SiO_2–TiO_2 THIN FILMS OBTAINED BY THE SOL-GEL METHOD

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Abstract

The hybrid silica-titania thin films, with different titania content, were prepared using the sol-gel technique. Their optical properties are presented. Thickness, refractive index and transmission spectra of the film have been measured. The titania precursor was used to increase the refractive index of the material. The more titania precursor for the synthesis has been used, the thinner layer with higher RI has been obtained. The SiO_2−TiO_2 matrix is porous and the dyes' molecules entrapped in it can interact with the surrounding media. Therefore, these thin films can be used as optical sensors. The sol-gel-derived layer has been doped with bromocresol green. The changes in absorption spectrum with increasing pH has been registered.

Keywords: silica-titania thin film, sol-gel method, optical sensor, bromocresol green

1. Introduction

The sol-gel technology allows to prepare glasses and glass-like materials that can be doped with organic compounds. It is very easy to prepare thin films using this method. They are characterized by good thermal and mechanical stabilities, porosity, high surface area, and good optical quality. Such films deposited on silicon substrates can be applied as planar or strip waveguides. Waveguides can be obtained using, for instance, silica-titania hybrids [1]. Control of the refractive index and film thickness is possible by changing starting precursors, solvents and temperature of thermal treatment. Waveguides doped with organic molecules can be used as optical sensors. Some of their applications are pH [2] or humidity sensing [3] and estimating isopropyl alcohol in water [4]. In this work, hybrid silica-titania thin films have been obtained via sol-gel technique. The optical properties of the films before and after thermal treatment are described. The layer was used as a matrix for immobilization of bromocresol green molecules. The changes of absorption spectra with increasing pH are shown.

2. Experimental

The silica (tetraethoxysilane, TEOS) and titania (titanium(IV) n-butoxide, TNBT and titanium(IV) isopropoxide, TIPO) precursors were obtained from Alfa Aesar. All other compounds were purchased from POCH SA. TEOS was mixed with proper amount of alcohol and hydrochloric acid [5] with the molar ratio of 1:8:0.05 for TEOS:ethanol:HCl. The compounds have been stirred on the magnetic stirrer for 30 minutes. Simultaneously, TNBT (or TIPO) was also mixed with alcohols (1:20:20:0.15

for TIPO:ethanol:isopropanol:HCl) [6] but this stage was shorter because of the higher hydrolysis rate of titania precursor [7]. Next, both solution was mixed together and the stirring was continued for one hour. The molar ratio of TEOS to TNBT/TIPO was 3:1, 2:1 or 1:1. The sol was aged for about 20 hours at room temperature. The SiO_2–TiO_2 films were deposited on microscopic glass slides (for transmittance measurements) and silicon wafers with a silica layer (for RI measurements) [5] by a modified dip-coating method [8]. The plates were dried in the air at 60ºC or heat-treated in 500°C for one hour. Thin film doped with bromocresol green was also prepared. The dye was added to the sol obtained as previously described and mixed. The film was coated on the glass after a few hours and dried at 60ºC to avoid the decomposition of organic dye.

The absorption spectra were recorded using a Varian Cary 2300 spectrophotometer. X-ray powder diffraction diagrams were recorded with Stoe diffractometer equipped with a position sensitive detector (Cu Kα radiation). The thicknesses and the refractive indexes of the films were measured at 632.8 nm wavelength ellipsometry.

3. Results and discussion

The sol-gel method was used to prepare transparent silica-titania thin films without cracks. They have good transmission properties in the visible range of the radiation. Figure 1 shows the absorption spectra of the films prepared with different titania content (with the SiO_2 to TiO_2 (TNBT) molar ratios of 3:1, 2:1 or 1:1). For the samples with more titania content, an absorption band with maximum at about 580 or 550 nm can be well seen. The best transmission (from 330 nm) has film with molar ratio of 3:1 after heat treatment. Other plates have higher absorbance after annealing, especially at higher wavelengths. All layers that were only dried at 60°C, have transmittance above 90%. Matrix with low titania content was chosen as material for optical sensors.

Fig. 1. Transmission spectra of thin films dried at 60°C or heat-treated at 500°C.

Sol-gel technology is relatively new method for fabricating passive devices for integrated optics purposes i.e. planar and strip waveguides. Propagation of a laser light in a waveguide can occur only when waveguiding layer has higher refractive index then adjacent layers (optical substrate and optical cladding), where also sufficient thickness for at least one optical mode excitement is needed. Defects in a waveguide structure can disturb the guided mode of light. Imperfections such as porosity, cracks, grain boundaries in polycrystalline film, refractive index inhomogeneity, or surface roughness can scatter light and promote optical losses. However, sol-gel technique allows achieving good quality films and therefore inexpensive and alternative method for preparing planar waveguides for integrated optics is available [9, 10]. Possibility of fabricating high refractive index glass at low process temperatures as well as feasibility of doping it with almost every material are another advantages of sol-gel technique. Tailoring of refractive index of sol-gel planar waveguide at desirable value is important for passive integrated optics. Since refractive index for silicon dioxide SiO_2 is n = 1.46 and for titanium dioxide TiO_2 is n = 2.7 (both values given for a laser light wavelength of 632.8 nm) the composition of these two compounds allows to obtain material with refractive index in range from 1.46 to 2.7.

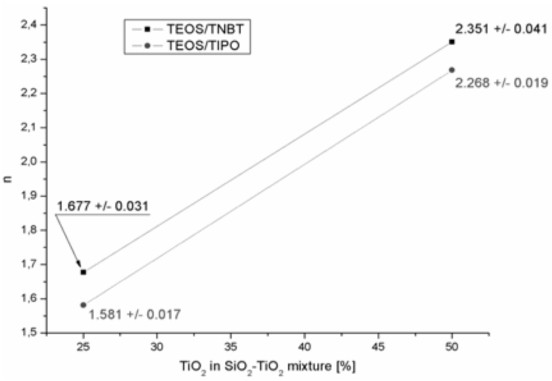

Fig. 2. Refractive index variation of sol-gel layers prepared with TEOS/TNBT and TEOS/TIPO precursors and annealed at 600°C.

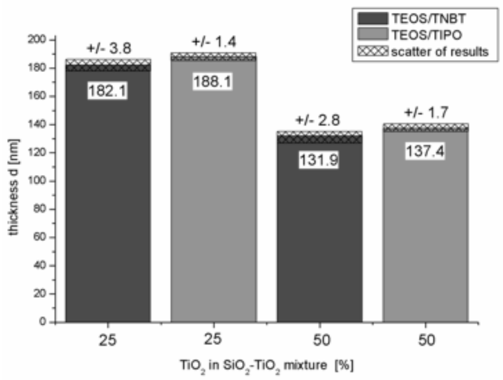

Fig. 3. Measured thickness of sol-gel layers prepared with two different precursors.

Figure 2 shows dependence of refractive index on the quantity of TiO_2 in final SiO_2−TiO_2 sol-gel layer. Square points represent layers fabricated by TEOS and TNBT precursors. Round points correspond to films prepared by TEOS and TIPO precursors. As can be seen, the refractive index for mixture 50% TiO_2–50% SiO_2 is clearly higher then for mixture 25% TiO_2–75% SiO_2, which is n=2.35 and n=1.67, respectively. In Figure 3, thickness of four different layers fabricated by different composition of silica to titania in SiO_2–TiO_2 mixture are presented. The scatter of the results is low, with average value of 2.4 nm, therefore very accurate thickness results were obtained.

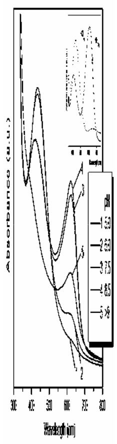

Fig. 4. Absorption spectra of SiO_2-TiO_2 film after immersing in water solution with different pH. The insert shows the spectra after exposition to gaseous ammonia and hydrochloric acid.

Low deviation of results and high homogeneity of layer thickness was achieved. Despite constant velocity during the withdrawing of layers, thin films which consist of 25% TiO_2 in SiO_2–TiO_2 mixture have higher thickness then 50% TiO_2 and 50% SiO_2

layers possibly due to lower flow resistant for titania precursors. When precursors were mixed in ratio of 3:1, the thickness was about 185 nm and when the ratio was set as 1:1, thickness was about 134 nm.

The doping of SiO_2-TiO_2 film (with the molar ratio for TEOS:TNBT of 3:1) with bromocresol green resulted in yellow and transparent layer. Its colour changed to blue when the film was immersed in water solution with pH>5. Figure 4 shows that in this case, one absorption band at 435 nm decreases and other band at 620 nm appears. This behavior was also observed when the plate was hold in gaseous ammonia. The changes were fully reversible after exposition to gaseous hydrochloric acid (see insert in Fig. 4). When the plate was placed in the basic solutions (pH>9), the sol-gel matrix started to decompose, the dye was washed and the absorption intensity of the film decreased (line 5 in Fig. 4).

4. Conclusions

The sol-gel method was used to obtain silica-titania thin films with good optical and mechanical properties. The layers have high transmittance in the visible region of the radiation. The addition of titania causes the increase of the refractive index (e.g. 2.35 for film with 50% TiO_2 and 50% SiO_2) thus this material could be used as planar waveguide. The refractive index and thickness of the film depend on the TiO_2 content. Samples with lower silica to titania molar ratio have higher refractive index and are thinner. The film prepared from tetraethoxysilane and titanium n-butoxide can be successfully used as a matrix for molecules of organic dye (bromocresol green). The dye can still change colour with increasing/decreasing pH, even though it is embedded in the sol-gel film. Waveguide obtained by the sol-gel process with molecules of pH indicator entrapped in the SiO_2-TiO_2 matrix could be used as an optical sensor.

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