Characteristics of laser-densified and conventionally heat treated sol–gel derived silica–titania films

Zhai Jiweia,*, Zhang Liangyinga, Yao Xia, S.N.B. Hodgsonb

aFunctional materials Research laboratory, Tongji University, 200092 Shanghai, PR China
bInstitute of Polymer Technology and Materials Engineering, Loughborough University, Loughborough, Leicestershire, UK

Received 16 March 2000; accepted 22 November 2000

Abstract

Thin films of various compositions in the system SiO₂–TiO₂ were prepared by the sol–gel method, with the effects of laser-densification and heat treatment being studied. The etch rate of the resultant coating films was found to change by a factor of almost 1000 for various heat treatment conditions in the temperature range 600–800°C. By combining laser sintering of selected areas and chemical etching techniques, the large difference between the etch rates of densified and undensified coatings can be used to produce channel waveguide structures. The etched coatings were characterized by X-ray diffraction, Fourier transform infrared spectra and micro-Raman spectra with these studies indicating that crystallization occurs in the region of laser scanning with dimensions corresponding approximately to the width of the beam used. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Film; Structure; Laser scanning; Chemical etch; Micro-Raman spectrum

1. Introduction

Optical quality dielectric films are a basic requirement for integrated optical devices fabricated on silicon substrates. TiO₂ and SiO₂ are commonly used materials for optical thin films in the visible and near-infrared wavelength ranges [1–5] due to their good transmission in these wavelengths. Thin films of these two materials have a large refractive index difference (n ≈ 2.4 and 1.45, respectively), and the large range of intermediate index values that can be obtained by mixing these materials makes them desirable in step index coatings. However, since TiO₂ and SiO₂ are immiscible in the crystalline form [1], any crystallization in these mixed films implies segregation or exodiffusion of Ti. Segregation and crystallization can degrade optical properties since the resulting inhomogeneous structure consisting of high refractive index crystalline TiO₂ embedded in the silica rich, low-index matrix can cause considerable scattering losses.

A number of methods have been applied to fabricate TiO₂–SiO₂ composite films, including e-beam evaporation [6], chemical vapour deposition [7], flame hydrolysis [8] and sol–gel [9,10]. The interest in the use of sol–gel methods is due to several advantages: good homogeneity, ease of composition control, low processing temperature, ability to fabricate large area coatings and low equipment cost. Sol–gel processing enables good control of composition and optical properties of the final materials, with good control of refractive index and thickness being particularly important to produce suitable materials for optical applications.

One attractive route for processing such materials in device form, is the use of laser technology as a method to obtain the densification of gel layers [11,12], in which waveguides or refractive index profiles may be written.
using laser heating techniques. The effects of laser heating on the film composition, structure and properties are of evident importance, but they are not yet well known.

The purpose of this work was to investigate and compare the properties of sol–gel derived TiO$_2$/SiO$_2$ thin films densified by laser and normal heating and to establish the heat treatment conditions and compositions required to prevent the formation of crystalline phases in this system. The etching behaviour of the thin films in dilute HF solution and the relationship between microstructure and processing conditions were also studied.

2. Experimental

The TiO$_2$/SiO$_2$ solutions were prepared using titanium butoxide $[\text{Ti(OC$_2$H$_5$)$_4}] \geq 98\%$, Shanghai Chemical Reagent Co.] and Si(OC$_2$H$_5$)$_4$ (TEOS; purity $\geq 99\%$, Shanghai Chemical Reagent Co.) precursors. Two compositions were used with TiO$_2$/SiO$_2$ molar ratios of 50:50, 8:92. The solutions were prepared by the following procedure. TEOS was mixed with isopropanol, water and several drops of HCl in the following proportions. TEOS/isopropanol/water/HCl = 1:4:4:0.03 (molar ratio). The solution was refluxed at 70°C for 60 min. In a separate container, titanium butoxide was mixed with acetylacetone (AcAc, purity $\geq 99\%$, Shanghai Chemical Reagent Co.) in the molar ratio Ti(OC$_2$H$_5$)$_4$/AcAc = 1:2. Each system was allowed to react for 30 min, after which the two solutions were mixed together, then diluted with isopropanol (analytically pure, Shanghai Chemical Reagent Co.) to give an equal volume solution. Films with various molar composition of Ti/Si were deposited onto Si(111) (Shanghai Silicon Materials Factory) and fused quartz (Shanghai Quartz Glass Factory) substrates of thickness 0.35 mm and 2.0 mm, respectively by spin-coating. Spin coating was performed in a class 100 clean room at a spin speed of 2500 rev. min$^{-1}$ for 20 s to produce an undensified coating thickness of approximately 0.3 $\mu$m for each deposition. A multi-cycle process was employed to deposit thick films. For each coating cycle, the wafer was spin coated with solution, annealed at a fixed temperature for 10 min then cooled to room temperature, prior to repeating the process.

Furnace-densified films (Ti/Si = 50:50) were prepared on fused-quartz substrates by a multilayer coating with heat treatment at various temperatures in the range 200 ÷ 500°C after each deposition. Samples for laser densification were obtained with the same procedure, but limiting the temperature to 300°C. A maximum of three layers could be deposited without cracking of the film occurring in this case. The laser used for heating was an 8 W CO$_2$ laser (Shanghai Institute of Optics and Fine Machines) focused on the film surface with beam diameter 300 $\mu$m. The porous oxide coating, as well as the substrate strongly absorbed the CO$_2$ laser light. Densification was performed by traversing the sample under the focussed beam at a velocity of 1 mm s$^{-1}$. Sample size was 15 $\times$ 15 mm$^2$.

Following laser irradiation of the selective removal of the non-irradiated and hence undensified regions was achieved by etching. The coated sample was immersed in a dilute, buffered hydrofluoric acid HF solution of composition: HF (analytically pure, Shanghai Chemical Reagent Co.)/NH$_4$F (purity $\geq 98\%$, Shanghai Chemical Reagent Co.)/H$_2$O = 3 ml:6 g:10 ml, which was further diluted 1:5 with water. This solution gave an etch rate of 0.1 $\mu$m/min. The etch rate was determined by covering half of the coating with a protective film of paraffin prior to etching and measuring the height of the resultant step with an interference microscope (Shanghai Optical Instrument Factory). In addition, the transverse profile was measured by profilometry (TENCOR, $\alpha$-STEP200).

Phase analyses of the prepared samples were performed using standard X-ray diffraction (XRD) techniques, with a Rigaku K/$\lambda$ max 2400 type diffractometer with CuK$\alpha$ radiation and a Ni filter. FTIR transmission spectra of the sol–gel derived films were measured using a Nicolet 60 SXR FTIR spectrophotometer. Raman microspectroscopy was also used to characterize the crystallization of the coating following both furnace and laser annealing heat treatments. The Raman spectra were obtained using a (Renishaw) 400 mW, JY U-1000 Raman microspectrometer with excitation wavelength 514.5 nm, at a scan rate of 3 cm$^{-1}$ s$^{-1}$. The samples were coated on Si(111) substrates, and either furnace annealed at 850°C for 30 min or sintered by laser scanning prior to analysis.

3. Results and discussion

3.1. The relationship between etch rate and densification temperature

Furnace heating was carried out in air, by placing the samples directly into the pre-heated furnace for 30 min. Densification changes not only the index, but also the etch rate of the sol–gel coatings. The etch rate varies rate with the heat treatment temperature by over two orders of magnitude, for the TiO$_2$-SiO$_2$ coatings, as shown in Fig. 1, with the etch rate being significantly affected by the composition used.

For the 92TiO$_2$-8SiO$_2$ coatings, the change in etch rate with sintering temperature is more evident than that of the 50TiO$_2$-50SiO$_2$ coatings (Fig. 1) The etch rate of the former changes by a factor of almost 1000 between 600° and 800°C, whilst the etch rate of the
92TiO₂–8SiO₂ coatings changes by a factor of only 600 over the same temperature range.

The large difference between the etch rates of densified and undensified coatings allows ridged structures to be produced, with the different etch rates being caused by the integral porosity present in the coatings heat treated at lower temperatures.

3.2. Structural evolution during heat treatment

The films of 8 mol.% TiO₂ content were found to be amorphous to X-rays for TiO₂ for heat treatment up to 900°C (Fig. 3a). For the films of 50 mol.% TiO₂, anatase, rutile phases and SiO₂ tridymite-M are formed (Fig. 3b). Crystallization of pure SiO₂ occurs at annealing temperatures higher than 1000°C which is consistent with the findings of other workers [15]. The formation the SiO₂ tridymite-M phase at 900°C in this sample, implies that this crystallization is due to the effect of the TiO₂ dopant. It is believed that this phenomenon is caused by the presence of highly dispersed microcrystallites of TiO₂, formed in the SiO₂ matrix. It is probable [16] that these small TiO₂ crystallites then induce the crystallization of SiO₂ at low temperatures by providing nucleation sites for growth of the tridymite SiO₂ phase.

The FTIR spectra of thin film coatings on Si(111) substrates, polished on two faces, are provided in Fig. 2a,b for the 8 mol.% and 50 mol.% TiO₂ compositions, respectively. The vibrational modes due to Si–O–Si asymmetric stretching and Si–O–Ti stretching (coupled with Si–O–Ti stretching) are observed at approximately 1100 cm⁻¹ and 955 cm⁻¹, respectively [13,14], with additional peaks related to Si–O–Si bands also observed at 800 cm⁻¹ and 440 cm⁻¹. The position of the Ti–O–Si band was 955 cm⁻¹ in the 8/92 sample and 937 cm⁻¹ in the 50/50 sample. Some peak shift and broadening effects were observed as the heat treatment temperatures were increased.

In the case of the film of composition 50 mol.% TiO₂/50 mol.% SiO₂, the FTIR spectra indicate that most of the Si–O–Ti bridges (≈937 cm⁻¹) remain intact for heat treatment in the 500–700°C temperature range, with the decrease in intensity of this band for higher temperatures suggesting that segregation of the TiO₂ to TiO₂ rich amorphous or anatase phases occur during heat treatment at temperatures of 750°C and above (compare with the corresponding X-ray spectra). The onset of TiO₂ crystallization would be anticipated to be accompanied by a reduction in the
number of Ti–O–Si linkages due to the immiscibility of these oxides in the crystalline form [1].

For the silica-rich sample, with TiO$_2$/SiO$_2$ mole ratio 8:92, the intensity of the absorption peaks associated with Si–O–Ti bridging stayed constant with increasing annealing temperatures. These findings are also consistent with the findings of the X-ray diffraction studies, with coatings of this composition found to be amorphous to X-rays for heat treatment temperatures up to 900°C.

Comparing the Raman spectra of the coated and uncoated Si(111) substrate in Fig. 4 after furnace annealing at 850°C for 30 min, the peaks at approximately 145, 196, 243, 396, 640 cm$^{-1}$ can be attributed to the coating film which comprised the molar composition 50% TiO$_2$/50% SiO$_2$.

The XRD results shown in Fig. 3b, confirm that the crystalline phase formed in these films consisted primarily of anatase, and the peaks at 145, 196, 396, 640 cm$^{-1}$ can thus attributed to this phase, in agreement with the findings of other studies [17,18]. The weaker peak at 243 cm$^{-1}$ (Fig. 4) was attributed [9] to a minor component of rutile, which was not observed using XRD.

3.3. Laser processing of coatings and Raman micro-spectra

Fig. 5 shows an SEM micrograph of the surface of a TiO$_2$–SiO$_2$ waveguide grating structure produced by CO$_2$ laser scanning and chemical etching of a sol–gel derived coating. The light regions are the grating ridges, and the dark stripes the troughs.

The surface profiles formed are shown for a typical 470-nm-thick 50TiO$_2$/50SiO$_2$ coating in Fig. 6. The trough was 180 nm deep and 300 µm wide. The profile formed comprised nearly vertical sides, which were 260 nm tall and 300 µm wide, with the latter dimension corresponding roughly to the width of the laser beam. As can be seen, the dimensions and shape are appropriate for optical propagation, if the refractive index is sufficiently higher than that of the substrate.

Due to the tendency of TiO$_2$ to crystallize in the TiO$_2$–SiO$_2$ system, with potential for deleterious scattering losses, micro-Raman spectroscopy was used for as an effective non-intrusive probe, with high spatial resolution, for characterizing the thin films after laser densification.

The Raman spectra in Fig. 6 were, respectively, obtained from the center (Fig. 7a) and margin portion...
Fig. 6. Transverse profile of (a) produced in TiO$_2$/SiO$_2 = 50$:$50$ coating after laser densification, and (b) after chemical etching.

Fig. 7. Raman spectra obtained from: (a) center, and (b) margin of the laser scanned region.

These results show that the at the center of the densified region, devitrification resulted in the formation of both anatase, rutile crystalline phases and some amorphous phase, with anatase peaks at 197, 396, 519 and 642 cm$^{-1}$, plus rutile peaks at 238, 443 and 614 cm$^{-1}$ [9]. In comparison, the crystalline phase formed at the margin of laser densified regions consisted exclusively of anatase, with peaks at 198, 398, 521 and 640 cm$^{-1}$. These structural differences across the laser densified region can be attributed to the power distribution profile of the laser spot, reflecting the fact that the power of the laser beam is higher at the center than at the margin. It has been shown [19] that the laser has a Gaussian profile, with this distribution of laser intensity, causing the variation in TiO$_2$ crystallinity in the scanned and densified regions.

4. Conclusions

Thin films of two binary titania-silica compositions have been prepared by the sol–gel method and their crystallization and etch resistance studied as a function of heat treatment conditions using both conventional and laser heating. The etch rate of the resultant coatings has been shown to change by a factor of up to 1000 over the temperature range 600–800°C for films of composition 50 mol.% TiO$_2$–50 mol.% SiO$_2$. The large difference between the etching rates of densified and undensified coatings can be used to produce channel waveguide structures by laser scanning on the coatings followed by chemical etching, with dimensions corresponding roughly to the width of the laser beam.

The difference of the etch rates was attributed to the density of coatings. Micro-Raman spectra also revealed that the crystallization in region of laser scanning has a distribution corresponding to the Gaussian profile of the beam intensity. At the center of the laser scanned region, the crystalline phase composition comprised
both anatase and rutile, whilst at the margin the crystalline phase present comprised solely anatase. Due to its tendency to crystallize, the TiO$_2$ component could cause high optical scattering losses. Further work is thus required to prevent the formation of crystalline phases in this system, either through a reduction in the heating temperatures used to densify the films and/or an increase in the stability toward crystallization via changes in formulation.

References