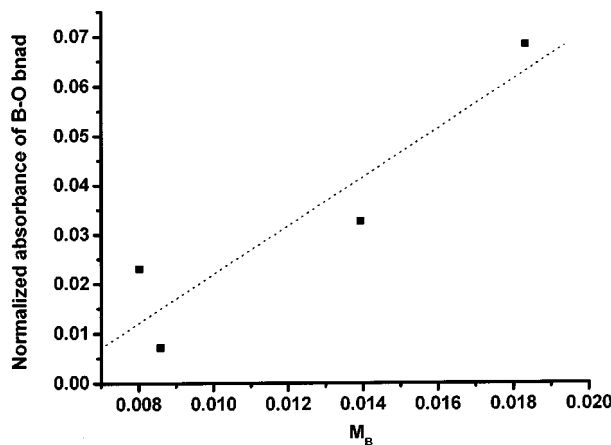


Fig. 6. Normalized absorbance of B-O band at various mole fraction for normalized extinction coefficient.

$$\frac{A_{B-O}}{A_{Si-O}} = \frac{\epsilon_{B-O}}{\epsilon_{Si-O}} \cdot \frac{C_{B-O}}{C_{Si-O}} \cong \epsilon_{B-O}^* \cdot M_B$$

Here, ϵ_{B-O}^* is the normalized absorption coefficient and M_B is an approximate value of the molar fraction of B. In this study, the concentration of B was relatively very small compared to the concentration of Si. Thus, $C_{Si-O}=1$ could be assumed within the experimental error.

Table 2 gives the absorbance of the B-O stretching

band, the Si-O asymmetric stretching band and the normalized B-O band absorbance at various BCl₃ flow rates in FHD film measured by the two-point base line method. In Fig. 5, the molar concentration of B in the sintered film measured by ICP-AES is shown as a function of BCl₃ flow rate. The B concentration generally increases with the flow rate of BCl₃. Here, the line is a guide for the eye and has no scientific meaning.

As mentioned above, the absorbance of the B-O stretching band was obtained by FTIR and absolute concentration of B was measured by ICP-AES. However, sample preparation of ICP-AES is not only complex in that the sample must be dissolved and diluted into an acid solution, but also a difficult method to obtain results quickly. This method is useful to calculate the absorption coefficient. Thus B concentration in silica film can be calculated indirectly by using only FTIR data.

Figure 6 shows the relationship between the normalized absorbance of the B-O stretching band and concentration of B. The normalized absorbance data and the concentration data were applied to the corrected Beer-Lambert law above. The ϵ_{B-O}^* of FHD silica film is 4.93. As shown in Fig. 6, the slope of the dotted straight line for normalized absorbance as a function of mole fraction is the normalized absorption coefficient in this research.

Conclusions

Silica soot and film that were fabricated by the Flame Hydrolysis Deposition process were analyzed through two methods. By analyzing absorbance spectra from FTIR, the compositional change of B-O, Si-O and H₂O (OH) in silica film were measured. The concentrations of these dopants were also measured by ICP-AES and were correlated with the FTIR results. Moreover, the quantitative relationship between the concentration of B and absorbance was clarified by comparing the FTIR analysis and ICP-AES analysis of each peak as functions of BCl₃ flow rate. A normalized absorption coefficient was then calculated. The normalized absorbance data and the concentration data were applied to the corrected Beer-Lambert law above. The ϵ_{B-O}^* of FHD silica film is 4.93. The higher the number of samples, the more precise normalized absorption coefficient becomes.

If the FHD standard process is established through controlled process parameters, the normalized absorption coefficient which was already calculated can be conveniently used to fabricate the optical passive device through controlling of the gas flow rate.

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