

Large Photoinduced Densification in Organically Modified Germanosilicate Glasses

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Organically modified germanosilicate (ORMOGSIL) glasses prepared by a sol–gel method showed a large refractive index change on ultraviolet exposure. The large photoinduced refractive index change in the ORMOGSIL glasses is mainly due to the structural densification caused by ultraviolet irradiation. The shifts in frequency of the Raman bands measured at room temperature reveal structural densification by reduction of the average intertetrahedral bonding angle θ in the ORMOGSIL glasses. Surface relief patterns by photoinduced densification were directly inscribed on the ORMOGSIL glasses.

I. Introduction

PHOTOSENSITIVE effect is a permanent change in the refractive index of a medium by exposure to light. The refractive index modulation in photograph polymers^{1,2} and photonic crystals^{3,4} can be accompanied with the surface relief modulation, induced by molecular structural changes. This regular surface modulation has attracted attention for optical device applications such as diffractive optical elements, optical switching devices, optical information storage, channel waveguides, and antireflection coatings, etc. Photosensitivity in germanium-doped silica glass has been investigated for grating-based devices with high reflectivities and broad bandwidths that have numerous applications in telecommunications and sensor networks.⁵ In this case, the refractive index changes through a defect reaction within the glass,^{6,7} but a surface relief pattern is rarely found. Some of the recent researches have been focused on making these glasses react more quickly to ultraviolet light and produce higher saturated index changes. In recent years, organically modified silica glasses have begun to receive attention because they can combine the properties of both inorganic and organic compounds, which promise numerous optical applications.^{8,9}

In the present work, we investigated the photosensitivity of organically modified germanosilicate (ORMOGSIL) glasses fabricated by the sol–gel method. We examined the effect of the organic modifier in the enhanced photosensitivity and directly inscribed the surface relief modulation on the ORMOGSIL glass by ultraviolet exposure through a quartz contact mask.

II. Experimental Procedure

Germanium isopropoxide ($\text{Ge}(\text{OC}_3\text{H}_7)_4$, GI) and diethoxydimethylsilane ($(\text{CH}_3)_2\text{Si}(\text{OC}_2\text{H}_5)_2$, DMDDES) were used as the starting precursors. The molar ratio of GI to DMDDES was 1:4. Since the hydrolysis reaction of GI was very fast compared with that of DMDDES, DMDDES was prehydrolyzed with hydrochloric acid as a catalyst for 2 h, and then GI diluted with isopropyl alcohol (1:2 molar ratio) was added to the solution. After being stirred for 24 h, the prepared sol solutions were gelled in a closed Petri dish at 50°C in air for 1 week, during which the inorganic precursor hydrolyzes and condenses into a gel–glass transition network. After sintering at 250°C for 8 h under reduced ($\text{H}_2/\text{N}_2 = 1:9$ volume ratio) atmosphere, we obtained optically transparent ORMOGSIL glasses. Two methyl groups in DMDDES can act as a modifier in the ORMOGSIL glass network, as can be seen in Fig. 1.

Ultraviolet (220–260 nm) light irradiation was performed with a 1000-W Hg/Xg lamp (82511, Oriel, Stratford, CT), which gives a power density of 45 mJ/cm². Refractive index was measured using a prism coupler (Model 2010, Metricon, Pennington, NJ) at 632.8 nm. The density of the ORMOGSIL glass was measured by the Archimedes method using a balance (LA120S, Sartorius, Goettingen, Germany). Raman spectra were measured with a 488-nm Ar–Kr ion laser (Coherent Innova 70 Series, Laser Innovations, Moorpark, CA) and double grating monochromator

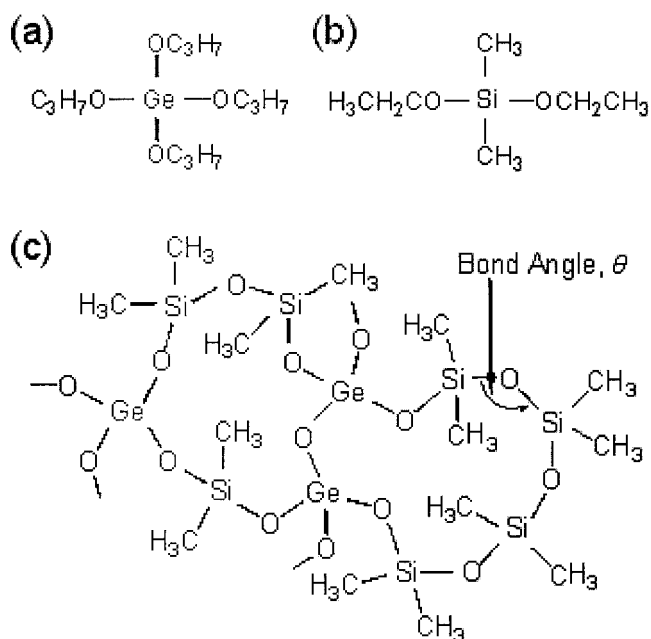


Fig. 1. Chemical structure of the sol–gel precursors and the ORMOGSIL glass: (a) germanium isopropoxide; (b) diethoxydimethylsilane; (c) ORMOGSIL glass. Methyl groups act as modifier in the silica glass network.

J. W. Fleming—contributing editor

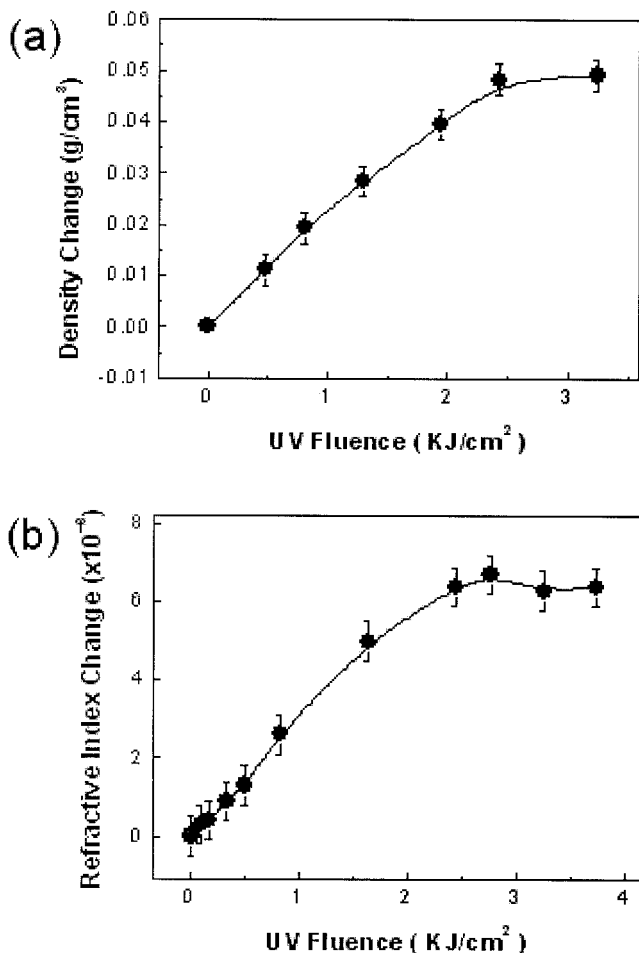


Fig. 2. Change in (a) refractive index and (b) density of the ORMOSIL glasses with the ultraviolet fluence of the 1000-W Hg/Xe lamp (220–260 nm, 45 mJ/cm²).

(U-1000, Jobin Yvon, Inc., Edison, NJ). The surface topology of the ORMOSIL glass was observed by atomic force microscopy (AFM; Autoprobe 5M, Park Scientific Instruments, Woodbury, NY) in a cyclic contact mode.

III. Results and Discussion

Figure 2 shows the refractive index change and the density change of the ORMOSIL glasses with the ultraviolet (UV) fluence. Refractive index increases linearly with the UV fluence up to 2500 J/cm² and then saturates at 6.5×10^{-3} . The density increases linearly up to 0.05 g/cm³ with the UV fluence, the same behavior as that seen for the refractive index change shown in Fig. 2(a). A refractive index change Δn is given by the differential form of the Lorentz–Lorenz equation:¹⁰

$$\Delta n = \frac{(n^2 - 1)(n^2 + 2)}{6n^2} \left(\frac{\Delta \alpha}{\alpha} - \frac{\Delta V}{V} \right) \quad (1)$$

Assuming that a change in polarizability of the ORMOSIL glass is zero with UV irradiation, a refractive index change can be written as follows:

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

The calculated refractive index change from the Lorentz–Lorenz equation is about 8×10^{-3} , which is in agreement with the experimental data.

Zachariassen's random network theory¹¹ provides the basic rules for the modeling of silica glass structures. The simple description of the silica glass structure is based on rings, which are closed circuits along nodal connections, for example through tetrahedra in the tetrahedral network. Angle θ between two neighboring tetrahedra (the Si–O–Si angle) is called the bond angle, as shown in Fig. 1. The densification of the glass structure is ascribed mostly to the variations in θ . Raman scattering spectroscopy was used to ascertain the structural changes of the ORMOSIL glasses with UV irradiation. The frequency shifts in the Raman bands reveal structural changes in the glass. The results are shown in Fig. 3.

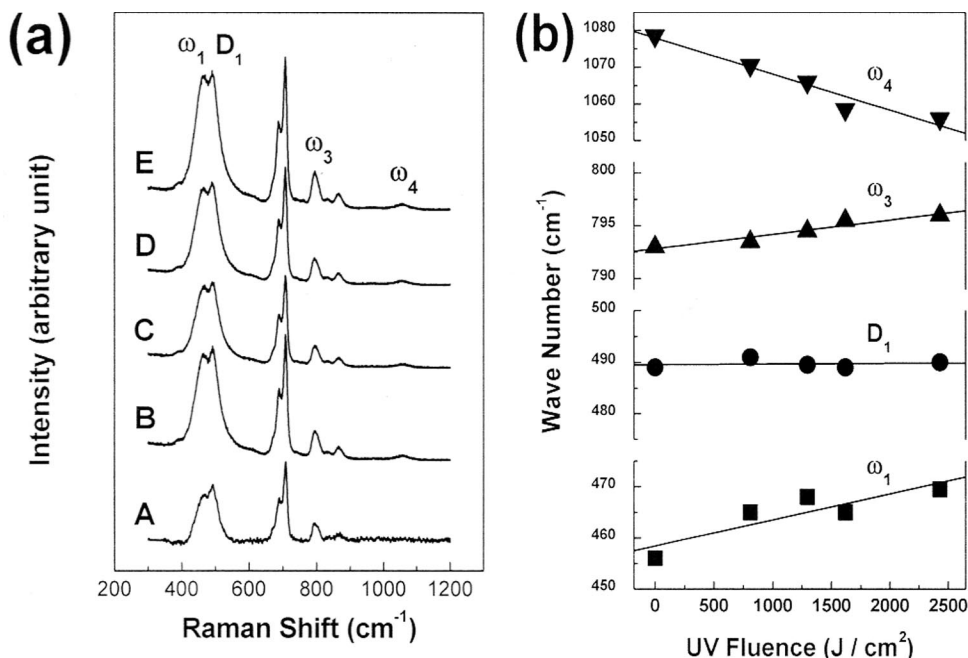


Fig. 3. (a) Stoke-scattered Raman spectra observed in ORMOSIL glasses with the ultraviolet fluence. Traces A–E are 0, 800, 1300, 1600, and 2500 J/cm², respectively. (b) Plot of the peak positions of the Raman features as a function of ultraviolet fluence. Lines drawn through the points are least-squares fits to the data.

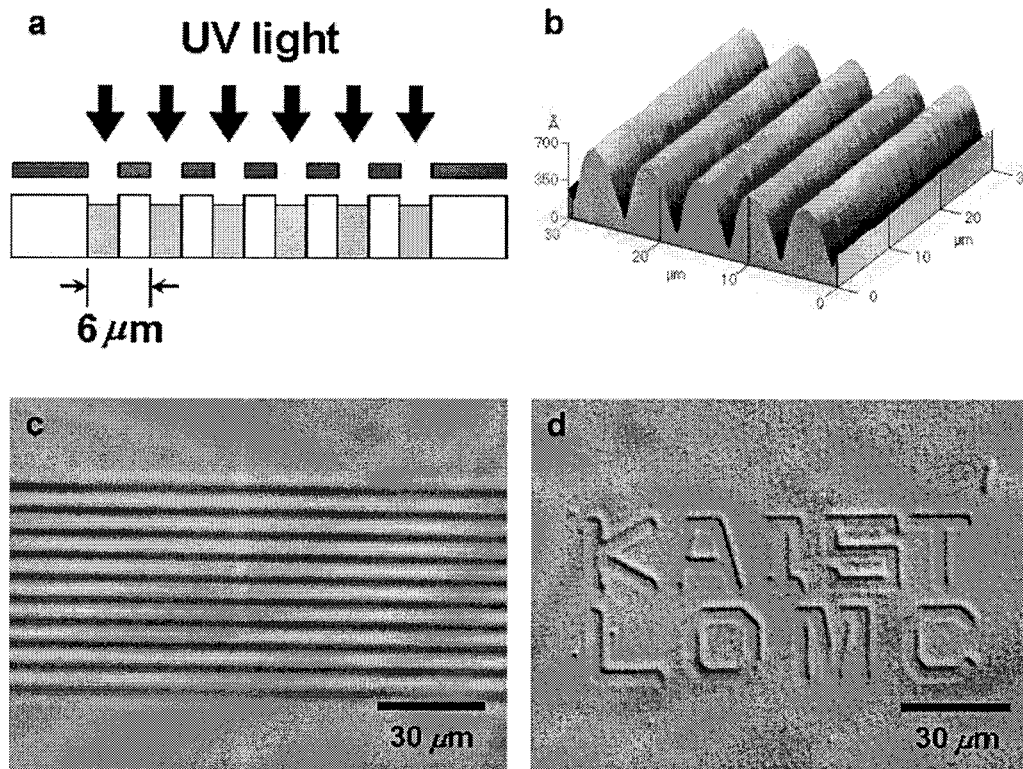


Fig. 4. (a) Schematic representation of ultraviolet direct patterning. Volume compaction occurs in the UV-illuminated regions. (b) AFM and (c, d) optical microscope images of direct photopatterning on the ORMOSIL glass.

460- and 490-cm⁻¹ bands have been assigned to the presence of six-membered rings and four-membered rings of SiO₄ tetrahedra, which are attributed to the Si–O–Si symmetric stretching vibration.^{12,13} The 700-cm⁻¹ band attributed to the methyl group acting as the organic modifier in the glass network is not affected by the UV irradiation. Figure 3(b) shows the change in frequencies of the Raman bands as a function of UV fluence. The ω_1 and ω_3 bands have shifted to the higher frequency side, while the ω_4 band has shifted to the lower frequency side upon UV illumination. However, the D_1 frequency has been found to be independent of UV fluence.

It is well-known that ω_i frequencies are related to the Si–O–Si bridging bond angle θ by a central-force idealized-continuous-random-network (CF-ICRN) theory.¹⁴ Assuming that all force constants are zero except for the Si–O bond-stretching constant α , the relationship between the shift in Raman frequencies $\Delta\omega_i$ and the change in bond angle $\Delta\theta$ is expressed as follows:

$$\Delta\omega_i = \pm(\alpha/m_O)(\sin \theta)(\Delta\theta/2\omega_i) \quad (3)$$

Here, ω_i is the angular frequency (rad/s) of Si–O–Si stretching while m_O is the mass of the oxygen atom. The sign is negative for $i = 1$ and 3 and positive for $i = 4$. Therefore, as shown in Fig. 3, $\Delta\omega_i$ is positive for ω_1 and ω_3 and negative for ω_4 and the intertetrahedral θ decreases from Eq. (3), indicating that the structural densification occurs in the ORMOSIL glass with UV irradiation. A molecular-dynamics simulation of Rino *et al.*¹⁵ indicates that SiO₄ tetrahedra organize in n -fold rings with $3 \leq n \leq 10$, $n = 6$ being the most frequent value in both amorphous and molten silica. And, also, the GeO₂ glass is mainly composed of six-membered rings of GeO₄ tetrahedra connected in a random three-dimensional network because of the larger size of Ge atoms compared with Si atoms. It is well-known that the Ge–O bonds are weaker than Si–O bonds and they can be more readily broken by low-energy radiation. Moreover, it was found in this study that the organically modified silica glass without germanium oxide was not photosensitive. Thus, the behavior of the ω_1 band with UV exposure is due to the breakup and rearrangement of the Ge–O

bonds in the ORMOSIL glass network. In addition, the decrease in connectivity of the three-dimensional network caused by the organic modifier facilitates the structural rearrangement of the ORMOSIL glass. The calculated Si–O–Si $\Delta\theta$ from $\Delta\omega_1$, which is related to six-membered rings of silica tetrahedra, is about -1.64° using $\alpha = 535$ N/m and $\theta = 130^\circ$.¹³ Although there are no data on the relationship between $\Delta\theta$ and the density change $\Delta\rho$ or Δn for the ORMOSIL glasses, Δn of the ORMOSIL glass can be roughly estimated using the relationship for the silica glass. Devine¹⁶ reported that $\Delta\rho$ and $\Delta\theta$ result in the relationship for the silica glass:

$$\Delta\rho = 0.0367 \times \Delta\theta \quad (4)$$

From the calculated bonding angle change, we can roughly estimate Δn of the ORMOSIL glass by using relations (1) and (4). The estimated refractive index change is about 10^{-2} which is in good agreement with the experimental data shown in Fig. 2(a). Therefore, Raman spectra confirm that the density change induced by a change in the bond structure of the silica network accounts for a major part of the photosensitivity in ORMOSIL glasses.

Surface relief patterning in the ORMOSIL glass was photofabricated by UV fluence of 2500 J/cm² through a quartz contact mask. Figure 4(b) represents an AFM image of the lined pattern inscribed on the surface of the glass, and Figs. 4(c) and (d) show $\times 400$ magnified views of the lined and illustrated patterns written on the ORMOSIL glass as imaged through the optical microscope. The three-dimensional view of AFM revealed that the volume compaction in the UV-illuminated region is associated with periodic pattern inscription. This is direct evidence for the photoinduced densification in the ORMOSIL glasses.

IV. Conclusions

We suggest that the large photoinduced refractive index change in the ORMOSIL glass is related to the structural densification caused by UV irradiation. The shifts in frequency of the Raman

bands reveal structural densification by reduction of the average intertetrahedral bonding angle θ in the ORMOSIL glass. Although the writing time for the periodic refractive index modulation is relatively slow, this large index change and the direct inscription of a relief pattern on the ORMOSIL glass have allowed easy development of grating-based devices that have a wide range of optical device applications.

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