

Optical properties of highly photosensitive hybrid sol-gel films

Jing Mao (毛靖), Weidong Shen (沈伟东)*, Yi Yin (尹伊), Yueguang Zhang (章岳光),
and Xu Liu (刘旭)

State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, Hangzhou 310027, China

*E-mail: adongszju@hotmail.com

Received July 1, 2009

A new organic-inorganic hybrid material, which shows photo-induced reduction of refractive index as well as volume contraction, is prepared using a sol-gel method. This material is coated on a Si substrate by spin-coating to manufacture film. After irradiated by ultraviolet (UV) light with a deuterium lamp for 5 h, the thickness of film decreases largely by 55%, and the refractive index of film changes from 1.484 to 1.445 at 550 nm. The film's optical thickness exhibits an exponential change with the increasing irradiation time. Furthermore, the photo-patterning of the organic-inorganic hybrid film without any further process (wet etching and thermal curing) is performed utilizing the volume contraction on UV-light irradiation. This film has potential applications for fabrication of patterned filter array and apodizing filter by direct light writing, and also demonstrates good temperature stability and immunity to visible light exposure.

OCIS codes: 160.5335, 310.6860, 100.4994.

doi: 10.3788/COL20100804.0435.

Over the past several decades, there is a growing concern in the use of photosensitive materials for a wide range of applications in optics including diffractive optical elements, optical recording, and antireflective coatings^[1–5]. In 2005, a thought about laser trimming of thin film filters was put forward^[6]. The use of photosensitive materials for manufacturing various functional optical filters would be a very attractive way for enabling the post trimming of such devices with the help of a light beam. It could not only correct some material deposition errors accurately to improve the production efficiency, but also create entirely new filtering devices with controlled spatial properties, such as apodizing filter and linear variable filters^[7]. The choice of a photosensitive material as a part of an optical filter should take into account a lot of constraints^[6], including small losses at design wavelength, mature film-forming process, long-term stability of the film's photo-induced changes, immunity to the visible light exposure, and large optical thickness change through the light process.

In this letter, a photosensitive organic-inorganic hybrid material which well meets the above-mentioned requirements has been prepared using a sol-gel method. This hybrid material shows a photo-induced reduction of refractive index as well as large volume contraction upon the ultraviolet (UV) light (190 – 280 nm) irradiation. Long-term stability of photo-induced changes and direct photo-patterning utilizing the volume contraction on light irradiation demonstrate that this material could be used to manufacture various reliable functional optical filters.

Fluorinated hybrid materials were synthesized by the use of 3-methacryloxy-propyl-trimethoxy silane (MPTS, Aldrich) and perfluorodecyl-trimethoxy silane (PFTS, Alfa Aesar) as precursors. MPTS and PFTS (3:1 in molar ratio) were mixed with distilled water in the presence of 0.01 N (normal concentration) hydrochloric acid (HCl), which acted as a catalyst for the sol-gel reaction. The solution was put into a water vapor-proof container,

which was immersed in the hot silicone oil to maintain the heating temperature. After stirring the solution for 24 h at 70 °C, a totally transparent solution was obtained. The solution was then left to stand for 30 min to remove gas bubbles resulting from the stirring. A single layer was deposited on Si substrate by a spin-coating method. As the refractive index of this hybrid material is close to that of glass substrate (1.52), and there is a better film-forming quality on Si substrate for this material, Si(100) substrate has been chosen for our experiment, which has a high refractive index. The spin speed was 500 rpm (round per minute) for 5 s and 3000 rpm for 30 s, respectively. The as-deposited film was first pre-baked for 1 min at 80 °C in order to improve the adhesion between the film and a native SiO₂ layer on the Si substrate^[8]. After pre-baking, the film was then cured thermally for 12 h at 150 °C.

Fluorinated hybrid materials are generally photosensitive to the UV light exposure around 190 – 280 nm^[9]. Thus, the as-deposited film was irradiated by a deuterium arc lamp which provided a radiation with a spectrum of 190 – 400 nm. During the UV irradiation, the spectral reflectance of the film was measured by a reflectivity spectrometer (USPM-RU, Olympus). The time interval for each measurement increased from 5 to 30 min with the augmented exposure time. The 100- μ m probing beam size of Φ is selected and the measurable spectral range is from 380 to 780 nm with a resolution of 1 nm. Based on the experimental reflectance curves, the refractive index n and physical thickness d are determined by the spectral curve fitting method with a global optimization algorithm^[10]. In the fitting process, the film's refractive index and extinction coefficient R are presumed by Cauchy dispersion model as

$$n(\lambda) = a + \frac{b}{\lambda^2}, \quad (1)$$

$$k(\lambda) = k_1 \exp\left(\frac{k_2}{\lambda}\right). \quad (2)$$

The optical constants (refractive index and extinction coefficient) of Si substrate are taken from Ref. [11]. The photometric method is widely used to characterize optical thin films with a relative high accuracy. In order to localize the probing area of the film accurately, a shadow mask with a small pinhole ($\Phi = 0.5$ mm) was tightly attached onto the film surface. With this method, we could ensure that the same point is measured after each irradiation.

It should be noticed that the temperature on the film was about 45 °C during the UV irradiation. The film's temperature stability had been investigated at temperature range from 25 to 140 °C in dark environment. The film was also exposed in natural light to study the influence of the film on the visible light.

Figure 1 shows the reflectance of bare Si substrate and monolayer film, which has been irradiated by UV light for different exposure times. In order to see more clearly, six curves are displayed in Fig. 1. As the exposure time increases, the reflectance curve is observed to shift gradually towards shorter wavelength. It indicates a negative photo-induced index change with increasing exposure time. It is confirmed that this material shows a rapid sensitivity to UV exposure. It can be also seen from Fig. 1 that the peak reflectances of the film at the half-wave points match those of bare Si substrate very well. It means the non-homogeneity of the film when the exposure could be ignored.

We obtained the optical constants of the film by fitting the reflectance curves. Figure 2(a) shows the refractive index and thickness of the film as functions of the exposure time of the deuterium lamp. The refractive index decreases from 1.484 to 1.445 as the UV fluence increasing. During the early stage of irradiation, the refractive index declines with a slight oscillation which is caused by measurement errors. Because the spectral reflectance curve fitting method is sensitive to the optical thickness of the film, it is difficult to distinguish a small variation of refractive index from the variation of optical thickness. After exposed for enough time, the refractive index declines rapidly until gradually saturated. Also, the film thickness decreases exponentially from 510.7 to 233.4 nm with the cumulated UV fluence.

Significantly, the film's optical thickness shows an exponential change from 758.0 to 337.4 nm by 55.4% with the irradiation time, as shown in Fig. 2(b). It provides us with the meaningful possibility of controlling this

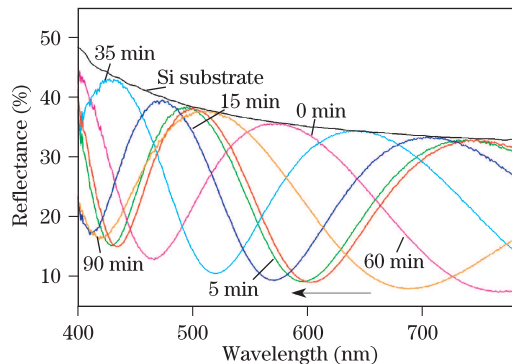


Fig. 1. Reflectance of bare Si substrate and monolayer film after different exposure times.

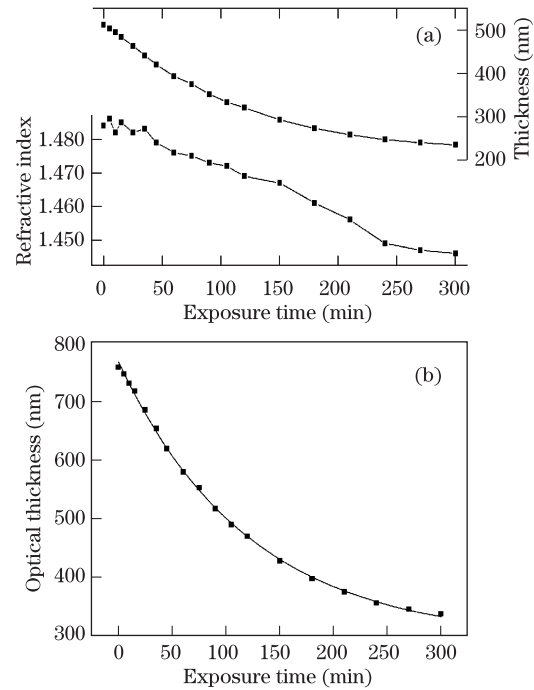


Fig. 2. Changes in (a) refractive index and thickness, (b) optical thickness of the hybrid material film with UV fluence from a deuterium lamp.

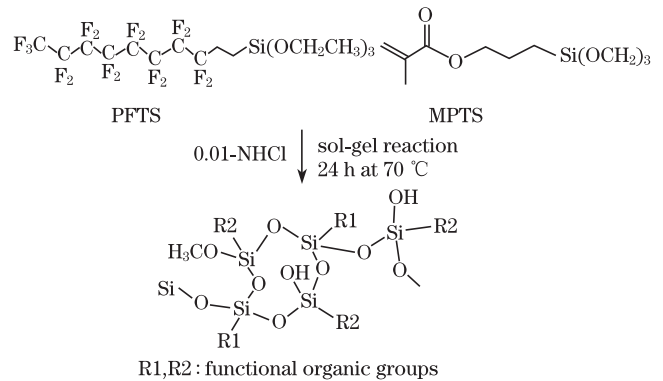


Fig. 3. Chemical structure of the sol-gel precursors and organic-inorganic hybrid Si-O-Si network.

film's optical thickness accurately by adjusting exposure time. Therefore, this material has potential applications to manufacture thin film components by light trimming and fabricate some special thin film devices such as linear variable filter and apodizing filter.

Photoinduced structural changes in this hybrid sol-gel material had been analyzed to explain the photosensitivity of the film. As shown in Fig. 3, during the sol-gel reaction, the two precursors hydrolyze, condense and finally comprise an organic-inorganic hybrid material which is composed of an inorganic Si-O-Si main chain and functional organic perfluoroalkyl and methacryl groups. These functional organic groups are covalently bonded to the inorganic Si-O-Si network to modify the silica network^[12].

When the film is irradiated by UV light with the deuterium lamp, methacryl groups will undergo a photoinduced decomposition resulting from the absorption of UV light in 190 – 280 nm region by the carbonyl group of

poly(methyl methacrylate)^[9]. Methacrylates are decomposed into small gas molecules such as CO₂ and CH₄, which diffuse out from the network. The refractive index change Δn of a material is given by the Lorenz-Lorentz equation^[13] as

$$\Delta n = \frac{(n^2 - 1)(n^2 + 2)}{6n^2} \cdot \left(\frac{\Delta \partial}{\partial} - \frac{\Delta \rho}{\rho} \right), \quad (3)$$

where $\Delta \partial / \partial$ and $\Delta \rho / \rho$ are the relative changes in material polarizability and density, respectively. The density of material before UV irradiation is 1.185 g/ml. On the assumption that the methacryl groups decompose completely after sufficient UV irradiation, the density of material would be 1.24 g/ml estimated by MPTS's molecular weight change. In the case of the methacryl groups decompose completely, the ultimate refractive index of the material would approach that of PFTS ($n = 1.342$ at 550 nm, Alfa Aesar). Whereas refractive index reduction calculated from Eq. (3) with the density change is about 0.013, which is much smaller than the expected value of ultimate refractive index change ($0.142 = 1.484 - 1.342$). Therefore, the impact of density change to the refractive index change is not significant in this hybrid material. On the other hand, carbonyl groups are very polar and hence result in high refractive indices of materials generally^[14]. These carbonyl groups are removed with the decomposition of methacryl groups in the hybrid material on UV irradiation. Consequently, the polarizability reduction by the removal of carbonyl groups contributes dominantly to the decrease in refractive index upon the UV light exposure. Meanwhile, the other functional group perfluoroalkyl is immune to UV light, so all the functional groups in the Si-O-Si networks would not decompose completely. On UV irradiation, the inorganic Si-O-Si frameworks experience photoinduced condensation reactions when the siloxane bond angles decrease^[15,16]. Therefore the film's thickness decreases largely owing to the shrinkage of the inorganic network. To summarize, the decomposition of methacryl groups causes the reduction of refractive index on UV irradiation while photoinduced densification in the inorganic framework causes the concurrent decrease of the film's thickness.

Because of the large photo induced decrease of the film's thickness, this hybrid material is photopatternable. A mask for the exposure was made based on a fused silica substrate which has a high transparency in the UV region. A chromium film with a thickness of 100 nm was first deposited on the substrate. Then, the pattern was transferred on it by a standard microfabrication processes, i.e., lithography and wet etching of Cr film. The mask was attached onto a film's surface, and then the film was directly irradiated by UV light for 2 h. After that, due to the photo induced change of physical thickness, a pattern on the surface was formed without any further processes, e.g., wet etching and thermal curing. Figure 4 shows a magnified view of the exposed pattern in the hybrid material film which is taken by an optical microscope. The linewidth of letters is about 65 μm and the image almost perfectly reproduces the shape of the mask. Consequently, more complicated and precise masks could be designed and manufactured to produce

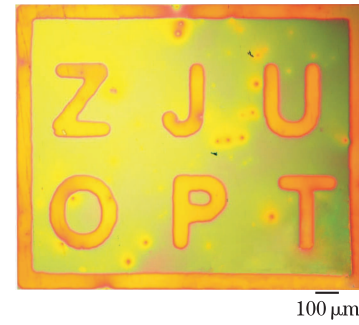


Fig. 4. Optical microscope image of the illustrated photoinduced pattern.

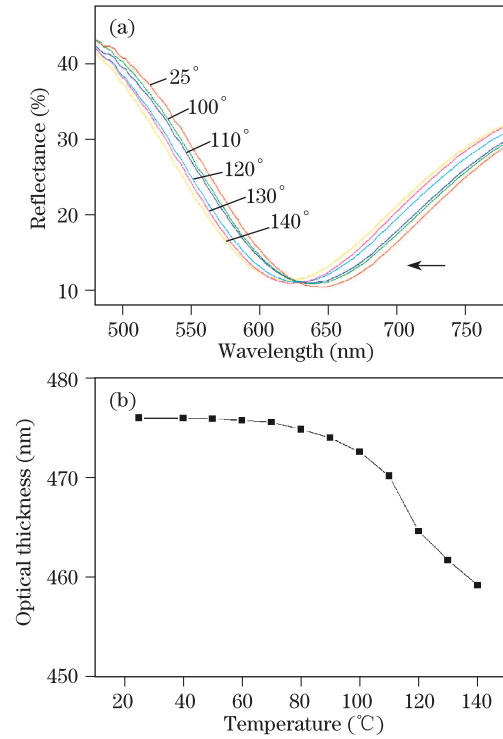


Fig. 5. (a) Reflectance and (b) optical thickness of the heated film at different temperatures.

various spatial optical filters based on this material.

The long-term stability of the film's photoinduced changes is very important for the future applications. The temperature stability of a film which has been irradiated for 2 h by UV light was measured. We heated the film at different temperatures for 1 h in dark environment and let it cool down naturally. The reflectance curves and optical thicknesses of the film at each temperature are measured, as shown in Fig. 5.

In Fig. 5(b), the film exhibits high temperature stability (with a variation of less than 0.8%) at the temperature of less than 100 °C. Therefore the film is suitable for general applications which usually work at room temperatures. When it approached to the annealing temperature of 150 °C, the film's thickness decreased as expected. The film was also exposed to the daylight for 24 h. The measurement result shows that the film is well immune to the visible light exposure. It means that the film is only photosensitive to UV light and stable for the visible light illumination.

In conclusion, the reduction in refractive index and thickness occurs upon UV-light irradiation in the photo-sensitive organic-inorganic hybrid material. The decomposition of methacryl groups causes the reduction of refractive index on UV irradiation while the photoinduced densification in the inorganic framework causes the concurrent decrease of film's thickness. The thickness of film decreases largely from 510.7 to 233.4 nm by 55%, and the refractive index of film changes from 1.484 to 1.445 at 550 nm. More meaningfully, the film's optical thickness shows an exponential change with the increasing irradiation time. Thus, we can precisely control of the film's thickness. Furthermore, this film has potential applications for fabrication of patterned filter array and apodizing filter by direct light writing without any further process. Finally, this film has the fairly good long-term stability of photoinduced changes.

This work was supported by the National Natural Science Foundation of China (Nos. 60708013 and 60778025), the China Post-Doctoral Funding (No. 20081463), and the Zhejiang Provincial Natural Science Foundation (No. Y5080094).

References

1. D. J. Kang and J.-U. Park, *Opt. Express* **11**, 1144 (2003).
2. M. W. Lee, C. G. Rillet, C. L. C. Smith, D. J. Moss, and B. J. Eggleton, *Opt. Express* **15**, 1277 (2007).
3. A. Draude, R. Meinhardt, H. Franke, Y. Zhao, and R. A. Lessard, *Chin. Opt. Lett.* **6**, 25 (2008).
4. C. Xue, K. Yi, C. Wei, J. Shao, and Z. Fan, *Chin. Opt. Lett.* **7**, 449 (2009).
5. M. Nenkov, B. Gyoeh, and T. Pencheva, in *Proceedings of ISSE* **30**, 377 (2007).
6. M. Lequime and J. Lumeau, *Proc. SPIE* **5963**, 60 (2005).
7. W. D. Shen, M. Cathelinaud, M. Lequime, F. Charpentier, and V. Nazabal, *Opt. Express* **16**, 373 (2008).
8. J.-U. Park, W.-S. Kim, and B.-S. Bae, *J. Mater. Chem.* **13**, 738 (2003).
9. J. A. Moore and J. O. Choi, in *Radiation Effects on Polymers* R. L. Clough and S. W. Shalaby, (eds.) (American Chemical Society, Washington, 1991).
10. W. Shen, X. Liu, Y. Zhu, T. Zou, H. Ye, and P. Gu, *Chin. J. Semiconductors* (in Chinese) **26**, 335 (2005).
11. E. D. Palik, *Handbook of Optical Constants of Solid* (Academic Press, New York, 1985).
12. C. Sanchez, G. J. de A. A. Soler-Illia, F. Ribot, T. Lalot, C. R. Mayer, and V. Cabuil, *Chem. Mater.* **13**, 3061 (2001).
13. A. K. Varshneya, *Fundamentals of Inorganic Glasses* (Academic Press, San Diego, 1994) p.459.
14. C. C. Ku and R. Liepins, *Electrical Properties of Polymers, Chemical Principles*, (Hanser Publishers, New York, 1987) p.41.
15. W. C. Chen, S. J. Lee, L. H. Lee, and J. L. Lin, *J. Mater. Chem.* **9**, 2999 (1999).
16. D. Blanc, S. Pelissier, K. Saravanamuttu, S. I. Najafi, and M. P. Andrews, *Adv. Mater.* **11**, 1508 (1999).