

## Fabrication and Characterization of Sol-Gel Ternary Titanium Silicate Waveguides

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Aluminum and zinc titanium silicate sol-gel films were fabricated for application of waveguide and the effect of additions of ZnO and Al<sub>2</sub>O<sub>3</sub> to binary titanium silicate films was investigated. During firing, the films are densified as they shrink and their refractive index increases in the range of 1.58-1.83 depending on the film composition. The attenuation of the waveguides is not sensitive to changes in composition except for zinc titanium silicate waveguides which have substantially higher attenuation. However, the increase in the attenuation with aging of the waveguides depend upon the composition of waveguides. The addition of Al<sub>2</sub>O<sub>3</sub> or the reduced SiO<sub>2</sub> content in the composition appears to slow the deterioration of the waveguides due to the formation of more stable bonds and increased acidity on the film surface. Also, the wavelength dependence of the attenuation of the waveguides varies with composition. The attenuation of the waveguides except for the 65SiO<sub>2</sub>·35TiO<sub>2</sub> composition are not Rayleigh scatter limited, suggesting the absorption loss of the waveguides due to the effects of residual carbon and structural defects in the films.

**Key words :** Aluminum, Zinc, Titanium silicate, Sol-gel film, FTIR, Waveguide, Attenuation

### I. Introduction

Sol-gel processing has been recently applied to the fabrication of planar optical waveguides.<sup>7</sup> Although waveguides of a variety of oxide compositions have been fabricated by sol-gel processing, the most often studied oxide system as solution derived are compositions in the binary TiO<sub>2</sub>-SiO<sub>2</sub>.<sup>1-7</sup> The advantage of the sol-gel titanium silicate waveguide is the broad range of refractive indices possible as a function of TiO<sub>2</sub> content, as well as the commercial availability of SiO<sub>2</sub> and TiO<sub>2</sub> precursor solutions. Also, the sol-gel waveguide can easily form grating structures and channel waveguides by embossing and laser densification techniques.<sup>1-7</sup>

Lukosz et al.<sup>2,4</sup> fabricated titanium silicate waveguides with a variety of TiO<sub>2</sub> content (33, 50, 67 and 75 mol%) waveguides by mixing commercially available SiO<sub>2</sub> and TiO<sub>2</sub> precursor solutions. The attenuation ranging 0.2-2.5 dB/cm did not vary strongly with TiO<sub>2</sub> content, except for the 75 mole% TiO<sub>2</sub> waveguides which had substantially higher attenuation. The measured attenuation as a function of wavelength did not meet the Rayleigh limited criteria. It suggested the absorption was not negligible in these waveguides. Guglielmi et al.<sup>5</sup> fabricated multi-layer titanium silicate waveguides with 35 mole% TiO<sub>2</sub> by dip coating and measured the attenuation as a function of firing temperature and thickness. The attenuation was the lowest for the film fired to 800°C and increased as the thickness of the waveguide increased.

However, miscibility gap exists in the binary TiO<sub>2</sub>-SiO<sub>2</sub>

system and this insolubility limits the range of glass compositions that can be fabricated conventionally. Thus, phase separation of the components can be an issue in sol-gel films as well which can affect waveguiding characteristics of the films.

One method to inhibit the phase separation tendency is to add a third component to the composition.<sup>8,10</sup> The additions chosen were Al<sub>2</sub>O<sub>3</sub> and ZnO in the present study. Based on the analysis of Nakagawa and Itzutani,<sup>9</sup> these oxide additions are expected to lower the tendency to the phase separation while maintaining a high refractive index. Thus, in this work, aluminum or zinc titanium silicate sol-gel films were fabricated for application of waveguide. Their structural evolution and densification behavior of the films with firing temperature was examined. The attenuation of the waveguides was measured depending on aging and wavelength and the effect of additions of ZnO and Al<sub>2</sub>O<sub>3</sub> to binary titanium silicate films was investigated.

### II. Experimental Procedure

#### 1. Preparation of solutions

Two binary (65SiO<sub>2</sub>·35TiO<sub>2</sub>, 50SiO<sub>2</sub>·50TiO<sub>2</sub>) and four ternary (50SiO<sub>2</sub>·35TiO<sub>2</sub>·15Al<sub>2</sub>O<sub>3</sub>, 50SiO<sub>2</sub>·25TiO<sub>2</sub>·25Al<sub>2</sub>O<sub>3</sub>, 50SiO<sub>2</sub>·35TiO<sub>2</sub>·15ZnO, 50SiO<sub>2</sub>·25TiO<sub>2</sub>·25ZnO) composition solutions were prepared.

For the binary composition solution, 0.045 moles of tetraethoxysilane (TEOS) was dissolved in ethanol, in a molar ratio of 4:1 alcohol:Si. The diluted TEOS was

slowly pre-hydrolyzed with acidified water (0.15N HCl), until a molar ratio of the water:Si was 1:1, then reacted for 15 mins. at 50°C. In a separate flask, titanium(IV) ethoxide (TET) is dissolved in ethanol, for a molar ratio of 8:1 alcohol:Ti, then slowly poured into the TEOS solution and reacted for 4 hrs at 50°C. The solution was diluted with ethanol to 20 wt% oxide concentration. The higher concentration yielded waveguides thick enough to support a lowest order mode in single coating.

For the  $\text{SiO}_2\text{-TiO}_2\text{-Al}_2\text{O}_3$  ternary composition solution, aluminum secbutoxide (ASB) was used as the Al source. The butoxide was chosen rather than the ethoxide due to the rapid reaction and low solubility of aluminum ethoxide in ethanol. The appropriate molar ratio of the TET and the ASB were mixed together in a clean and dry flask for 15 mins. An exothermic reaction occurred as the two alkoxides reacted, presumably due to alcohol exchange reaction, and the creation of some sort of stabilizing, complex structure of the two molecules. The double alkoxide mixture was slowly diluted with an equal volume of distilled ethanol. If the dilution was too rapid, small white precipitates formed. The diluted aluminum and titanium alkoxide mixture was stirred for 20 mins. prior to the slow addition of the TEOS solution, then was stirred overnight at room temperature. The TEOS solution was added to the aluminum and titanium alkoxide solution since precipitates formed when the double alkoxide solution was added to the prehydrolyzed solution. The oxide concentration of the solution was 15 wt%.

For the  $\text{SiO}_2\text{-TiO}_2\text{-ZnO}$  ternary composition solution, zinc ethoxide was used as the Zn source. Zinc ethoxide was produced by transferring diethyl zinc (1.0 M solution in hexane) through a spectrum into a flask containing TET dissolved in excess ethanol. Reaction with the TET was required to produce a clear colorless solution. When the diethyl zinc was added to the ethanol alone, small white precipitates formed. As with the aluminum solutions described above, apparently the zinc and titanium alkoxides reacted to form a complex structure within the solution. The complex titanium and zinc alkoxides solution was then poured into the pre-hydrolyzed TEOS solution and stirred overnight at room temperature in a sealed flask. The oxide concentration of the solution was 15 wt%. All the solutions were stored after removal from the reaction flask in clean dry vials in a desiccator until deposition.

## 2. Film coating and characterization

The films were deposited using spin coating on Si wafer, Corning 7059 glass or quartz substrate. The deposited films were fired at various temperatures for 15 mins. Thicknesses and refractive index of the films on Si wafer substrate were measured using an ellipsometer (Gaertner L116B). Prism coupling technique, which was described in detail previously,<sup>11</sup> was used to determine

the waveguiding attenuation of the films on glass or quartz substrate. FTIR spectroscopy (Perkin Elmer 1725 $\times$ ) analyses were performed in transmission on the films on Si wafer substrate.

## III. Results and Discussion

### 1. FTIR analysis

Figures 1, 2 and 3 present transmission FTIR analysis for  $50\text{SiO}_2\text{-}50\text{TiO}_2$ ,  $50\text{SiO}_2\text{-}25\text{TiO}_2\text{-}25\text{Al}_2\text{O}_3$ , and  $50\text{SiO}_2\text{-}25\text{TiO}_2\text{-}25\text{ZnO}$  compositions, respectively, after firing at 500, 600, 700, and 800°C. First of all, in the 3000~3800  $\text{cm}^{-1}$  range, a large and broad band associated with the stretching of M-OH structural bond is seen in the low temperature spectra of all the compositions.<sup>12</sup> As the films are fired at higher temperature, the band area decreases in all the compositions until the peak is no longer present at 800°C. Thus, the films continue to shrink and densify until dehydroxylation is complete after 800°C.

The principle spectral bands, at approximately 1050, 940 and 800  $\text{cm}^{-1}$ , are associated with the Si-O (TO) stretching, Si-O-Ti stretching, and Si-O-Si bending vibrations, respectively.<sup>12,13</sup> The Si-O (TO) band has a shoulder at higher frequencies assigned to the Si-O (LO)

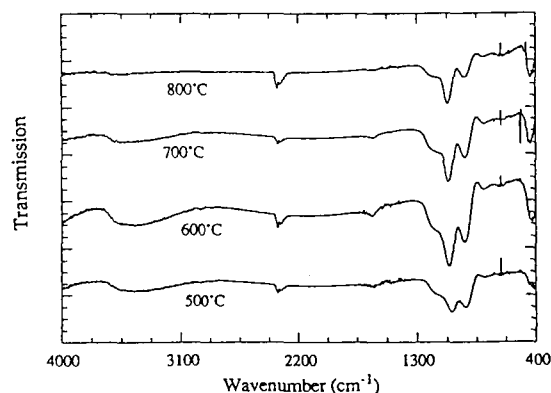


Fig. 1. FTIR spectra for  $50\text{SiO}_2\text{-}50\text{TiO}_2$  composition films fired at 500~800°C.

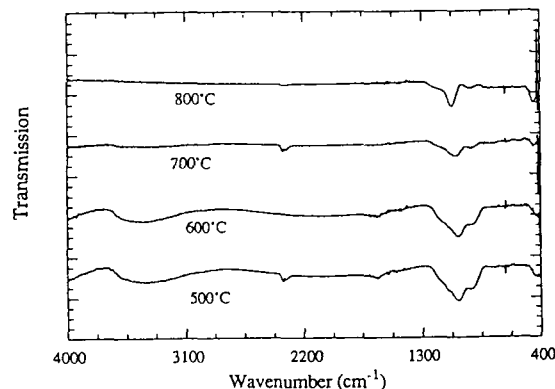
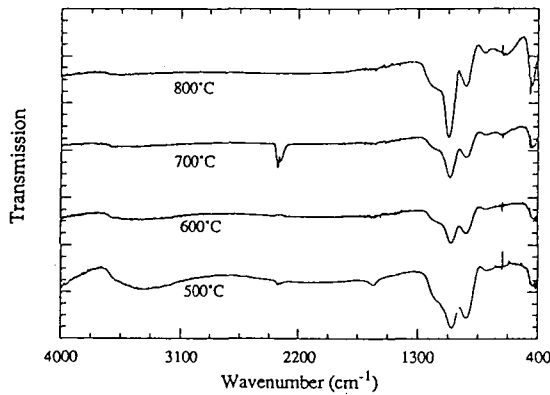


Fig. 2. FTIR spectra for  $50\text{SiO}_2\text{-}25\text{TiO}_2\text{-}25\text{Al}_2\text{O}_3$  composition films fired at 500~800°C.



**Fig. 3.** FTIR spectra for 50SiO<sub>2</sub>·25TiO<sub>2</sub>·25TnO composition films fired at 500~800°C.

**Table 1.** FTIR Position of Si-O (TO) Stretching Vibration Band as a Function of Firing Temperature for Each Composition (cm<sup>-1</sup>)

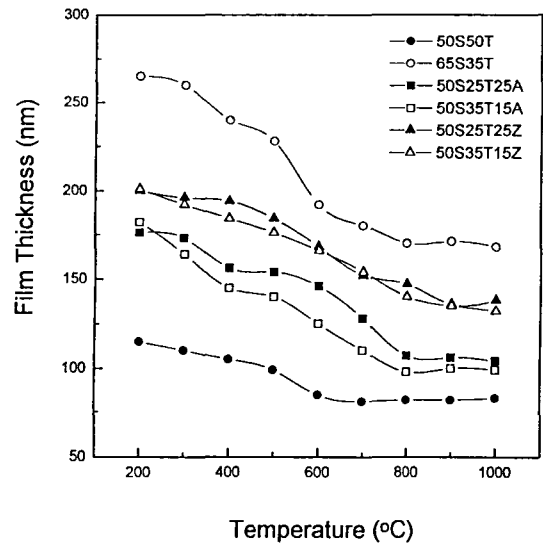
Firing temperature	50SiO <sub>2</sub> ·50TiO <sub>2</sub>	50SiO <sub>2</sub> ·25TiO <sub>2</sub> ·25ZnO	50SiO <sub>2</sub> ·25TiO <sub>2</sub> ·25Al <sub>2</sub> O <sub>3</sub>
500°C	1045	1050	1030
600°C	1060	1050	1030
700°C	1065	1065	1050
800°C	1075	1070	1070

stretching vibration. No separate bands are present which can be assigned to Al-O or Zn-O bonds. The position of the Si-O (TO) stretching vibration band is listed as a function of firing temperature for each of the compositions in Table 1. The band moves to higher wavenumber with increasing firing temperature for all compositions. The shift in the band positions may result from structural or compositional changes. The presence of hydroxyls in the microstructure broadens and shifts the position of the Si-O vibration band to lower wavenumbers. As the hydroxyls are removed and bridging bonds are formed, the position of the Si-O vibration band shift to greater wavenumbers.<sup>13)</sup> The peaks in the 500 and 600°C spectra for Al ternary composition are further red shifted than any other composition as shown in Table 1. The shift in the position of the Si-O band, associated with the SiO<sub>2</sub> network, suggests that the Al<sup>3+</sup> ions have been incorporated into the glass network forming Si-O-Al bonds.<sup>13)</sup>

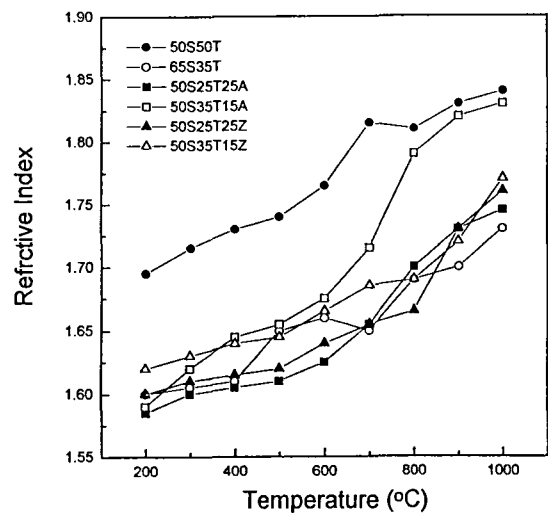
Compared to other compositions, the fundamental band in the Al ternary composition spectra is broad. This band broadening may be due to the presence of hydroxyls and Al-O-Ti bonds in the structure.

**2. Densification behavior**

The densification behavior of the films is shown in figure 4 as film thickness versus firing temperature. Each data point represents an individual film spun and fired for each composition. As expected in FTIR analyses, the film thickness decreases monotonically with increasing



**Fig. 4.** Film thickness plotted as a function of firing temperature for each composition films.



**Fig. 5.** Refractive index plotted as a function of firing temperature for each composition films.

firing temperature until certain temperature and then remains constant, although there is scatter in the data. This transition temperatures of the ternary compositions are higher than those of the binary compositions. The shrinkage of the films during firing is caused by evaporation of water and organic components. Thus, it is found that removal of organic and water residues for the ternary compositions complete at higher temperature with low rate than for the binary compositions.

The refractive indices of the films as a function of firing temperature are plotted in figure 5. For all the compositions, the refractive index of the films are in the range of 1.58~1.83 and increase monotonously with firing temperature, though the scatter in the data vary with composition. The increase in the refractive index of

**Table 2.** Optical Propagation Losses Measured for Various Composition Waveguides Fired at 500°C and 800°C (dB/cm)

Composition	500°C	800°C
50SiO <sub>2</sub> ·50TiO <sub>2</sub>	0.5 - 1.5	5 - 9
65SiO <sub>2</sub> ·35TiO <sub>2</sub>	0.5 - 1	5 - 8
50SiO <sub>2</sub> ·25TiO <sub>2</sub> ·25ZnO	3 - 4	3 - 4
50SiO <sub>2</sub> ·35TiO <sub>2</sub> ·15ZnO	2 - 3	2 - 3
50SiO <sub>2</sub> ·25TiO <sub>2</sub> ·25Al <sub>2</sub> O <sub>3</sub>	1 - 2	1 - 2.5
50SiO <sub>2</sub> ·35TiO <sub>2</sub> ·15Al <sub>2</sub> O <sub>3</sub>	0.5 - 1	0.5 - 1.5

the films is expected due to the film densification as well as the removal of organic and water residues at higher temperature. The refractive index of the films can be controlled over the broad range by composition and firing temperature.

### 3. Attenuation of waveguides

Average optical propagation losses of the films at 632.8 nm wavelength for the various compositions are shown in Table 2. The optical propagation loss for firing at 500°C was measured for the films on glass substrate and for firing at 800°C for the films on quartz substrate. The attenuation was determined by averaging the optical propagation loss measured at several points on the film.

With the exception of the 50SiO<sub>2</sub>·25TiO<sub>2</sub>·25ZnO composition, the attenuation of the films fired at 500°C is within the range 0.5~2 dB/cm, though it should be noted that the losses of the 50SiO<sub>2</sub>·35TiO<sub>2</sub>·15ZnO composition waveguide are higher than 2 dB/cm. In general, binary and Al ternary composition waveguides fired at 500°C with propagation loss of < 1 dB/cm could be fabricated under the correct set of conditions. Thus, the attenuation of the waveguides at 632.8 nm wavelength is not significantly sensitive to changes in composition, except for the Zn ternary composition. This results suggest that for these waveguides, the contribution of the substrate and processing differences dominates the propagation loss over any difference induced by the composition.

Firing the films at 800°C increase the attenuation of the waveguides, except for the Zn ternary composition waveguides. This increase in attenuation is caused by formation of crystalline phase in the films which has higher refractive index and acts as a scattering source in the waveguides. Actually, in the 50SiO<sub>2</sub>·50TiO<sub>2</sub> composition waveguide, the small TiO<sub>2</sub> crystals were detected by TEM and its effect on propagation loss was established before.<sup>6,7)</sup> The high propagation loss of the Zn ternary composition waveguides suggests that the structure of the films are not homogeneous due to inhomogeneous solution or non-uniform volatilization of zinc in the films.

Sometimes, the propagation loss of the waveguides was found to increase during storage. The increased propagation loss is not due to dirt settling on surfaces of the waveguides during storage, as the surfaces were

**Table 3.** Optical Propagation Losses Measured as a Function of Aging Time (dB/cm)

Composition	Initial	1 month	2 months	5 months
50SiO <sub>2</sub> ·50TiO <sub>2</sub>	1.0±0.1	1.0±0.1	1.0±0.1	4.2±0.2
65SiO <sub>2</sub> ·35TiO <sub>2</sub>	0.5±0.1	1.2±0.1	1.2±0.1	2.0±0.1
50SiO <sub>2</sub> ·35TiO <sub>2</sub> ·15Al <sub>2</sub> O <sub>3</sub>	0.5±0.1	0.5±0.1	0.5±0.1	0.5±0.1

thoroughly cleaned prior to measuring the propagation loss. Table 3 compares the effect of aging on the propagation loss characteristics of several composition waveguides. The initial propagation loss measurement was done in the first week after the waveguides were fabricated. After fabrication, the samples were stored in opaque plastic containers under ambient laboratory conditions. The ambient temperature and relative humidity of the laboratory during the experiment varied in the range of 18~24°C and 40~65% RH. As shown in the Table 3, the attenuation of the binary composition waveguides increase as they aged in storage. The 65SiO<sub>2</sub>·35TiO<sub>2</sub> composition waveguide deteriorates the fastest exhibiting four time increase in propagation loss after 5 months. The propagation loss of the 50SiO<sub>2</sub>·50TiO<sub>2</sub> composition waveguides remains constant for 4 months, then dramatically increases in the fifth month. In contrast, after 5 months of storage, the quality of the 50SiO<sub>2</sub>·35TiO<sub>2</sub>·15Al<sub>2</sub>O<sub>3</sub> composition waveguide, as measured by the attenuation at 632.8 nm wavelength, is unchanged. Thus, the addition of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> to the composition appears to slow the deterioration of the films, but the effect of the addition of the Al<sub>2</sub>O<sub>3</sub> is greater.

A possible cause of the deterioration in the films is the degradation of the film surface with time due to reaction with the ambient humidity and the components of the air. The reaction of humidity with glass surface can be modeled as the dissolution or corrosion of the glass. The reaction of water and atmospheric gases with glass, resulting in the breaking or modifying of the glass structure is well known. The reaction is diffusion limited as the gas molecules dissolve or diffuse into the glass surface, reacting with the network bonds. The reaction requires the breaking of bonds, which will weaken the network structure, and thus the rate will depend upon the density of SiO<sub>2</sub>. The presence of either chemisorbed or physisorbed gas molecules will affect the reaction between the water and the surface as well, along with temperature.

The surface of the sol-gel film fired to 500°C is not dense, and is covered with hydroxyls. Studies of the sol-gel derived SiO<sub>2</sub> with Raman spectroscopies and NMR have shown that the concentration of silanol at the surface remains high even after firing to 600°C.<sup>10)</sup> Reaction of the absorbed gas molecules and the hydroxyls may be similar to the water/glass reaction referred to above. Thus, the addition of TiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> in the SiO<sub>2</sub> surface

would decrease the hydroxyl concentration or the reactivity of the surface, resulting in variation of aging effect with composition. Specially, the addition of  $\text{Al}_2\text{O}_3$  may improve the aging characteristics of the waveguides by altering the surface chemistry, forming Si-O-Al or Al-O-Ti linkages that may be more resistant to attack. Although the exact nature of the reactions of the gases and the water with the surface of waveguides are not known, possible absorption sources that might result from the break up of the film structure are considered.

The fastest rate of deterioration of the films is observed in the  $65\text{SiO}_2\cdot 35\text{TiO}_2$  composition waveguide, which contains the highest relative percentage of  $\text{SiO}_2$  in the composition, and thus had the most basic surface chemistry. As the relative amount of  $\text{SiO}_2$  in the composition is reduced, the acidic character of the film increases. Thus, the surface of higher acidity would be more resistant to acid attack of the atmosphere. This suggests that the composition containing lower content of  $\text{SiO}_2$  increases the acidity of the surface and may improve the environmental durability of the film.

The attenuation measured for the several composition waveguides as a function of wavelength is given in figure 6. If the attenuation is limited by the intrinsic or Rayleigh scattering of the material, the measured propagation loss should have a  $\lambda^{-4}$  dependence. An absorptive film would be expected to have a dependence of  $\lambda^{-n}$  where  $n \gg 4$ . However, if the increased propagation loss is due to the increased scattering, the wavelength dependence would be expected to be  $\lambda^{-n}$  where  $n \ll 4$ . The power coefficient of the wavelength dependence ( $n$ ) for the  $65\text{SiO}_2\cdot 35\text{TiO}_2$  composition waveguide in the first week after its synthesis is approximately  $n=4$ . This indicates that the propagation loss of the waveguide is limited initially by the intrinsic scattering in the films. However, the power

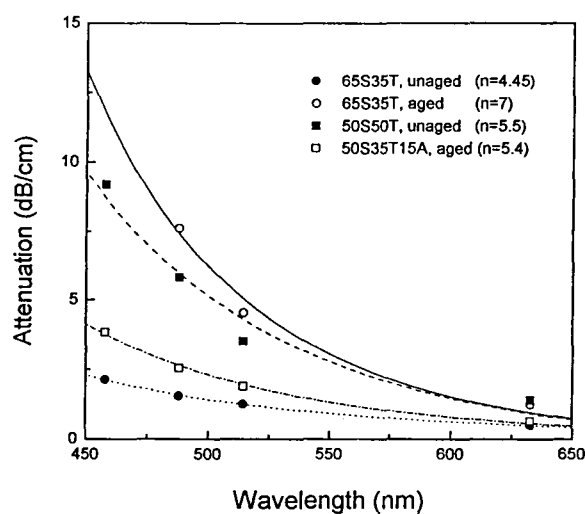
coefficient for the  $65\text{SiO}_2\cdot 35\text{TiO}_2$  composition waveguide after one month in storage is found to be  $n=7$ . This suggests that absorption in the film is no longer negligible. In addition, the power coefficient for the  $50\text{SiO}_2\cdot 50\text{TiO}_2$  and  $50\text{SiO}_2\cdot 35\text{TiO}_2\cdot 15\text{Al}_2\text{O}_3$  composition waveguides is higher than expected, 5.5 and 5.4, respectively. The higher fit coefficient suggests that the propagation losses may not be Rayleigh scatter limited and the assumption of negligible absorption is of questionable validity for these composition waveguides.

There are many possible sources of absorption in the films. The presence of transition element impurities, even in trace amounts, would increase the absorption in the visible region. However, the effect of the impurities should be evident immediately after fabrication equally in all the waveguides since the chemical precursors were the same for all the waveguides. But the initial wavelength dependence of the  $65\text{SiO}_2\cdot 35\text{TiO}_2$  composition waveguide indicates the absorption is negligible. Therefore, impurities are discounted as the source of the absorption in the waveguides.

The absorption spectra of reduced  $\text{Ti}^{3+}$  ions extends well into the visible wavelengths. However, thermodynamically,  $\text{Ti}^{3+}$  ions would not be stable in hydrous and porous network such as in the waveguides, in which the diffusion of water would be rapid. The equilibrium state for the Ti ion is  $\text{Ti}^{4+}$  in octahedral coordination, and the  $\text{Ti}^{3+}$  ion would tend to be oxidized. It seems unlikely that a reducing environment could be maintained in the thin films.

In addition, the presence of carbon or non-bridging oxygens (NBO) in the film structure might account for the absorption losses. The absorption edge of amorphous carbon extends to energies of 3-4eV into the blue visible range.<sup>15)</sup> Also, a weak absorption band centered at 622 nm wavelength was identified in silicate glass and assigned to the interaction of the light with NBO defects in the structure.<sup>16)</sup> As the film reacts with atmosphere and humidity, bridging oxygen bonds are broken and carbon is incorporated into the microstructure, increasing the content of hydroxyls, carbon, and perhaps the defects in the structure. Thus, as the concentration of these defects increases, the absorption in the films will be increased. Absorption due to the residual carbon or structural defects may explain the initial wavelength dependence of the  $50\text{SiO}_2\cdot 50\text{TiO}_2$  and  $50\text{SiO}_2\cdot 35\text{TiO}_2\cdot 15\text{Al}_2\text{O}_3$  composition waveguides. The concentration of residual carbon in these waveguides is below the detection limit for the techniques used. Because of the very strong absorption associated with carbon, only a very small concentration would need to be present to increase the absorption loss.

An increase in the defect concentration of the film structure due to the addition of Ti or Al ions is also a possibility. The Ti and Al ions prefer octahedral coordination in the structure in the absence of alkali or al-



**Fig. 6.** Attenuation of the waveguides as a function of wavelength. The curves included on the plot are an exponential fit of the data points and  $n$  is the power coefficient of corresponding exponential fit.

kaline earth for charge compensation within the structure.<sup>17)</sup> Thus, the incorporation of the octahedral units into the SiO<sub>2</sub> tetrahedral network structure by addition of Ti or Al ions may result in an increased number of NBOs and an increased absorption loss due to the defects in the structure.

#### IV. Conclusions

The ternary titanium silicate sol-gel films are densified during firing as they are shrunk and their refractive index grows. The attenuation of the binary and ternary titanium silicate waveguides is not significantly sensitive to changes in composition, except for the zinc ternary composition. However, the increase in the attenuation with aging of the waveguides depend upon the composition of the waveguides. The addition of Al<sub>2</sub>O<sub>3</sub> to the titanium silicate waveguides incorporation appears to slow the deterioration of the waveguides due to the formation of stable bond in the structure. The increased resistance to the deterioration of the decreased concentration of SiO<sub>2</sub> present in the composition might be due to the enhanced acidity of the surface. Also, the wavelength dependence of the attenuation of the waveguides varies with composition. The attenuation of the waveguides except for the 65SiO<sub>2</sub>·35TiO<sub>2</sub> composition are not Rayleigh scatter limited, suggesting the absorption loss of the waveguides. The effects of amorphous carbon and structural defects are considered the most likely absorption mechanisms in these films.

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