Large photosensitivity in SnO_2/SiO_2 thin film fabricated by sol-gel method

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SnO_2/SiO_2 (90%mol SnO_2) thin film was prepared on the silica substrate by sol-gel method. The SnO_2/SiO_2 thin film was irradiated by xenon lamp. Then the transmission spectra of the sample were measured. The refractive-index expressions were figured out for irradiated and non-irradiated SnO_2/SiO_2 thin film, respectively. According to refractive index curves, the refractive index change between irradiated and non-irradiated thin film was approximately up to 0.05.

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1. Introduction

Glass photosensitivity is the permanent change in refractive index following by UV irradiation. For some fiber applications, such as fiber filters and fiber dispersion compensators [1], a stronger photosensitivity would be desirable. For volume optical holographic data storage, inexpensive materials with high optical quality, large refractive index change, and long shelf life are still necessary. Also a large photosensitivity in glass would make it possible to fabricate planar waveguide devices by direct UV-writing.

In 1978, K. O. Hill and his colleagues first observed permanent refractive index change in germanosilicate glass fibers [2]. The preponderance of the investigations used to be devoted to GeO_2-doped silica glass [3, 4, 5]. The maximum photo-induced index change Δn, is about 0.01 for hydrogen-loaded germanosilicate glass fibers with limited stability at elevated temperature [6].

The observation of large photosensitivity for lead silica glass has been done in the past years [7 8]. Long and Brueck wrote permanent gratings in lead silicate glasses through a phase mask by irradiation with a pulsed KrF exciter laser (248 nm) and a Q-switched YAG laser (266 nm), respectively [9]. The refractive index change Δn can be evaluated by measuring the diffraction efficiency of the gratings. The largest index change (Δn = 0.21±0.04 at 633 nm) was obtained in SF59 glass (57mol% PbO). But most of the experiments are not related to waveguide structure, which limits its practical values.

We know that SnO_2/SiO_2 also has a good photosensitivity [10 11]. Most experiments on SnO_2/SiO_2 photosensitivity are conducted by using CVD technique. In case of crystallization in the chemical compound, the lower Sn concentration is conditioned by CVD technique. Shivakiran Bhaktha et al. [12] studied formation of SnO_2 nanocrystals in SiO_2-SnO_2 film fabricated by sol-gel method after exposed to the 266 nm UV laser, but did not study the change of refractive index before and after UV exposure.

In this paper, the process of preparation of high SnO_2 concentration SnO_2/SiO_2 thin film by sol-gel method was simply described. Prepared film was exposed to xenon lamp. Then the transmission spectra of the sample were measured. With the introduction of the transmittance formula and classic Cauchy expression for refractive index, the experimental spectra were fitted. It finally got the refractive index.

2. Basic theory

Since dip-coating process is introduced for the film preparation, it means that the film is doubled-coated on substrate. The double-coated thin film model consists of five regions, air-film-substrate-film-air.

The expression for the transmittance (T) is presented as follows [13 14].

$$T=\left\{\frac{A}{Be^{4\pi kd/\lambda}+C\cos 4\pi nd/\lambda+De^{-4\pi kd/\lambda}}\right\}^2 \quad (1)$$

Where

$$A=16n^2n_g$$

$$B=(n+1)^2(n+n_g)^2$$

$$C=-2(n^2-1)(n^2-{n_g}^2)$$

$$D=(n-1)^2(n-n_g)^2$$

were k is the extinction coefficient, d is the thickness of thin film deposited on substrate, n and n_g are the refractive index for thin film and substrate, respectively. The substrate material is made of quartz glass.

Generally speaking, Cauchy equation is a classic expression for refractive index n in thin film system if the measured transmission spectrum is nearly not in the absorption region. For this reason, the expression for n is shown as:

$$n(\lambda) = a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} + ... \quad (2)$$

Based on these mentioned above, n is substituted from Eq. (1) into Eq. (2). The experimental transmission curve is fitted by computer. From the calculated results, the expression for n is acquired, which helps us draw the refractive index figure and analyze the change between irradiated and non-irradiated films.

3. Experimental

SnO_2/SiO_2 thin film was prepared by sol-gel method. The ethyl orthosilicate was a kind of metal lakeside. Absolute ethyl alcohol was as solvent. Ammonia water with 28% concentration was as catalyst. These chemical materials were used for the preparation of SiO_2 sol. At the same time, $SnCl_2$ • $2H_2O$ and absolute ethyl alcohol were ready for SnO_2 sol. Finally, the two kinds of sols mentioned above were mixed together with high SnO_2 composition (90 mol% SnO_2). Also stirring them well enough was a plus. After that, these samples were thermally treated at 1,022°F for half an hour. Since the calculation needs a certain amount of external points, the thickness of the thin films must reach to a certain number. Given this, it is impossible to fulfill this acquirement by dipping only for one time. The repetition of dip-coating process could increase the thickness. The number of coating layers is 14. The flow chart is as follows.

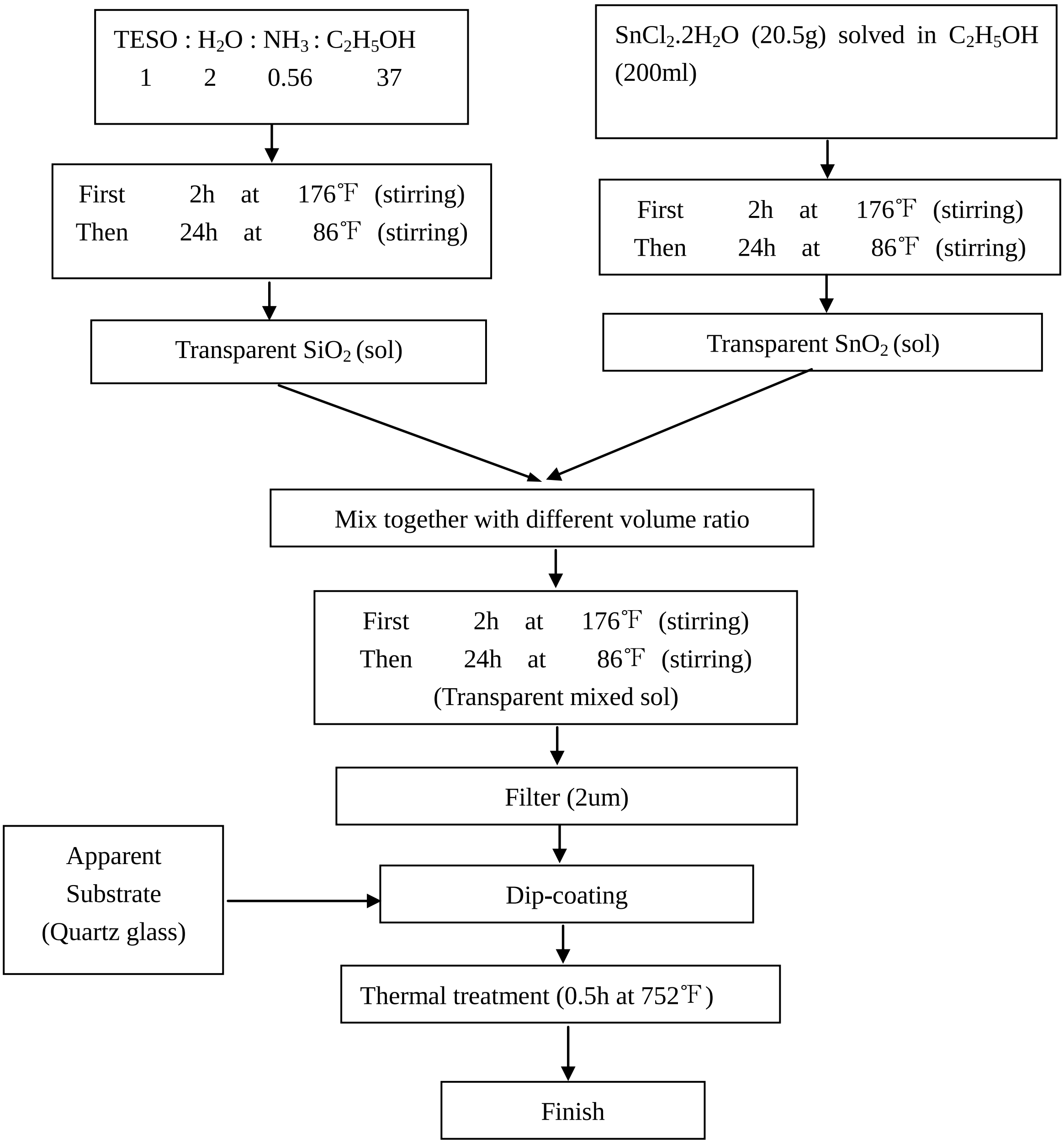

Fig. 1. The flow chart for fabricating the SnO_2/SiO_2 thin film.

The SnO_2/SiO_2 film was exposed to xenon lamp (25 mw, 190-900 nm) for an hour (half an hour for each side). The diameter of the light spot of the xenon lamp is about 5 mm. The irradiated region on surface of the film is marked with a circle. Then the transmission spectra were measured by spectrometer (Cary5000, USA). The irradiated and non-irradiated spectra are shown together in Fig. 2.

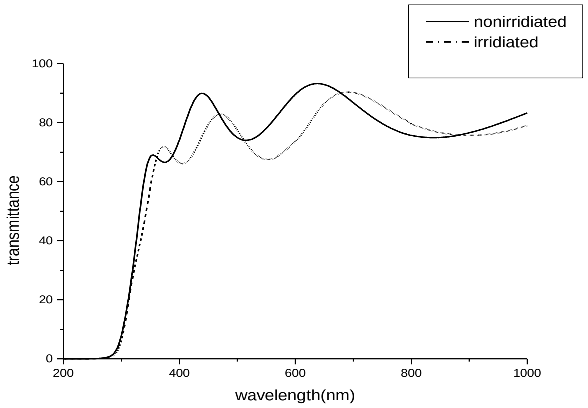

Fig. 2. The irradiated and non-irradiated transmission spectra.

From Fig. 2, it's easy to distinguish that the transmission curve is shifted and decreased after exposure under xenon lamp. As transmittance formula has been introduced, the irradiated and non-irradiated experimental curves are fitted. From calculated results, the expressions for refractive index are obtained. The comparison of them is illustrated in Fig. 3.

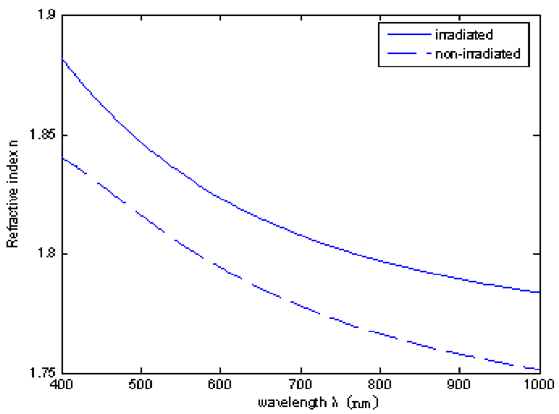

Fig. 3. The irradiated and non-irradiated curves for refractive index n VS wavelength λ..

To analyze these two curves, they are approximately parallel from 400 nm to 900 nm wavelength range. The refractive index becomes higher after exposure by xenon lamp. Refractive index change Δn is up to 0.05.

The film thickness was also obtained by data fitting. Thickness of non-irradiation and irradiation was 359 nm and 379 nm, respectively. To discuss its effect, the AFM (atomic force microscope) is used for detecting surface topography as shown in Fig. 4.

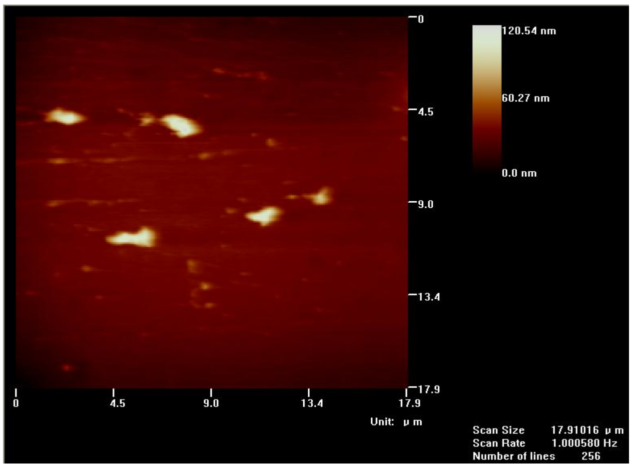

Fig. 4. The AFM topography for the SnO_2/SiO_2 thin film surface.

It shows a color-coded map of surface topography detected by AFM, along with a histogram showing the depth on film surface. The uniformity of the film surface is better than 50 nm except some discrete spots. Generally speaking, the refractive index of the thin film influences the heights and the positions of the peaks in transmission spectrum, and the thickness of the film only influences the positions of the peaks in transmission spectrum. The height of the peaks in transmission spectrum changed obviously in Fig. 2, so we believed this was because of the changes of refractive index.

4. Conclusion

In this paper, the SnO_2/SiO_2 films were prepared by sol-gel method which allowed large SnO_2 dopant. The concentration of SnO_2 in the compound is 90%. The transmittance formula is introduced for refractive index calculation. The transmission spectra of irradiated and non-irradiated thin film are measured. The refractive index is expressed by Cauchy equation. According to the transmittance formula and experimental data, the original transmittance curve is fitted. The expression for refractive index is obtained. By the above method, we have already figure out the refractive index for both irradiated and non-irradiated thin film. The refractive index of SnO_2/SiO_2 films is increased ($\Delta n \approx 0.05$) after irradiation by xenon lamp.

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