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Sol−Gel-Processed SiO_2/TiO_2/Poly(vinylpyrrolidone) Composite Materials for Optical Waveguides

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SiO_2/TiO_2/poly(vinylpyrrolidone) (PVP) composite materials processed by the sol−gel technique were studied for optical waveguide applications. Change of refractive index through the range 1.39−1.65 at 633 nm (optical wavelength) was achieved by varying the ratio between the SiO_2 and TiO_2 concentrations. To produce low optical propagation loss in the waveguide, it was necessary to avoid the precipitation of TiO_2 particles caused by the fast hydrolysis reaction of titanium alkoxide. By using titanium ethylhexoxide as a titanium alkoxide together with acetic acid and 2-propanol as the solvent, the precipitation of TiO_2 was avoided in the TiO_2 concentration range of up to 30 wt %, resulting in low optical propagation losses in the slab waveguide configuration. In the higher TiO_2 concentration range, an additional measure, peptization was necessary. With this method, we could produce optical waveguides possessing optical propagation losses of 0.62 dB/cm or lower at 633 nm. Low optical propagation loss in all the TiO_2 concentrations, from 0% TiO_2/50% SiO_2/50% PVP to 50% TiO_2/0% SiO_2/50% PVP was achieved. The reactions of the sol−gel precursors were also studied using UV−visible and FT-IR spectroscopy.

Introduction

Increasing interest in optical integrated circuit has stimulated studies on optical waveguide materials. Many researchers have spent a great deal of effort to realize useful materials for optical waveguides. The sol−gel processing is one approach because of high optical quality of materials produced and freedom to impregnate them with a variety of additives to modify their optical characteristics. The sol−gel reaction is a technique to make metal (semi-metal) oxide compounds through chemical reactions without high-temperature processing. The precursor solution is an alkoxide, such as silicon alkoxide or titanium alkoxide, that is reacted with water containing an acid or a base catalyst. A hydrolysis reaction takes place followed by a polycondensation reaction, resulting in a three-dimensional oxide network.

Pure inorganic sol−gel materials, such as SiO_2 and TiO_2, have been investigated for optical applications, including optical waveguides.[1−7] Weisenbach et al. states that sol−gel processed SiO_2/TiO_2 (50/50 wt %) slab waveguides typically have less than 0.5 dB/cm at 633 nm in wavelength.[7] The thickness of the waveguide was 0.18 μm. These materials have excellent optical quality and provide the freedom to change their indexes. However, pure inorganic sol−gel materials are difficult to be produced as thicker than 0.2 μm, because a large shrinkage of the material during the thermal densification process causes cracking in thicker films. Such films are too thin to guide modes in the waveguides, so several repeated coatings are necessary.

Sol−gel processed organic:inorganic composite materials are capable of producing thick enough films by single coating without cracking. Some researchers have used organically modified alkoxysilanes (ORMOSIL) and tetraalkoxysilanes to produce organically modified silicates, called ORMOCERs or Polycerams.[8−14] Motakef et al.[14] recently achieved an optical propagation loss of 0.15 dB/cm at 633 nm in wavelength with a slab waveguide. This consisted of a composite material of poly(dimethylsiloxane), SiO_2 and TiO_2, with a thickness of 1.55 μm. Another approach is mixing a prepolymerized material (polymer) into the sol−gel precursors.[15−20] In this case, it is important to avoid phase separation throughout the sol−gel reaction by a careful selection

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of solvents and optimized material processing conditions.

Poly(vinylpyrrolidone) (PVP) is one of the ideal prepolymerized materials due to its solubility in polar solvents and its thermal cross-linking characteristics. The solubility in polar solvents is a preferable characteristic for mixing with the sol−gel precursors, since the sol−gel reaction uses polar solvent(s) and water and produces alcohol in the reaction. So PVP is expected to provide a homogeneous solution in sol−gel processing, avoiding phase separation. The cross-linking of PVP is another advantage because it is expected to have better thermal stability than many un-cross-linked polymers. The cross-linked PVP also allows us to employ some etching techniques using water-based etchants to pattern channel waveguide structures from slab waveguides, so the conventional photolithographic technique can be applied. Sheirs et al. studied the cross-linking mechanism of PVP.[21] PVP is cross-linked by a radical reaction originated by residual hydrogen peroxide which is used to initiate the polymerization reaction. The cross-linking takes place during a 120 °C 24 h thermal treatment.

Many sol−gel processed materials employ TiO_2. TiO_2 is known as a high refractive index material, so it is used to increase the refractive index of the system. Titanium isopropoxide is one of the most widely used titanium alkoxides as a TiO_2 source in the sol−gel reaction; however, its high hydrolysis rate results in precipitation of TiO_2 particles, causing severe scattering loss. Therefore, 2,4-pentanedione (acetylacetone) is often used to reduce the reaction rate through the formation of a complex. This complex has a strong absorption band in the visible region, so even after the sample is baked at 300 °C, the residual of the complex still absorbs in the visible wavelengths, resulting in a high optical loss at 633 nm. To avoid using 2,4-pentanedione and to reduce the reaction rate, acetic acid was used as a solvent for titanium alkoxide. Acetic acid works not only as a solvent but also as a reagent to produce a relatively stable acetyl compound.[22−25] Doeuff et al. have found that acetic acid reacts with titanium alkoxide and forms a polymeric precipitation through an exothermic reaction.[23] The compound was studied by FT-IR and NMR spectroscopy and was found to be titanium oxo-acetate, $TiO(OAc)_2$. Another approach to avoid the formation of TiO_2 precipitation is “chemically controlled condensation”, which was introduced by Schmidt et al.[26] This concept uses ethanol and acetic acid to prepare a Ti precursor. Acetic acid slowly reacts with ethanol to form an ester and water. This water contributes to the hydrolysis reaction of Ti alkoxide.

In our previous work,[20] we studied the sol−gel-derived SiO_2/PVP composite material for optical waveguide application. We found that the incorporation of sol−gel-derived SiO_2 provides a relatively inert environment for PVP and prevents its thermal decomposition, resulting in high optical transparency even after thermal cross-linking. An optical propagation loss of 0.2 dB/cm at 633 nm in a slab waveguide configuration was achieved. This composite system also showed considerable thermal stability.

In this paper, we have succeeded to impregnate TiO_2 into the PVP/SiO_2 system to realize the manipulation of refractive index which provides an extended freedom for designing optical waveguides.

Experimental Section

A variety of titanium alkoxides: titanium isopropoxide (99.999%) from Aldrich, titanium *n*-butoxide from Tokyo Kasei, titanium isobutoxide from Gelest Inc., and titanium 2-ethylhexoxide from Gelest Inc. were used as TiO_2 sources. We used them without any further purification. Other chemicals such as acetic acid, poly(vinylpyrrolidone) (average molecular weight: 40 000 g/mol), tetraethoxysilane, hydrochloric acid (37 wt % in water), *N*,*N*-dimethylformamide, and 2-propanol were obtained from Aldrich.

Titanium precursors were prepared as follows: 4.5 mmol of titanium alkoxide and 2.15 mL of acetic acid were mixed and stirred at room temperature for 10 min to allow the oxoacetate compound to be formed; 2.15 mL of 2-propanol was then added to the solution. For a comparison, the titanium acetylacetate complex was prepared by mixing titanium isopropoxide and 2,4-pentanedione with a molar ratio of 1:2. Herein after our titanium precursor containing titanium oxoacetate is called titanium acetate precursor to distinguish it from the titanium acetylacetate complex.

Sol−gel precursors for making slab waveguides were prepared as follows. Four separate titanium acetyl precursors were first prepared by using four kinds of titanium alkoxides. The titanium alkoxide (5 mmol) and acetic acid (3 mL) were mixed and allowed to react for 10 min under vigorous stirring. 2-Propanol (3 mL) was then added to dilute the solution and avoid the formation of polymeric titanium oxoacetate precipitate. The silicon precursor was prepared separately from the titanium precursors. Tetraethoxysilane (TEOS, 20 mmol) and hydrochloric acid (1 N, 8 g) were mixed and stirred for 1 h to accomplish the hydrolysis and polycondensation reactions. A PVP solution was also prepared separately by dissolving PVP with *N*,*N*-dimethylformamide (20 wt %). These three solutions (titanium precursor, silicon precursor and PVP solution) were mixed to have different TiO_2:SiO_2 concentration ratios; however, the concentration of PVP was fixed to be 50 wt % of the resultant products. So 50 wt % TiO_2 means 100% replacement of SiO_2 by TiO_2. According to our previous work,[20] 50 wt % of PVP was necessary to avoid cracking in the waveguides if the thickness is 1 μm or thicker. The weight percent was calculated under an assumption that all the titanium and silicon precursors convert to TiO_2 and SiO_2 after baking. The precursors were spin-coated on glass substrates at proper spinning rates, typically 1500 rpm, to achieve 1.5−3 μm in thickness. The samples were dried and aged overnight at room temperature and densified at 220 °C for 10 min under argon atmosphere. According to our previous work, baking at 220 °C was not only preferable to transform titanium acetyl precursor to TiO_2 but also necessary to crosslink PVP.[20] Baking at temperatures higher than 250 °C produced PVP decomposition, resulting in high absorption losses.

UV−visible transmission spectra were collected on a Shimadzu UV−vis−NIR scanning spectrometer, Model UV-3191PC.

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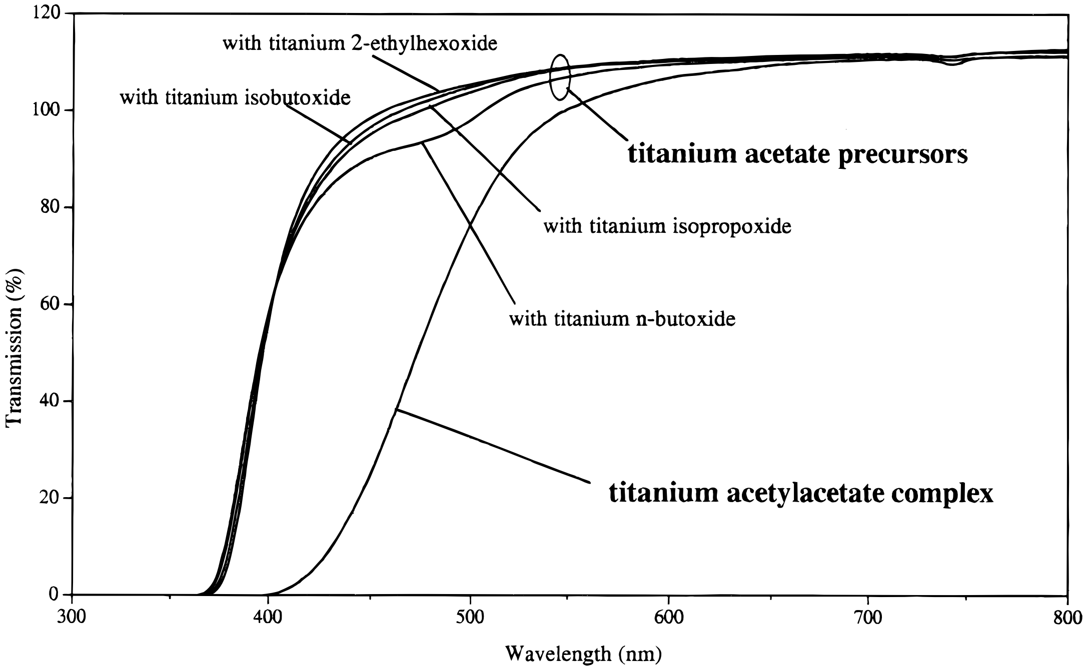

Figure 1. Transmission spectra of various titanium acetate precursors and the titanium acetylacetate complex. The titanium acetate precursors were prepared with a reaction of titanium alkoxides and acetic acid, followed by dilution with 2-propanol.

FT-IR spectroscopy was performed on a Mattson Alpha Centauri Model IR-10300 spectrometer, with KBr windows.

The optical waveguides were prepared on soda-lime glass plates manufactured by Corning (number 2947). If the refractive index of the waveguide was lower than that of the substrate, the waveguide was fabricated on the substrate with a cladding layer (refractive index 1.39).

The refractive index of waveguide samples were calculated from coupling angles measured by the prism coupling technique using a TiO_2 rutile prism and a He–Ne laser (wavelength 632.8 nm; output power 3 mW).[26] Two propagation modes are necessary for each sample to calculate the refractive index, so the thickness must be 1–2 μm. The optical propagation loss was measured by looking at the optical intensity decay of the streak line with a CCD camera. The decay was digitized and plotted in dB units with respect to the displacement of the steak line in cm unit. The slope is the optical propagation loss in dB/cm units.

Results and Discussion

Titanium Sol–Gel Precursors. Acetic acid was used to stabilize the titanium alkoxides, because the yielded compound has little absorption in the visible wavelengths, unlike the case when 2,4-pentanedione was reacted with titanium alkoxide producing acetylacetate complex. However, at room temperature an excess of acetic acid produces a polymeric precipitate: titanium oxoacetate, $TiO(OAc)_2$, in several hours.[24] This causes scattering loss in the resultant optical waveguides. Therefore, 2-propanol was added to avoid formation of high molar mass polymers. We found that when the volumetric ratio of acetic acid and 2-propanol was 1:1 and the molar ratio of titanium isopropoxide to acetic acid was 1:10, the solution remained transparent for a week without the formation of a precipitate. The same was true for all titanium alkoxides used.

To find the best titanium alkoxide for our purpose, several titanium precursors were prepared using a variety of commercial titanium alkoxides, and the optical absorption characteristics were measured. The evaluated titanium alkoxides were titanium isopropoxide, titanium *n*-butoxide, titanium isobutoxide, and titanium 2-ethylhexoxide. Figure 1 shows the transmission spectra of titanium acetate precursors prepared from a variety of titanium alkoxides and titanium acetylacetate complex. They clearly show that the titanium acetate precursors have little absorption at 400 nm and longer wavelength, whereas the acetylacetate complex has a significantly larger absorption up to 600 nm. The titanium acetate precursors are, therefore, expected to produce more transparent waveguides than those prepared from the titanium acetylacetone complex.

These data also show an interesting characteristic of titanium oxoacetate. Figure 2 shows enlarged spectra of that in Figure 1 in the wavelength range 360–430 nm. Here, every spectrum crosses the same point (403 nm in wavelength) which is attributed to be an isosbestic point. On the longer wavelength side of this point, transmission is higher for the stronger electron donating groups and more bulky groups attached to titanium in the alkoxides. The order was 2-ethylhexoxide > isobutoxide > isopropoxide > *n*-butoxide. At the shorter wavelengths than the crossing point, the order was reversed. This may suggest that the reaction between titanium alkoxide and acetic acid produces a single product, titanium oxoacetate, whatever the original titanium alkoxide is, and that titanium oxoacetate has two different forms depending on the condition.

The transmission spectra of pure titanium alkoxides were collected to see the difference from those of the resultant titanium acetyl precursors stated above. Figure 3 shows the transmission spectra of the pure titanium alkoxides diluted with 2-propanol. The solutions were prepared by diluting 4.5 mmol of each titanium alkoxide with 4.3 mL of 2-propanol to have the same alkoxide concentration as the titanium acetyl precursors. The results show that all the titanium alkoxides have better transmission than the titanium precursors shown in Figure 1. It suggests that all titanium alkoxides have reacted with acetic acid and

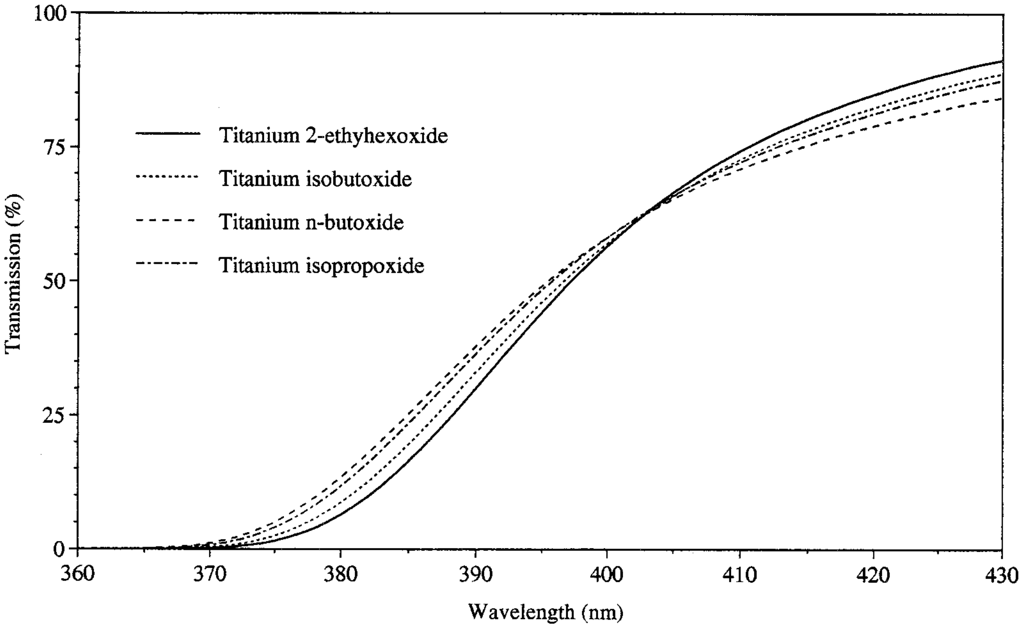

Figure 2. Enlarged spectra of Figure 1 between 360 and 430 nm.

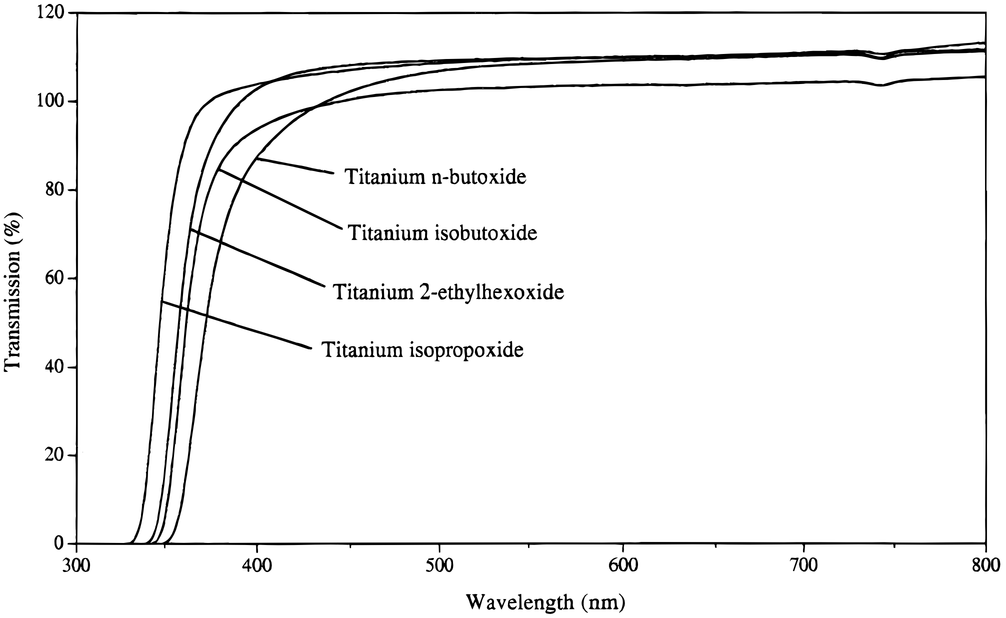

Figure 3. Transmission spectra of titanium alkoxides diluted with 2-propanol.

produced a new species having an absorption peak around 370 nm. This corresponds to titanium oxoacetate.

FT-IR spectroscopy was carried out to detect the presence of titanium oxoacetate in the titanium acetyl precursors. Figure 4 shows the spectra of titanium 2-ethylhexoxide, acetic acid, and a product obtained from the reaction of titanium 2-ethylhexoxide and acetic acid in a molar ratio of 1:1.5. The peaks at 1450 and 1580 cm^{-1} are due to symmetric and asymmetric vibrations of $C(=O)O^-$, and the frequency separation of 130 cm^{-1} indicates the presence of $CH_3C(=O)O^-$ bidentate ligands;[21] however, it is not clear if it is a bidentate chelating or bidentate bridging group. This is the same as what Doeuff et al. reported in their work using titanium n-butoxide and acetic acid.[21] This observation suggests that acetic acid produces direct covalent bonding with titanium in our titanium acetate precursor as well.

The oxidation behavior of titanium oxoacetate was studied by two methods: FT-IR and TGA. The titanium oxoacetate was prepared by a reaction of titanium 2-ethylhexoxide, acetic acid, and 2-propanol. To prepare samples for FT-IR, the titanium oxoacetate solution was spin-coated on KBr plates, and baked at different temperatures in an Ar flow for 10 min. The results of FT-IR are shown in Figure 5. The peaks at 1450 and 1570 cm^{-1}, indicating $C(=O)O^-$ bidentate covalent bonding with titanium, still exist after baking at 260 °C; however, the peaks became much weaker than the original peaks observed after baking at 220 °C. This suggests that even 260 °C is not enough to oxidize titanium oxoacetate totally to TiO_2; however, most of the organic parts are decomposed to TiO_2 at 220 °C.

The titanium oxoacetate solution was subjected to thermogravimetric analysis (TGA). TGA was carried out with a temperature ramp rate of 10 °C/min and in an inert atmosphere. The results are shown in Figure

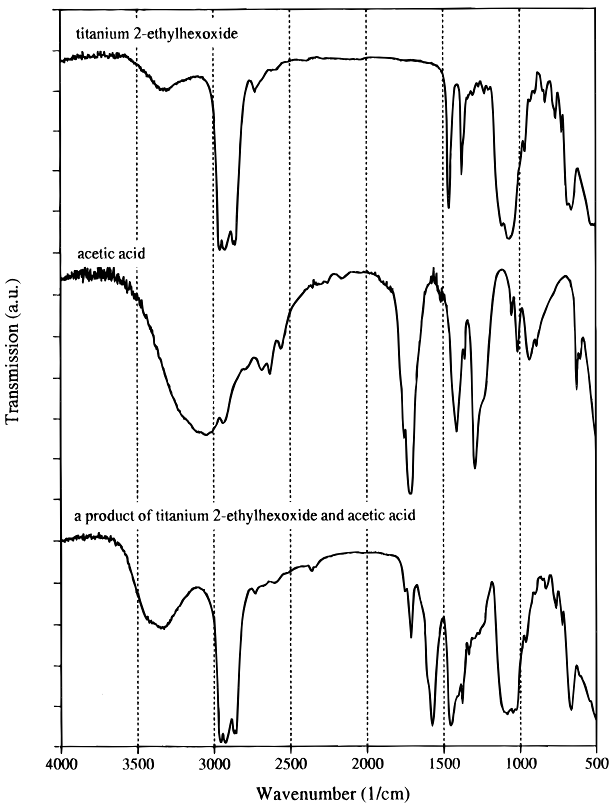

Figure 4. FT-IR spectra of titanium 2-ethylhexoxide, acetic acid, and the product obtained by mixing them in a molar ratio of 1:1.5.

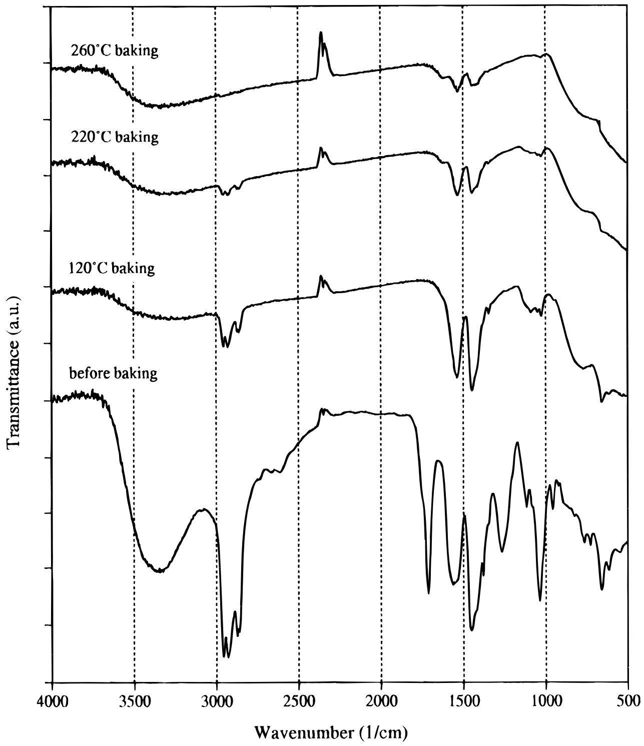

Figure 5. FT-IR spectra of titanium acetate precursor spin-coated on a KBr substrate and being baked at different temperatures for 10 min.

6. Two large peaks are due to evaporation of 2-propanol and acetic acid, and the weight loss is saturated at 280 °C. This suggests that titanium oxoacetate is mostly decomposed to titanium oxide at 280 °C.

Fabrication and Evaluation of Waveguides Using Titanium Acetyl Precursors. The first series of precursors we prepared were 30 wt % TiO_2:20 wt % SiO_2:50 wt % PVP, here in after called 30% TiO_2. The optical propagation loss was evaluated by the prism coupling technique. However, the only waveguide sample possessing low enough optical propagation loss to be measured was that from titanium 2-ethylhexoxide. All other samples had severe scattering losses due to TiO_2 particles. All the precursors were homogeneous and did not show any presence of precipitation before spin-coating, so the TiO_2 particles must be produced during the drying stage. In this stage, 2-propanol evaporates first, followed by the hydrolysis of titanium oxoacetate with the moisture in the air. Here, the concentration of titanium becomes higher than in the original solution, and the titanium compound has a better chance to react with the moisture. The hydrolysis and polycondensation reaction of titanium oxoacetate take place more rapidly compared to the silicon alkoxide, and its heterogeneous reaction yields large TiO_2 particles. Because the titanium oxoacetate may aggregate at first, or form oligomers, and turn to TiO_2 with a reaction of moisture. The bulky 2-ethylhexoxide side group in the titanium precursor seems to help in providing a slow hydrolysis reaction of titanium, resulting in a uniform microstructure which avoids the formation of large TiO_2 particles.

10% and 20% TiO_2 waveguides were also produced using titanium 2-ethylhexoxide by the same way the 30% TiO_2 waveguide was fabricated; they also did not exhibit any scattering losses. However, with 40% or more TiO_2 concentration, titanium 2-ethylhexoxide also yielded waveguides having scattering loss due to the formation of large TiO_2 particles.

It was seen that if the titanium concentration was 20% or less, titanium isopropoxide was also capable of producing waveguides without scattering loss.

To avoid the formation of large TiO_2 particles in the resultant waveguides in high TiO_2 concentration range, peptization was attempted using hydrochloric acid. Peptization with inorganic acid is often used in the sol—gel technique to deaggregate the large hydrolyzates, and to produce fine powders.[28-31]

Peptization of Titanium Acetate Precursor. Peptization was applied to the 30% TiO_2 precursor prepared from titanium isopropoxide. Four sets of the titanium acetate precursor, total volume of 5 mL each, was first prepared by following the procedure mentioned above, and then 1, 2, 3, and 5 drops (1 drop ~ 30 mg) of concentrated hydrochloric acid (37 wt %) were added, respectively. These precursors were spin-coated on glass substrates, followed by baking at 220 °C under argon atmosphere for 10 min. This is the same procedure mentioned above. According to the results of prism coupling, all samples showed very little scattering. However, the waveguide prepared from the precursor with 5 drops of HCl had a high optical propagation loss, 2.40 dB/cm, and that of the waveguides from 1, 2, and 3 drop (HCl) added precursors were 0.41, 0.73, and 0.76

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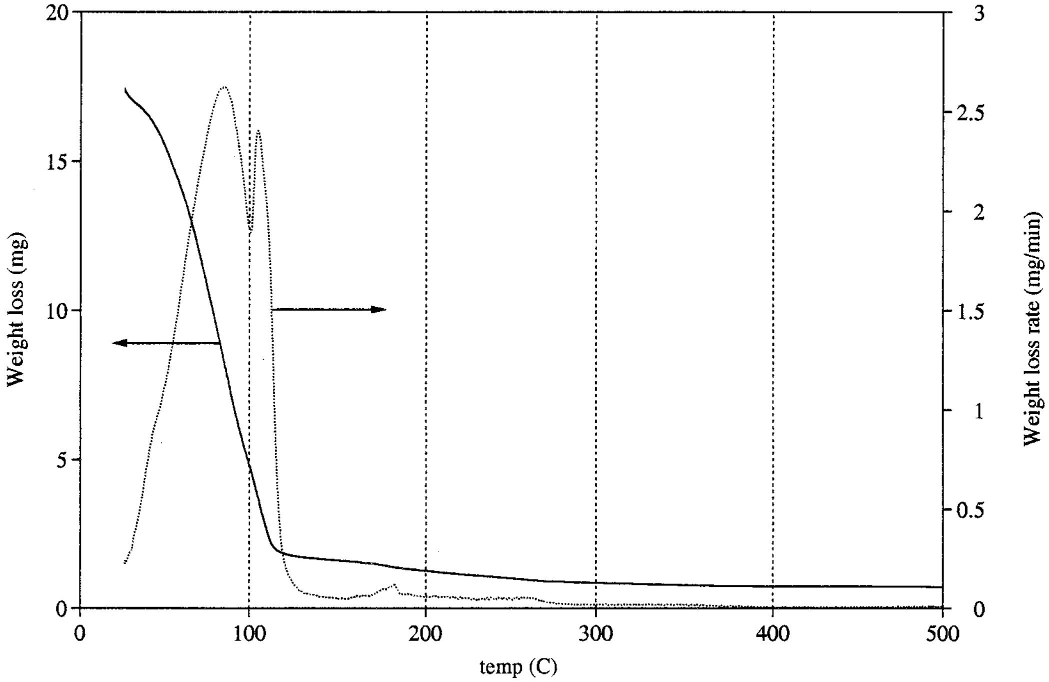

Figure 6. Thermogravimetric analysis (TGA) curve of titanium oxoacetate being prepared from titanium 2-ethylhexoxide, acetic acid, and 2-propanol.

Table 1. Summary of Optical Propagation Loss and Refractive Index Values for Titanium 2-Ethylhexoxide Derived (SiO_2)/(TiO_2)/PVP Composite Waveguides at the Wavelength of 633 nm[a]

TiO_2 wt %	0	10	20	30	40	50
SiO_2 wt %	50	40	30	20	10	0
optical propagation loss (dB/cm)	0.20	0.20	0.43	0.45	0.62	0.52
refractive index	1.490	1.520	1.551	1.584	1.618	1.647

[a] The concentration of PVP was fixed to be 50 wt %.

dB/cm, respectively, at 633 nm. Therefore, the higher the HCl concentration, the higher the optical propagation loss. This high propagation loss is due to the absorption loss of the waveguide. Adding too much hydrochloric acid oxidizes PVP at an elevated temperature during the heating process, and the absorption edge of the decomposed PVP reduces the optical transparency. One drop of HCl to 5 mL was enough to avoid scattering loss in the titanium isopropoxide-derived precursor; however, it is better to avoid peptization if possible, since it oxidizes PVP, resulting in a high absorption loss. Therefore, using titanium 2-ethylhexoxide is a better approach than using titanium isopropoxide with peptization to prepare 30% TiO_2 waveguides.

The same peptization was applied to the 40% and 50% TiO_2 precursors prepared with titanium 2-ethylhexoxide, but 1 drop of HCl was added to the 5 mL of the precursor. The resultant waveguides did not show any severe scattering or absorption loss. Resulting optical propagation losses were 0.62 and 0.52 dB/cm for 40 and 50% TiO_2 waveguides, respectively. Table 1 summarizes the results of optical propagation losses in titanium 2-ethylhexoxide-derived composite waveguides, together with the results of measured refractive indexes. The refractive indexes are also plotted in Figure 7 as a function of concentration of TiO_2. The data for a 0% TiO_2 waveguide was taken from our previous work on PVP/SiO_2 composite materials.[20] For all the titanium concentrations, propagation losses of 0.62 dB/cm or lower were achieved by avoiding both scattering and absorption losses. Additionally, a manipulation of refractive index in the range 1.39−1.65 was accomplished by changing the ratio of SiO_2 and TiO_2. The variation of the refractive index was proportional to the concentration of TiO_2. Figure 8 shows an example of the results from the optical propagation loss measurement.

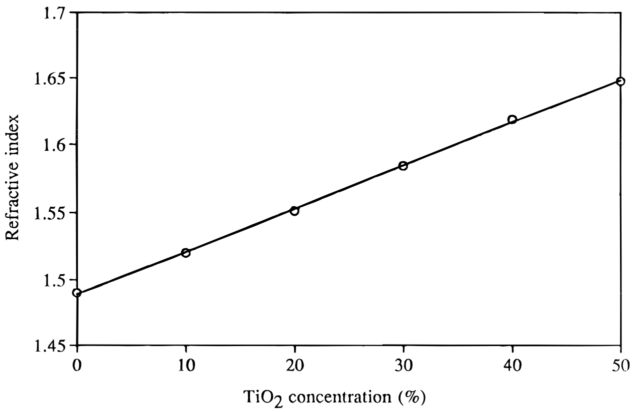

Figure 7. Refractive index change of the titanium 2-ethylhexoxide derived (SiO2)/(TiO2)/PVP waveguides as a functional of the TiO2 concentration. The concentration of PVP was fixed at 50 wt %. The TiO_2 and SiO_2 concentrations were calculated under an assumption that all the titanium and silicon atoms were present as TiO_2 and SiO_2, respectively.

We employed FT-IR spectroscopy to study the reaction of the sol−gel precursor with HCl in the peptization reaction. Titanium 2-ethylhexoxide and acetic acid were mixed in the 1:1.5 molar ratio to a total volume of 5 mL, and stirred for 10 min to allow to produce titanium oxoacetate. One drop of HCl was added to the solution. Surprisingly, the solution turned opaque and formed precipitate immediately. The FT-IR spectra of the solution before and after the addition of HCl are shown in Figure 9. The two spectra did not show any difference. This result suggests that HCl catalyzes the formation of titanium oxoacetate and does not work for

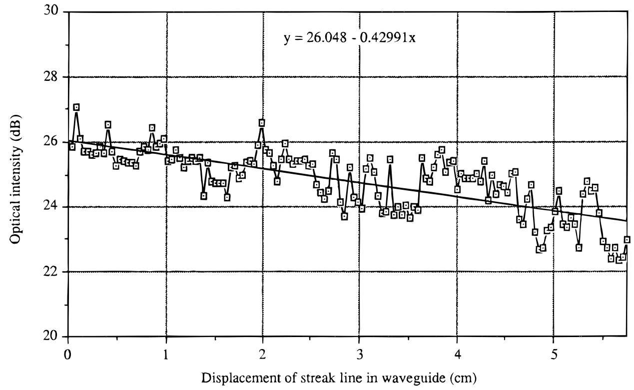

Figure 8. Optical intensity decay of a streak line with respect to the displacement in a 20% TiO_2 waveguide. The slope of the line, 0.43, is the optical propagation loss in units of dB/cm.

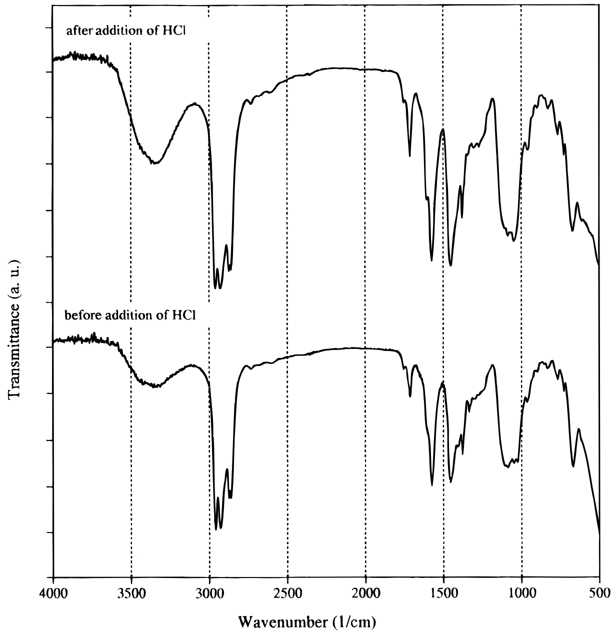

Figure 9. FT-IR spectra of a solution before and after the addition of 1 drop of HCl. The solution is prepared from titanium 2-ethylhexoxide and acetic acid with a molar ratio of 1:1.5.

peptization in this case. We then prepared the titanium acetyl precursor from titanium 2-ethylhexoxide, acetic acid, and 2-propanol, by following the same procedure stated above. One drop of HCl was added to it. The solution did not turn opaque and stayed clear. The FT-IR spectra of this solution before and after the addition of HCl are shown in Figure 10. The triangle marks in the spectrum indicate peaks of pure acetic acid (936, 1015, 1294, 1414, and 1713 cm^{-1}). This suggests that the addition of HCl reproduces acetic acid. This must be due to the hydrolysis of titanium oxoacetate to acetic acid and titanium hydroxide and/or titanium chloride. So this result supports that the addition of HCl to the titanium acetyl precursor deaggregates the titanium oxoacetate oligomers. Therefore, peptization avoids the formation of large TiO_2 particles in the resultant waveguides.

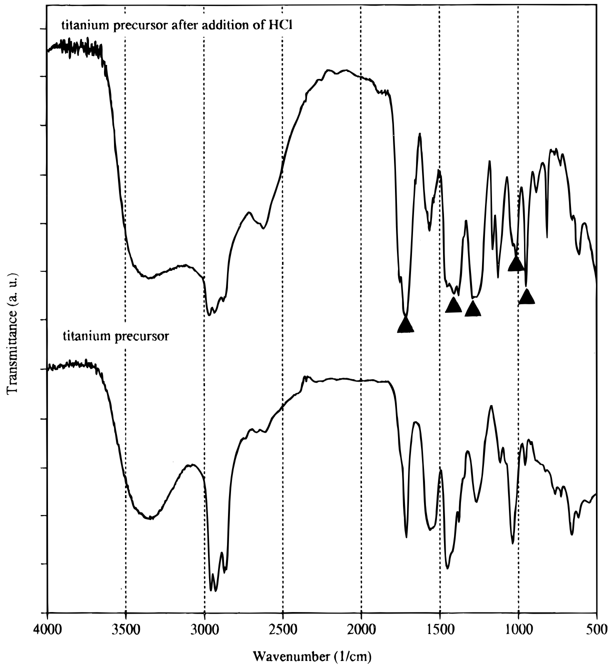

Figure 10. FT-IR spectra of the titanium acetate precursor and that after addition of 1 drop of HCl for peptization. The triangles indicate peaks due to acetic acid.

Conclusions

A composite material system, SiO_2, TiO_2, and PVP, was studied in the optical slab waveguide configuration. Minimization of both absorption and scattering losses were studied in this paper. Titanium alkoxides have fast hydrolysis and easily produce large TiO_2 particles which cause severe scattering losses in resultant optical waveguides. Acetic acid reacts with titanium alkoxides to produce a relatively stable compound, titanium oxoacetate. The formation of titanium oxoacetate was confirmed by FT-IR and UV–visible spectra. The compound forms polymeric precipitate after several hours which causes scattering losses. However, we found the solution keeps it homogeneous when the same amount of 2-propanol was added to the solution. Among many titanium alkoxides, titanium 2-ethylhexoxide was found to be the best for producing a homogeneous precursor, since it has bulky side groups which provide steric hindrance to slow the hydrolysis rate. The combination of acetic acid as a solvent and titanium 2-ethylhexoxide as a titanium alkoxide was capable of producing waveguides with low optical propagation losses, 0.45 dB/cm or lower at 633 nm. However, at the high TiO_2 concentration, 40% or more, it provided waveguides showing severe scattering losses due to large TiO_2 particles. Peptization was applied in this range. Peptization with small amount of hydrochloric acid breaks up oligomers of titanium oxoacetate. This precursor yielded transparent waveguides having optical propagation losses of 0.62 dB/cm or lower. The FT-IR spectra suggested that peptization reproduces acetic acid. With our approach, it was possible to manipulate the refractive index from 1.39 to 1.65 by changing the concentration of TiO_2 with respect to SiO_2, keeping optical propagation losses low.

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