Articles

The Effect of Processing Variables on Structural Changes and Optical Properties of SiO_2-TiO_2 Sol-Gel Derived Films

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The structural evolution during the thermal treatment of $70SiO_2$-$30TiO_2$ (mole%) sol-gel derived powders and films was investigated by FT-IR, Raman and XPS, and XRD. From these results, the TiO_2-rich regions involving Ti^{4+} ions in octahedral coordination were confirmed to be amorphous at 600 °C. However, Raman spectra along with XRD patterns indicated that at high temperature (above 700 °C), the amorphous TiO_2 was segregating to form anatase crystal. Also, the effect of experimental variables such as thermal treatment, heating rate and exposure to water vapor on structural changes, refractive index and thickness of the film coated on soda-lime-silicate glass were investigated.

Introduction

Sol-gel processing has attracted wide attention due to its capability to control the structure and microstructure of product. Also this technology offers one of the promising means of preparing films of amorphous and crystalline metal oxides which can be used in many optical devices.[1,2] Sol-gel processing of silica-titania gel films is of significant technological interest since it enables fine control of refractive index and thickness for optical application such as antireflection, planar waveguides for integrated optics and weather resistant optical memory discs.[3-5] SiO_2-TiO_2 glasses are known to exist with interesting properties, *i.e.*, up to about 10 mol% TiO_2 with titanium in fourfold coordination and up to 16 mol% in a metastable state with titanium separated in a second phase and octahedrally coordinated.[6]

A larger amount of titanium is not retained in the amorphous network and separates as a crystal phase. The sol-gel process has provided a unique method to prepare TiO_2-SiO_2 glasses with high TiO_2 concentration. When SiO_2-TiO_2 films or powders are prepared through sol-gel method, inhomogeneities may arise due to different reactivities of silicon and titanium alkoxides. Homogeneity of the gel phase depends on the chemical procedure and the experimental parameters. In this study, effects of experimental variables such as temperature and duration of heat treatment, heating rate and prevailing atmosphere on structural changes, refractive index and thickness of the films coated on soda-lime-silicate glass were investigated. Also we studied structural evolution of $30TiO_2$-$70SiO_2$ sol-gel derived powders and films which occurred during thermal treatment by FT-IR, Raman, XPS and XRD. The refractive index and the thickness of the film were obtained from the fringe pattern of the UV-VIS transmission spectra using Envelope method.[7]

Experimental Section

The preparation procedure of the $70SiO_2$-$30TiO_2$ (mole%) sol-gel derived powders and films was essentially the same as that described in the literature.[8] The starting solution of $Si(OC_2H_5)_4$, ethanol and HCl was partially hydrolyzed for 2 hrs before addition of titanium isopropoxide, $Ti[OCH(CH_3)_2]_4$, diluted with ethanol. Next, water was added until the final molar ratio (Rw) of water to alkoxides reached one. The solution was stirred for 2 hrs at room temperature and passed through a 0.2 μm pore filter attached to a syringe to remove foreign particles before the solution was applied to the substrate.

We used soda-lime-silicate glasses as substrates and they were ultrasonically cleaned in acetone and ethanol, rinsed with de-ionized water and dried in oven. Films were deposited on the substrate by spin coating at 2000 rpm for 30 seconds and heat treated at 300 °C for 1 min after each deposition. After drying, the coated films were immediately placed into the furnace preheated at the desired temperature and held for 1 hr. Gel powders were obtained from the solutions poured into petri-dishes and maintained in oven for 7 days at 100 °C.

The coated films or powders were characterized by differential thermal analysis (DTA), thermogravimetric analysis (TGA), X-ray diffractometry (XRD), X-ray Photoelectron Spectroscopy (XPS), UV-Visible spectroscopy (UV-VIS), Fourier transform infrared spectroscopy (FT-IR), and Raman spectroscopy. DTA and TGA were performed using a TA instrument SDT 1500 on the powders at a heating rate of 5 °C/min. XRD was carried out for the powders and films using a Philips PW 3719 diffractometer equipped with a thin film attachment. The X-ray radiation source was Cu K_α, operated at 40 kV and 25 mA. The FT-IR spectra of the coated films and powders were measured with a Bio-Rad FTS-155 in the range 400 cm^{-1}-4000 cm^{-1} with a resolution of 2 cm^{-1}. The Raman spectra of the gel powder in a capillary tube were obtained with a double monochrometer (SPEX) using 514.5 nm Ar^+ exciting line. The UV-VIS. transmission spectra were taken from $70SiO_2$-$30TiO_2$ films in the range of

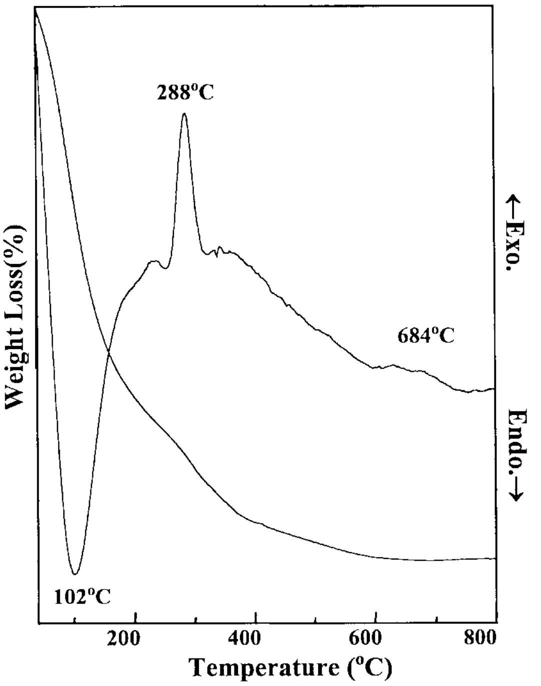

Figure 1. DTA-TGA curves of $70SiO_2$-$30TiO_2$ (mol%) gel powders (heating rate: 10 °C/min, in air).

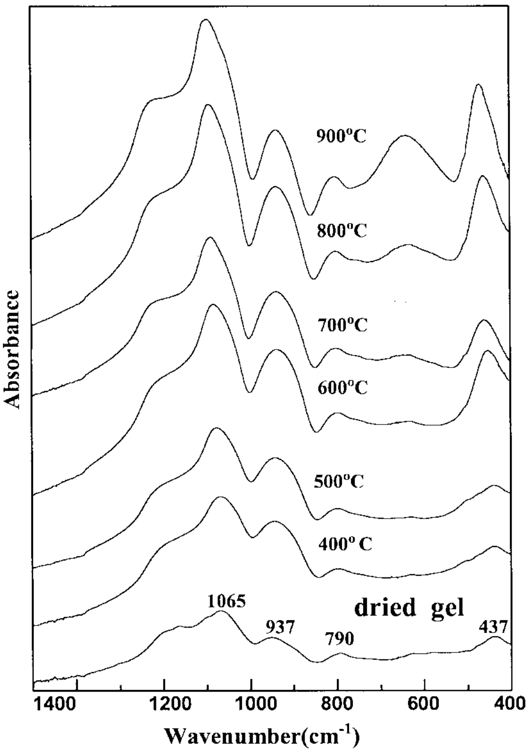

Figure 2. FT-IR spectra of 70 SiO_2-$30TiO_2$ (mol%) gel powders sintered at various temperatures for 1hr.

300-800 nm by a Shimadzu UV 2401.

Results and Discussion

SiO_2-TiO_2 gel powders. DTA and TGA curves obtained from gel powders are shown in Figure 1. At around 100 °C an endothermic effect due to the evaporation of water is observed. The major weight loss below 200 °C is considered to be due to the evaporation of adsorbed water, the vaporization and the thermal decomposition of the organic solvents. The strong exothermic peak at about 290 °C is attributed to combustion of $-OC_2H_5$ groups in organic compounds. Between 300 °C and 600 °C, the gradual weight losses are ascribed to the further combustion of organic compounds such as $-OC_3H_7$ groups, and $-OCH_3$ groups. Since there is no significant weight loss above 600 °C, it can be concluded that the organic groups in the sample have been completely burnt off. Another weak broad exothermic peak is present at around 608 °C which is possibly related to the phase transformation of TiO_2 from amorphous state to anatase crystalline state.

Figure 2 illustrates the FT-IR spectra of $70SiO_2$-$30TiO_2$ (mol%) binary system after thermal treatment at various temperatures. As shown in this spectra, dried gel powder possesses characteristic bands at ~437, 790, 937 and 1065 cm^{-1}. The main band at the frequency of about ~1065 cm^{-1} is assigned to Si-O-Si anti-symmetric stretching and the lower frequency peak near 450 cm^{-1} is assigned to rocking motions of the oxygen atoms perpendicular to the Si-O-Si plane.

The band at 799 cm^{-1} is ascribed to Si-O-Si symmetric stretching vibration. The strong band at the frequency of about ~950 cm^{-1} which becomes more intense upon heating is attributed to stretching vibrations of Si-OH or Si-O- groups superimposed to Si-O-Ti stretching.[9,10] Condrate *et al.* investigated the titanium coordination in SiO_2-TiO_2 glasses containing up to 65 mole% TiO_2 by Raman spectroscopy.[11] They suggested that a nominal concentration of Ti^{4+} ions can be incorporated into the silica network in tetrahedral coordination and the remainder of TiO_2 will be found in the TiO_2-rich glass phase.

Figure 3 and 4 illustrate the Raman spectra and XRD patterns of a thermally treated $70SiO_2$-$30TiO_2$ gel powder at various temperatures, respectively. Below 700 °C, the gel powder exists in the amorphous phase. Significant change of the spectra occurs after heat treatment at 700 °C. The intense peak at 144 cm^{-1} in Figure 3 is, in general, a sensitive indicator for the presence of anatase crystal since its intensity is at least 25 times larger than other TiO_2 bands. Thus observed peaks at 144 cm^{-1}, 399 cm^{-1}, 516 cm^{-1} and 653 cm^{-1} of the Raman spectra are attributed to characteristic peaks of anatase crystals.[12]

However, the relative intensities of bands at ~940 cm^{-1} and ~1090 cm^{-1} of IR peaks in Figure 2 associated with vibrational modes involving SiO_4 units linked with titanium atoms remain unchanged after thermal treatment at 700 °C. These facts indicate that most of the Si-O-Ti bridges remain intact in the glass, and the amorphous TiO_2 in the TiO_2-rich phase is segregating to form anatase above 700 °C.

Also, additional broad band at about 650 cm^{-1} associated with the formation of anatase crystals was evident in the figure, particularly at high temperature. This band which was

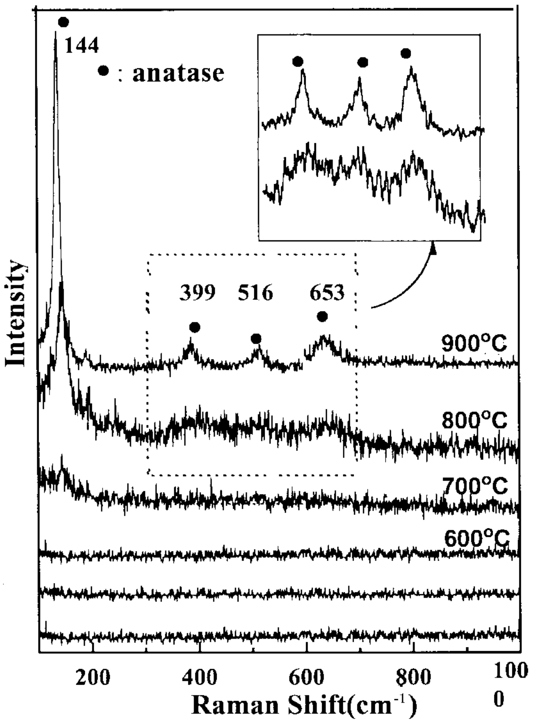

Figure 3. Raman spectra of 70SiO_2-30TiO_2 (mol%) gel powders sintered at various temperatures for 1hr.

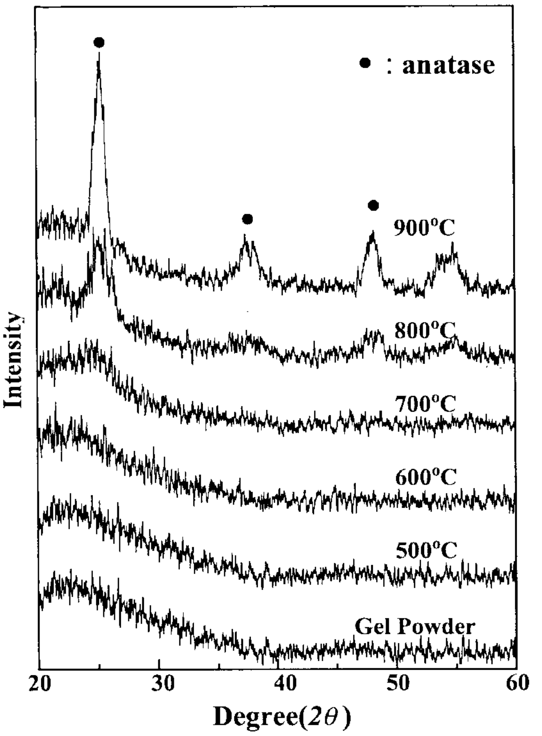

Figure 4. XRD patterns of 70SiO_2-30TiO_2 (mol%) gel powders sintered at various temperatures for 1hr.

absent below 700 °C was assigned to Ti-O-Ti/Ti-OR vibration. This interpretation is consistent with the result obtained from XRD patterns of SiO_2-TiO_2 in Figure 4.

SiO_2-TiO_2 gel film

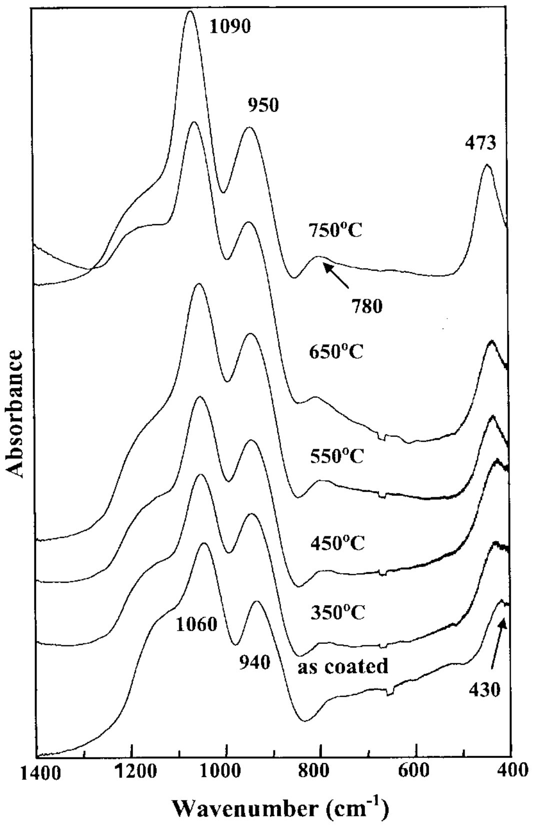

Figure 5. FT-IR spectra of 70SiO_2-30TiO_2 (mol%) thin films heat-treated at various temperatures for 1hr.

The effect of heating temperature: Figure 5 shows the FT-IR spectra of as-coated and heat-treated films at various temperatures for 1 hr. The absorption bands associated with the Si-O-Si antisymmetric stretching and Si-O-Si out-of-plane bending mode were observed at 1060 cm^{-1} and 473 cm^{-1}, respectively. These peaks move toward higher wavenumbers as the thermal treatment temperature increases. The shift to higher frequency and the sharpening of the bands indicate that the gel-glass film is strengthened by bond shortening and a reduction in mean Si-O-Si bond angle and angular distribution for this feature.

The refractive index and the thickness of film prepared with different experimental conditions such as temperature and duration of heat-treatment, heating rate and prevailing atmosphere were obtained from fringe pattern of the UV-VIS spectra using Envelope method.[7] One can write the refractive index and the thickness as

$$d = \frac{M\lambda_1\lambda_2}{2[n_{\lambda_2}\lambda_1 - n_{\lambda_1}\lambda_2]} \qquad n = [N+(N^2 - n_0^2n_1^2)^{1/2}]^{1/2}$$

d : film thickness, λ : incident wavelength
N : complex refractive index of film
n : refractive index of film, n_0 : refractive index of air
n_1 : refractive index of substrates
M : the number of oscillations between the two extrema

The film thickness and refractive index of the sample as a

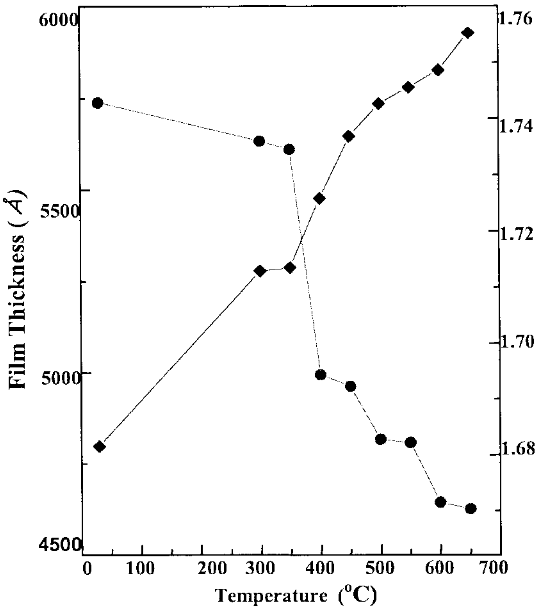

Figure 6. Film thickness (●) and refractive index (◆) of 70SiO$_2$-30TiO$_2$ (mol%) thin films heat-treated at various temperatures for 1 hr.

function of heating temperature are shown in Figure 6.

The decrease in film thickness from ~5700 Å to ~4600 Å and increase in refractive index from ~1.68 to 1.76 are observed as the heating temperature is increased. Also, the effect of duration of thermal treatment on refractive index and thickness of the films heat-treated at 600 °C were determined (Table 1).

When the films were heat-treated up to 2 hrs, the refractive index of films increased along with the decrease in the film thickness. However, when the films were heat-treated longer than 2 hrs, the refractive index decreased while the film thickness remains unchanged.

It was reported that sodium ions diffused from glass substrate into SiO$_2$-TiO$_2$ film, lowering the refractive index of film.[13] In order to clarify whether this phenomenon really occurs, XPS analysis of films was performed at various baking times and illustrated in Figure 7. When the film was heat-treated longer than 2 hrs at 600 °C, sodium ions diffused from the soda-lime glass substrate towards the film layer.

The photoelectron spectra of Na(1s) electron show a symmetric single peak for the SiO$_2$-TiO$_2$ thin films. The binding energy of Na(1s) peak is 1072 eV.

Table 1. The variation of refractive index and thickness of the films heated at 600 °C for various holding time

Sample (holding time)	Refractive index	Film thickness (Å)
10 min	1.726	2975
30 min	1.731	2915
60 min	1.735	2887
120 min	1.751	2730
2400 min	1.745	2735
4800 min	1.741	2730

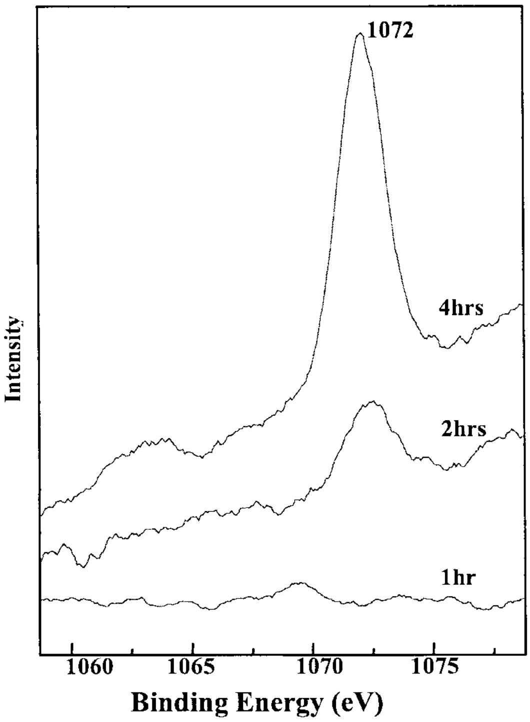

Figure 7. XPS Na (1s) region for 70SiO$_2$-30TiO$_2$ (mol%) thin films heat-treated at 600 °C for different holding times.

The effect of the heating rate: The effect of the heating rate on the refractive index and the thickness of film is shown in Table 2. As shown in the table, the refractive index of the film prepared by direct insertion method showed a larger value than that of the film heat-treated by low heating rate, 5 °C/min. Also, the thickness of the film prepared by the direct insertion method was thinner than that prepared by the low heating rate.

Therefore, we can conclude that the direct insertion method induces a higher packing density while the slow heating process produces a rather open structure due to slow shrinkage of the gel film. Also larger quantities of sodium ions have diffused by the slow heating process which contributes partially to the lower refractive index of the film compared with that of the film prepared by the direct inser-

Table 2. The variation of refractive index and thickness of the films heated at various temperature with different heating rate

Sample (°C)	Refractive index		Film thickness (Å)	
	5 °C/min	direct insertion method	5 °C/min	direct insertion method
300	1.713	1.740	5632	4763
350	1.714	1.746	5610	4516
400	1.726	1.750	4994	4457
450	1.737	1.750	4962	4439
500	1.743	1.752	4816	4256
550	1.746	1.753	4807	4275
600	1.749	1.759	4643	3966
650	1.755	1.775	4625	3616

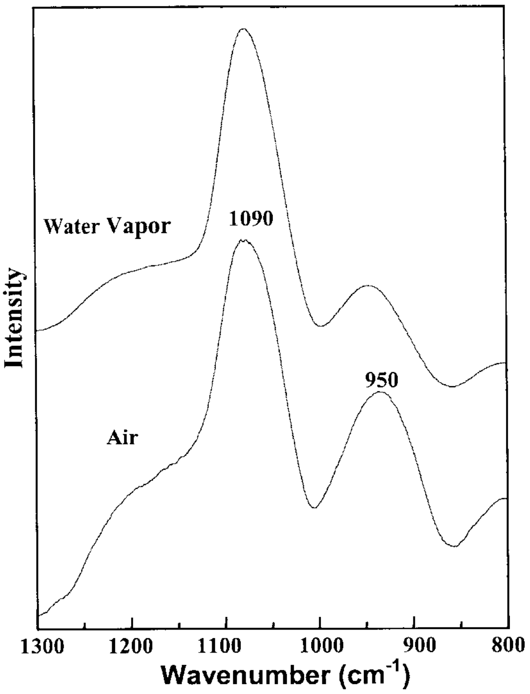

Figure 8. FT-IR spectra of $70SiO_2$-$30TiO_2$ (mol%) thin films prepared with different atmosphere.

tion method.

The effect of water vapor: Structure of sol-gel derived SiO_2 and TiO_2 films were reported to be modified by the exposure to water vapor.[14,15] In order to investigate the effect of water vapor on structure of SiO_2-TiO_2 films, the samples were heat-treated at various temperatures for 1hr with and without water vapor.

Hirashima suggested that water vapor attacked strained M-O-M (M: Si or Ti) bonds in the gel network and induces a cleavage of the bonds with hydrolysis reaction.[14]

The bond cleavage increases the flexibility and promotes the rearrangement of the network. Finally, relatively stable bonds are formed by the condensation which causes removal of water molecules as given by

$$\text{M-O-M (strained)} + H_2O \rightarrow \text{M-OH HO-M} \rightarrow$$
$$\text{increasing flexibility}$$
$$\text{M-OH HO-M} \rightarrow \text{M-O-M (stable)} + H_2O \rightarrow$$
$$\text{densification or crystallization}$$

Figure 8 shows the changes in the intensity of the absorption peak at 950 cm^{-1} due to Si-O-Ti and Si-OH stretching vibration in the two different atmospheres.

Intensity of this peak decreased by exposure to water vapor indicating that the Si-O-Ti bonds are easily dissociated by the attack of water vapor. Stable M-O-M bonds are formed by the condensation which causes the removal of water accompanied with densification and/or crystallization.

The higher refractive index and thinner thickness of the film by the exposure to water vapor compared with the dry atmosphere in Figure 9 support the above mentioned assumption.

Conclusion

The structural evolution during thermal treatment of $70SiO_2$-$30TiO_2$ (mole%) system has been examined by FT-IR and Raman spectroscopy. Also, structural changes and physical properties of the films were investigated in connection with the processing conditions.

Major findings of this work are as follows.

1. The FT-IR spectra of TiO_2-SiO_2 powder and films exhibited same peaks as those present for vitreous silica at ~437, 790 and ~1065 cm^{-1}. As the heating temperature

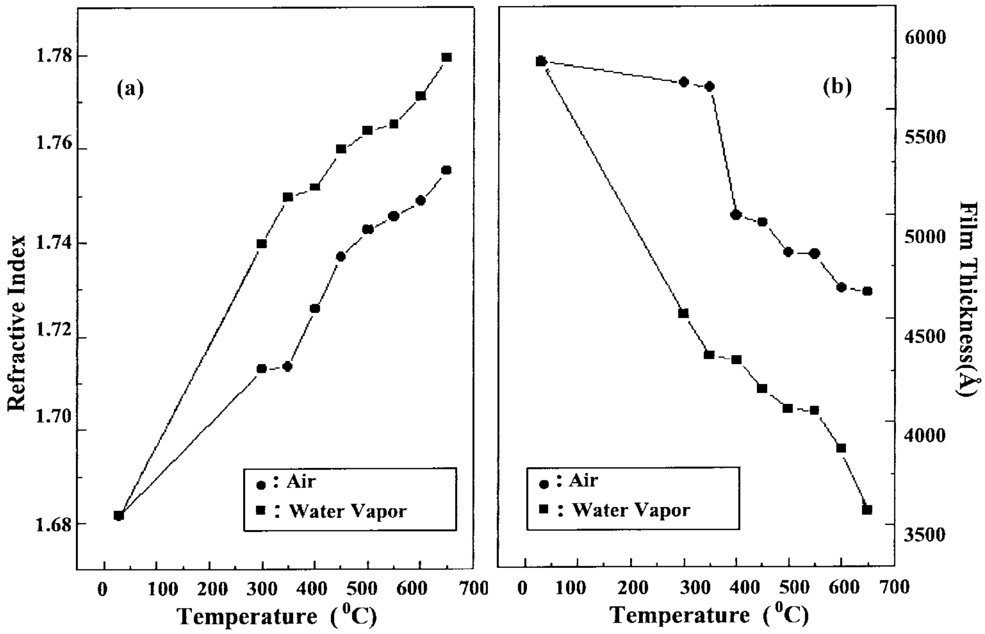

Figure 9. (a) Refractive index and (b) film thickness of $70SiO_2$-$30TiO_2$ (mol%) thin films heat-treated at various temperatures for 1hr with different atmosphere.

increased, the sharpening of the bands and the shift to higher frequency were observed. This indicates that bond shortening and a reduction in mean Si-O-Si bond angle occurred with increasing thermal temperature.

2. The TiO_2 coordination in $70SiO_2$-$30TiO_2$ (mole%) system was investigated with infrared and Raman spectroscopy along with X-ray diffraction. A limited concentration of Ti^{4+} ions were incorporated into the silica network and the remainder of TiO_2 in the TiO_2-rich phase octahedrally coordinated were confirmed to be amorphous at 600 °C. At high temperature (above 700 °C), the amorphous TiO_2 in the TiO_2-rich phase was segregating to form anatase crystal.

3. When films were heat-treated up to 2 hrs at 600 °C, the refractive index of films increased while the film thickness decreased. However, when the films were heat-treated longer than 2 hrs at 600 °C, the refractive index decreased due to diffusion of sodium ions from glass substrate into the film. This fact was confirmed by XPS measurement (BE Na(1s)=1072 eV).

4. The refractive index of the film prepared by direct insertion method showed a larger value than that of the film heat-treated by low heating rate, 5 °C/min.

5. The effect of water vapor on structure of SiO_2-TiO_2 films, refractive index and the thickness of the films heat-treated at various temperatures for 1hr with and without water vapor were measured. The intensity of the absorption peak at 950 cm^{-1} due to Si-O-Ti stretching vibration decreased by exposure to water vapor indicating a cleavage of the bonds with hydrolysis reaction.

When the films were exposed to water vapor, films with higher refractive index and thinner thickness were obtained compared with the dry atmosphere.

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