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The optical waveguiding properties of TiO_2–SiO_2 composite films prepared by the sol–gel process

Zhai Jiwei [a,*], Yang Tao [b], Zhang Liangying [a,b], Yao Xi [a,b]

[a] *Functional Materials Research Laboratory, Tongji University, Shanghai 200092, China*
[b] *Electronic Materials Research Laboratory, Xi'an Jiaotong University, Xi'an 710049, China*

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Abstract

We have studied the optical waveguide properties of sol–gel coated TiO_2–SiO_2 composite thin films. With increasing TiO_2 content the loss of thin films was increased. The loss of thin films was increased and then decreased with increasing annealing temperature. FT–IR spectra, XRD, AFM, and SEM analyses showed that this loss resulted from the scattering of segregations and non-uniform distribution in the films. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

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1. Introduction

Optical quality dielectric films are a basic requirement for integrated optical devices fabricated on silicon substrates. TiO_2 and SiO_2 are commonly used materials in optical thin film in the visible and near-infrared wavelength ranges. Thin films of these materials have a large refractive index difference. The large range of intermediate index values that can be obtained by mixing these materials makes them desirable in step index coatings. A number of methods have been applied to fabricate TiO_2–SiO_2 composite films, including e-beam evaporation [1], chemical vapor deposition [2], flame hydrolysis [3] and sol–gel [4]. The interest in the use of sol–gel methods is due to several advantages: good homogeneity, ease of composition control, low processing temperature, large area coatings, and low equipment cost.

Sol–gel glass has been successfully used in thin planar layer [4]. Segregation and crystallization can degrade optical properties since the resulting inhomogeneous structure consisting of high refractive index ($\sim$2.4) crystalline TiO_2 embedded in the silica rich, low-index matrix can cause considerable scatter. A major factor of the waveguide loss is the surface roughness and inhomogeneity. In addition to the nature of the alkoxide precursors, the physical properties of a sol–gel film are dependent on the processing conditions, firing temperature, and the cleanliness of preparing environment.

The purpose of this work is to investigate the effects of TiO_2 crystallization on films microstructure, processing conditions and their waveguiding properties.

2. Experimental procedure

A silica–titania solution was made using the following procedure. TEOS was mixed with isopropanol, water and several drops of HCl to bring the pH to 2. TEOS:isopropanol:water:HCl = 1:4:4:0.03. The solution was refluxed at 70°C for 60 min. In a separate container, titanium butoxide was mixed with acetylaceton (AcAc). Titanium butoxide/AcAc = 1/2, was allowed to react for 30 min, after which the solutions were mixed together, then diluted as equal to volume solution with isopropanol. Films with various molar composition of Ti/Si were deposited onto SiO_2/Si(111) substrates (the thickness of SiO_2 is 1000 nm) by spin-coating at 2500 rpm for 20 s in 100 clean room. The films were coated about eight times and final thickness was about 1.8 μm of the annealing. The films were heat treated at various temperatures, in the 500–850°C temperature range for 30 min. Phase analyses of the prepared samples were performed using standard X-ray diffraction techniques, with a Rigaku K/max 2400 type diffractometer with Cu K_α radiation and a Ni filter. FT-IR transmission spectra

* Corresponding author.

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of sol–gel films were measured using a Nicolet 60 SXR FT–IR spectrophotometer. Microstructure was examined using a Hitachi S-2700 scanning electron microscope (SEM).

3. Results and discussion

The waveguiding loss was determined by the light scattering method [5]. Assuming the scattering in the films is uniform, hence the intensity $I(x)$ of the guided mode is proportional to the scattering intensity $I_{sc}(x)$ at the same position, and the attenuation coefficient α in units of dB/cm will be

$$\alpha = -\frac{10\log\left[\frac{I_{sc}(x)}{I_{sc}(0)}\right]}{x}$$

Waveguiding loss for films after different heat treatment temperature and different TiO_2 content are shown in Tables 1 and 2. With increasing TiO_2 content the waveguiding loss of thin films were increased. The loss of $50TiO_2$–$50SiO_2$ films were increased and then decreased with increasing heat treatment temperature.

Table 1
TiO_2 content versus optical waveguide loss (650°C, 30 min)

Ti/Si	20/80	30/70	50/50	100/0
Loss (dB/cm)	2.2	5.3	11.4	42

Table 2
Heat treatment temperature versus optical waveguide loss

Heat treatment temperature (°C)	500	650	750	850
Loss (dB/cm)	7.4	11.4	13.2	8.6

For a given heat treatment condition, films with 50 mol% titania developed amorphous state into crystalline anatase, and from mixtures of anatase and rutile into rutile, as shown in Fig. 1. The grain size of TiO_2 is calculated from X-ray diffraction line broadening using the Scherrer formula, where the broadening due to non-uniform stress is neglected. Table 3 shows variation of the particles size of TiO_2 with heat treatment temperature. The particle scattering can be neglected. For instance, crystallites smaller than 7.6 nm at 850°C for 30 min are only 1/83 of the wavelength of light of 632 nm. The crystalline particles are too small to affect the optical properties.

FT–IR spectra were acquired from both the coated (three layers) and uncoated wafer to enable the Si absorption background to be subtracted. The FT–IR spectra of $x$$TiO_2$–$(100-x)SiO_2$ ($x=0\sim100$) thin films coating to two side polished Si(111) substrates are provided in Figs. 2 and 3. The silica sample, exhibits the symmetric stretching vibration band at 809 cm^{-1} and the asymmetric vibration band at 1090 cm^{-1} of the tetrahedral SiO_4^{4-} structure unit. The band at about 550 cm^{-1} is representative of titanium dioxide [6]. The absorption peak at 955 cm^{-1} in the $8TiO_2$–$92SiO_2$ films is a result of overlapping of the bands due to Si–OH and Si–O–Ti vibrational modes [7]. The position of this Ti–O–Si band is 955 cm^{-1} in the 8/92 sample and 937 cm^{-1} in the 50/50 sample. As the annealing temperature was increased, this band shifted to higher frequencies 1090 cm^{-1} and broadened. The intensity trend indicates that most of the Si–O–Ti bridges remain intact in the films when heat treatment temperature is in the 500~700°C

Table 3
Grain size of TiO_2 versus different heat treatment temperatures

Heat treatment temperature (°C)	700	750	850	900	950
Grain size (nm)	2.8	3.8	7.6	11.5	14.0

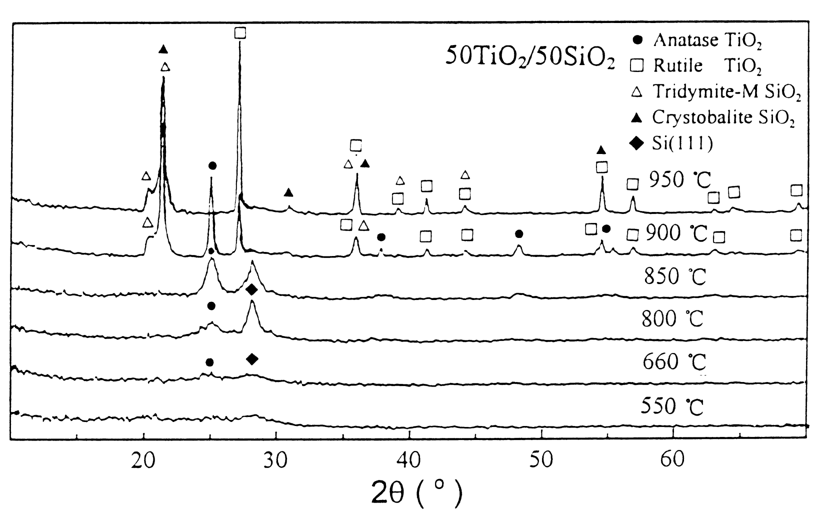

Fig. 1. XRD spectra for $50TiO_2$–$50SiO_2$ films versus heat treatment temperature.

range. One can conclude that mainly titanium oxide in the TiO_2-rich phase is segregating to form anatase in the films during heat treatment at 750°C. The characteristic bands for the Si–O–Ti bridges decrease with increasing heat treatment temperature (750–850°C temperature range). The band intensity decreased at elevated temperature, which is emphasized because the onset of TiO_2 crystallization should be accompanied by a reduction in Ti–O–Si linkage. From Table 1 one can conclude that the waveguiding loss was obviously affected by the segregation. The origin of the shifted-broadening may be thermal oxidation of Si–OH to Si–OH, which absorbs in the 930–960 cm^{-1} region [8].

AFM image of $50TiO_2$–$50SiO_2$ films show that the surface of films roughness is lower than 2 nm of the annealing at 650°C for 30 min. After annealing at 850°C for 30 min the roughness is only 4 nm. Therefore the roughness of surface did not obviously affect the waveguide loss. Scanning electron microscopy was used to examine the surface morphology of films. The image of film surface annealed at 650°C for 30 min in O_2 is shown in Fig. 4a. The image of film surface annealed at 850°C for 30 min in O_2 shown in Fig. 4b was devoid of structure and homogeneous down to the sub-micrometer scale. In contrast, an inhomogeneous, phase separated surface morphology was observed in the image of the sample annealed at 650°C. From Table 3 one can observe that the optical waveguiding loss is increased and then decreased with heat treatment temperature. The waveguiding loss results from the submicrometer inhomogeneous film surface.

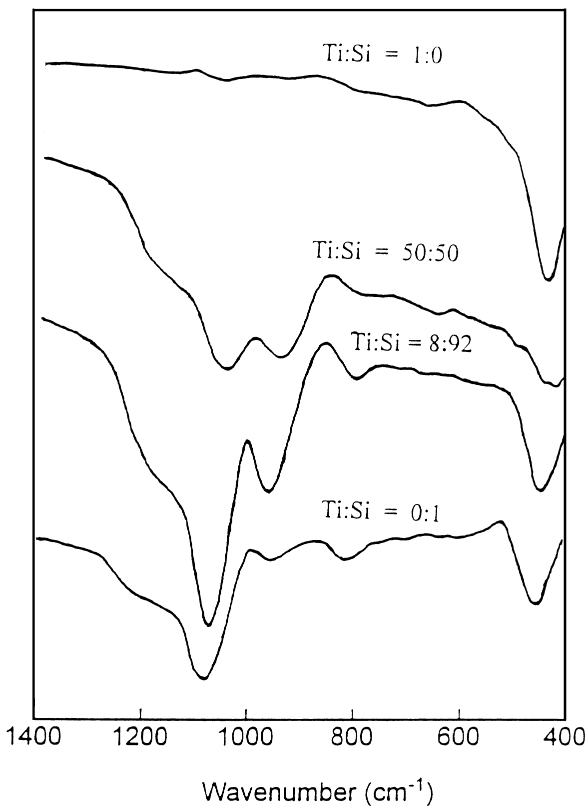

Fig. 2. FT–IR spectra of films with various TiO_2 contents at 500°C for 30 min.

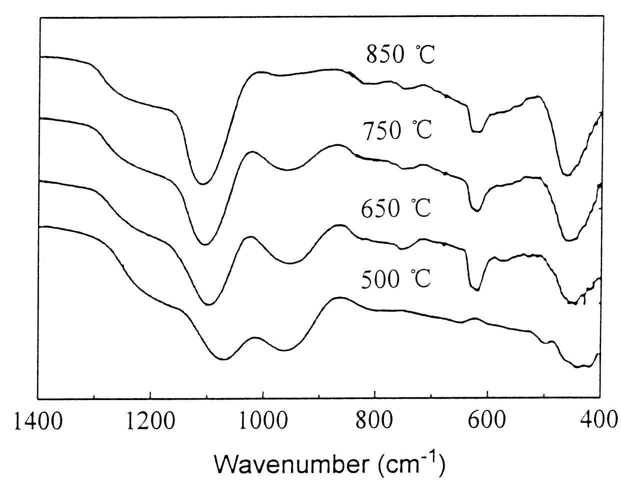

Fig. 3. FT–IR spectra for $50TiO_2$–$50SiO_2$ films versus heat treatment temperature: (a) 650°C, 30 min in O_2; (b) 850°C, 30 min in O_2.

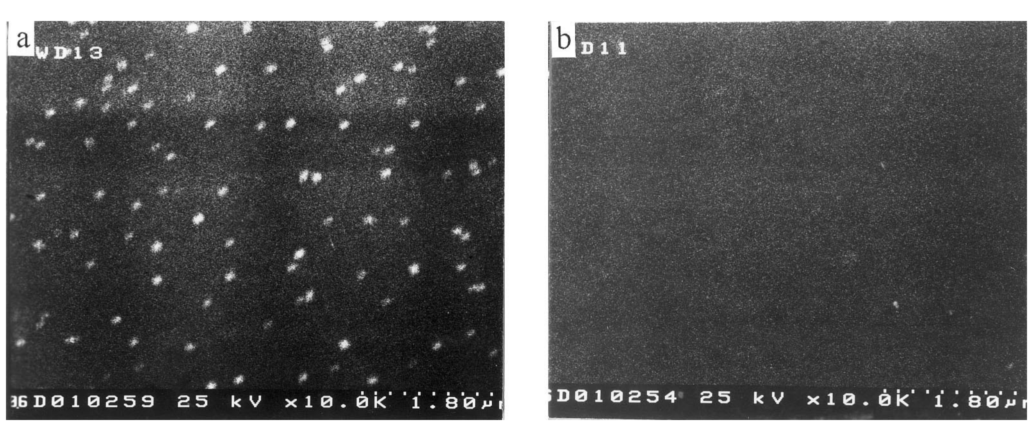

Fig. 4. SEM images of film surface.

4. Conclusions

TiO_2–SiO_2 composite thin films have been prepared by the sol–gel process and their optical waveguiding properties were characterized. The optical waveguiding loss is increased at increased TiO_2 content. With increasing of annealing temperature the waveguiding loss is increased and then decreased. Analyses showed this loss being the result of segregation effects and non-uniform distribution in the films.

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