Surface characteristics of SiO_2-TiO_2 strip fabricated by laser direct writing

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SiO_2-TiO_2 sol-gel films are deposited on SiO_2/Si by dip-coating technique. The SiO_2-TiO_2 strips are fabricated by laser direct writing using an ytterbium fiber laser and followed by chemical etching. Surface structures, morphologies and roughness of the films and strips are characterized. The experimental results demonstrate that the SiO_2-TiO_2 sol-gel film is loose in structure and a shrinkage concave groove forms if the film is irradiated by laser beam. The surface roughness of both non-irradiated and laser irradiated areas increases with the chemical etching time. But the roughness of laser irradiated area increases more than that of non-irradiated area under the same etching time. After being etched for 28 s, the surface roughness value of the laser irradiated area increases from 0.3 nm to 3.1 nm.

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SiO_2-TiO_2 films have been widely used for a variety of applications, including catalysis[1], ceramic[2] and optoelectronics[3,4], etc. because of their many virtues, such as controlled structure, high surface-to-volume ratio and good optical and dielectric properties. Especially, the sol-gel derived SiO_2-TiO_2 films with benefits of good control on refractive index, low cost and low temperature are ideal materials for functional optical elements and thus have received much attention in recent years[5−7]. The traditional technique to fabricate SiO_2-TiO_2 functional elements is photolithography and followed by etching. However, the expensive equipments and multi-step, time-consuming processes limit their applications. Comparatively, the technique of laser direct writing is a method with virtues of maskless, flexibility and time saving, which is mainly based on the selective modification of SiO_2-TiO_2 sol-gel films induced by laser irradiation[8,9].

There are many reports about the preparation of SiO_2-TiO_2 sols and the effects of laser processing parameters on the sol-gel film composition, structure and refractive index. However, the performance of optical elements fabricated by laser direct writing is not as good as that obtained by photolithography, which limits its application in the field of optoelectronics. Moreover, the factors which affect the performance of optical elements have not been investigated systematically. It is well known that the interface and surface roughness of optical elements is an important factor to affect the optical properties. Up to now, there are few reports on the surface characteristics of optical elements fabricated by laser direct writing. In this work, SiO_2-TiO_2 sol-gel films were prepared on SiO_2/Si surfaces, and then three-dimensional (3D) strips were obtained by laser direct writing and followed by chemical etching. The surface morphologies, structures and surface roughness of the films and strips were characterized.

Following the previous reports[10,11], the SiO_2-TiO_2 sols with 50 mol-% Ti in concentration were prepared with the precursors such as $Si(OC_2H_5)_4$, tetraethoxysilane (TEOS), $Ti(OC_4H_9)$ (tetrabutoxytitanate, TiBOT), and $C_5H_8O_2$ (acetylacetone, AcAc), etc.. The concrete synthesis procedure is shown in Fig. 1.

The SiO_2-TiO_2 sol was filtrated by an percolator with an aperture of 0.2 μm, by which large grain impurities can be removed. Then the SiO_2-TiO_2 coating was deposited on SiO_2/Si surface by dip-coating technique at a drawing speed of 8 cm/min in the environment of N_2 gas. After each deposition, the film samples were heat-treated at 200 °C for 30 min. Finally, the SiO_2-TiO_2 sol-gel films were irradiated by laser beam, which makes the density of the irradiated area higher.

A continuous-wave ytterbium fiber laser with a wavelength of 1070 nm was used for writing the sol-gel films directly. The laser power can be adjusted continuously within the range of 0 − 50 W. The whole laser direct writing process was conducted on a computer numerical control (CNC) working table set up in a class-100 clean

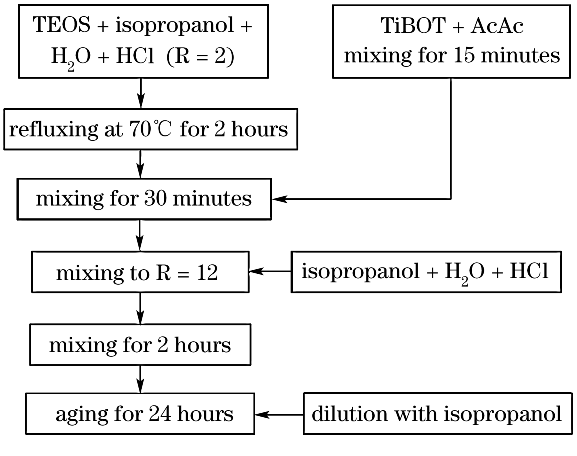

Fig. 1. Schematic description of the solution preparation.

room[12]. The SiO_2-TiO_2 strips were patterned by laser beam with a defocused spot size of 60 μm. After the laser treatment, a dilute hydrofluoric acid solution with HF:NH_4F:H_2O in a proportion of 2 mL:10 g:40 mL was used to etch the irradiated films, in which parts of the laser irradiated areas were kept in-site while other areas were dissolved in the chemical solutions due to the difference of the chemical etching rate.

The prism coupler (Metricon Model 2010) was used to determine the thickness of sol-gel films. The transverse morphologies of the films were observed by a scanning electronic microscope (SEM, Sirion 200), in which the operating voltage is 20 kV. The film surfaces were characterized by an atomic force microscope (AFM, Nano Scope IIIa, Digital Instrument Co.) operating in the tapping mode. The silicon nitride (Si_3N_4) pyramidal tip on a cantilever with a 0.37 N/m force constant was used to scan each sample. The transverse profiles of the SiO_2-TiO_2 3D strips were characterized by a Dektak IIA profilometer.

Figure 2 is a typical SEM photograph of cross section for a SiO_2-TiO_2 film on SiO_2/Si, in which there is a distinct interface between the SiO_2-TiO_2 film and SiO_2 film, as pointed out by two arrows. The lower side of the interface is a SiO_2 film prepared by wet oxidation method, while the upper side of the interface is a SiO_2-TiO_2 film deposited by dip-coating technique. It is significant that although the SiO_2-TiO_2 film is multilayer, no apparent interface can be observed in the all sol-gel films, which means that multilayer structure of SiO_2-TiO_2 film does not affect the optical properties of optical elements, for example, the interface scattering loss when the light propagates in the SiO_2-TiO_2 film.

Figure 3 shows the surface morphology of the SiO_2-TiO_2 film by AFM. The surface roughness of the root mean square (RMS) of the core layer is about 0.31 nm.

In general, there are a lot of interior nanoscale pores in the SiO_2-TiO_2 films by sol-gel technology[13]. These nanoscale pores will become smaller or even disappear under the heating effect, which results in the film shrinkage for their high surface-to-volume ratio. According to the ultraviolet-visible (UV-vis) transmission spectra of SiO_2-TiO_2 sol-gel films (the spectra is not given here), the absorption of the SiO_2-TiO_2 film and SiO_2 film to the wavelength of 1070 nm is very small. The energy of laser beam is absorbed not by SiO_2-TiO_2 film and SiO_2 film directly but by Si substrate. Then the SiO_2-TiO_2 films are densified by the heat conducted from Si substrates and the different patterns can thus be realized.

Figure 4 is the cross section profile of the laser irradiated area in the SiO_2-TiO_2 film at a power density of 1.03×10^6 W/cm^2 and a scanning velocity of 1 mm/s. The thickness of the SiO_2-TiO_2 film is 510 nm. The shrinkage takes place and a concave groove forms in the laser irradiated area. The depth of the shrinkage groove is 123.3 nm. This phenomenon can be explained as follows. As the energy distribution of the laser beam used is Gaussian distribution, most laser energy is centralized in the beam spot center. Therefore, the shrinkage extent becomes larger in the center of the laser spot than around area to form a converse Gaussian shape groove. Figure 5 is an AFM photograph of the center area in Fig. 4. Its RMS roughness is about 0.30 nm, which is basically the same as that of the non-irradiated area in Fig. 3. Summing up, the irradiated area will become more compact in structure after laser selected densification.

Compared with the non-irradiated area, the chemical etching rate of laser irradiated area will decrease much

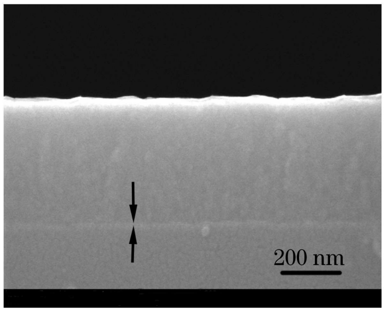

Fig. 2. SEM image of cross section for a planar waveguide.

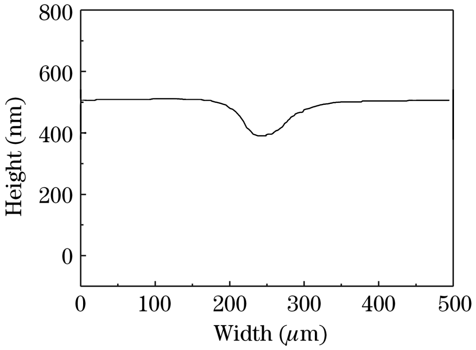

Fig. 4. Profile of the laser irradiated area.

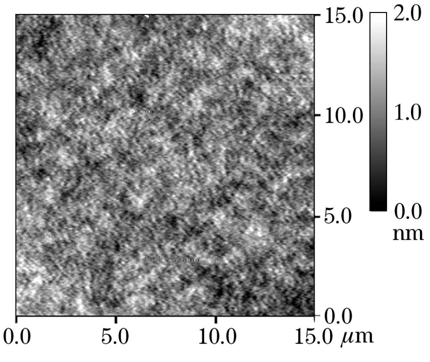

Fig. 3. AFM image of the surface for a planar waveguide.

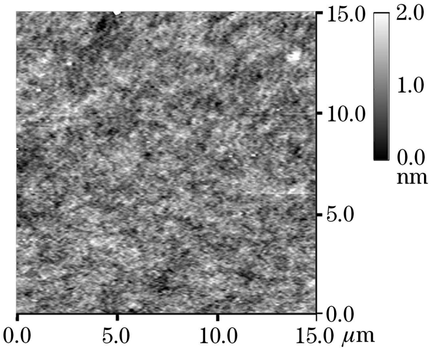

Fig. 5. AFM image of the irradiated area surface.

greater due to the more compact structure caused by laser irradiation. Thus, the shrinkage groove will become gibbous gradually with the increase of the chemical etching time, and finally form the SiO_2-TiO_2 strip at a proper etching time.

Figure 6 shows the cross section profiles of the strips etched by hydrofluoric acid solution at different etching times based on Fig. 4. Before the chemical etching, the thickness from the bottom of the shrinkage groove to the interface between the SiO_2-TiO_2 film and SiO_2 film is 386.7 nm. It means that the final height of 3D strip should be controlled to the theoretical value of 386.7 nm at least. As shown in Fig. 6, obviously, the etching time of 18 s is not enough to get ideal profile of strips and the relative height is only 228.2 nm. When the etching time increases to 28 s, the patterned 3D strip is ideal and the relative height is 386.9 nm. Here, the height of the strip is almost equal to the theoretical height, which indicates that the chemical etching time of 28 s is sufficient and proper to get a well-patterned SiO_2-TiO_2 strip. Importantly, the ideal chemical etching time is not a fixed value, which can be changed according to the preheat treatment temperature of sol-gel films and laser writing parameters.

Figure 7 shows the AFM images of different areas in Fig. 6. In order to compare the roughness of laser irradiated and non-irradiated areas at different chemical etching times, the concrete RMS roughness values of Figs. 3, 5 and 7 are summarized and listed in Table 1. It is distinct that the surface roughness of both the non-irradiated and laser irradiated areas increases with the increase of the chemical etching time. But the roughness of laser irradiated area increases much more than that of non-irradiated area under the same etching time, which indicates that the laser irradiation probably increases the roughness of the patterned SiO_2-TiO_2 strip. There may be two reasons that influence the chemical etching rate of the irradiated area and increase the surface roughness. One is that the densification extent of the irradiated area is different due to the non-uniform energy distribution of the laser beam. The other is inorganic carbon caused by laser irradiation emerges in the film material. These two factors will result in anisotropy of chemical etching rate in laser irradiated area. Especially, the anisotropy of chemical etching rate increases with the etching time, which makes the surface roughness of the irradiated area increase much more quickly than that of the non-irradiated area.

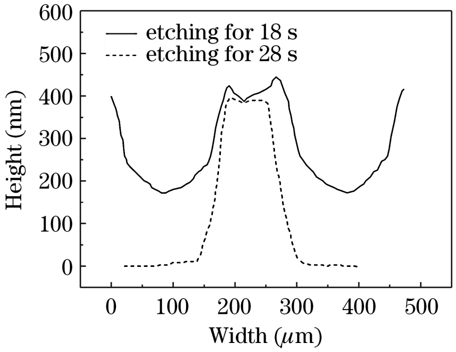

Fig. 6. Profiles of the SiO_2-TiO_2 strips gotten at different etching time.

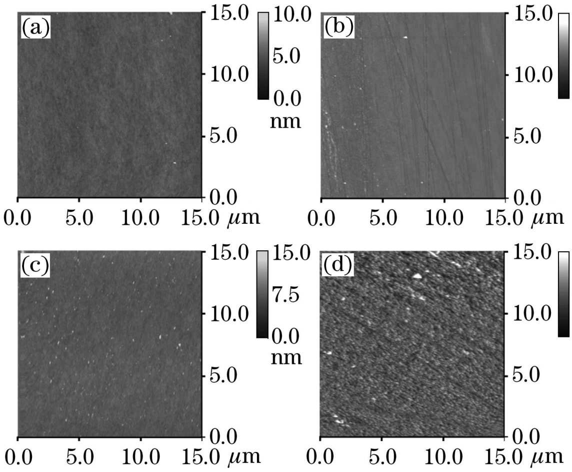

Fig. 7. AFM images of different area in Fig. 6, in which the images (a) and (c) are the non-irradiated area being etched for 18 and 28 s, images (b) and (d) are the laser irradiated area being etched for 18 and 28 s.

Table 1. RMS Roughness of the Core Layer Etched for Different Time

Etching Time (s)	RMS Roughness (nm) Non-Irradiated Area	Irradiated Area
0	0.31	0.30
18	0.43	0.98
28	0.61	3.07

In summary, SiO_2-TiO_2 strips based on sol-gel films are fabricated by laser direct writing followed by chemical etching. The SiO_2-TiO_2 sol-gel film is loose in structure and a shrinkage concave groove forms in the laser irradiated area. The chemical etching rate of the sol-gel film will decrease due to the laser irradiation. SiO_2-TiO_2 strips are fabricated by chemical etching to remove the non-irradiated area based on the difference of chemical etching rate. Besides, the surface roughness values of non-irradiated and laser irradiated areas increase with the increase of the chemical etching time. But the roughness of laser irradiated area increases much more rapidly than that of non-irradiated area under the same etching time.

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