

Photoinduced low refractive index in a photosensitive organic–inorganic hybrid material

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A new organic–inorganic hybrid material, that shows photoinduced reduction of refractive index as well as volume contraction, has been prepared using a sol–gel method. Whereas previous photosensitive materials show a photoinduced increase in refractive index, this hybrid material shows a significant decrease in refractive index *via* the decomposition of methacrylate on light irradiation. Moreover, this hybrid material is patternable. The reduction of refractive index measured with a prism coupler was about 0.045, with a low refractive index value of 1.385 being observed. The structural change of the hybrid material on UV-light irradiation as monitored by FT-IR and energy dispersive X-ray spectroscopy (EDS) is investigated. Direct imprinting of the organic–inorganic hybrid material without any further steps (wet etching, thermal curing, or UV fixing) is also performed utilizing the volume contraction on light irradiation.

Introduction

Photosensitivity leads a change in the refractive index or a surface modulation of a medium upon light illumination. Over the past several decades, interest has increased in the use of photosensitive materials for a wide range of applications including diffractive optical elements, optical recording, and antireflective coatings *etc.*^{1–4} So far, research in the field of photosensitivity is dominantly concentrated on silicate glasses and polymers, more particularly on germanosilicate glasses⁵ and azo-polymers.^{6–8} Photosensitivity occurs in those materials by photoinduced densification, defect formation, molecular structural change, *etc.* However, previous photosensitive materials show only a refractive index change or surface modulation without change of the refractive index on light illumination. Moreover, the photoinduced changes in refractive indices or film thicknesses of conventional photosensitive materials are small. For example, germanosilicate glasses, which have been generally used as refractive index-tunable materials by light irradiation for application of optical devices using Bragg gratings, show only small index changes, less than 0.01.⁹ Recently, various organic–inorganic hybrid materials have been synthesized to combine properties of organic and inorganic components in a unique hybrid material.¹⁰ The hybrid materials can be also photosensitive by crosslinking of organic components using photo-initiators.¹¹ While the organic–inorganic hybrid materials can show the changes in refractive index and film thickness at the same time upon light illumination, the photoinduced changes are small.

In this study, a photosensitive organic–inorganic hybrid material derived from a methacryl silicate has been prepared using a sol–gel method. This hybrid material shows a photoinduced reduction of refractive index as well as volume contraction. While previous photosensitive materials such as germanosilicate and general organic–inorganic hybrid materials show a photoinduced increase in refractive index, this hybrid material shows a significant decrease in refractive index ($\Delta n = 0.045$) upon the decomposition of methacrylate on light irradiation. Moreover, this hybrid material is patternable without any etching steps. Here, we show a large photoinduced refractive index reduction, with a final low refractive index value of 1.3853 being observed, comparable to the indices of

perfluorinated polymers (for example, PTFE[®]: 1.38¹²). We also carried out direct imprinting of the organic–inorganic hybrid materials, utilizing the volume contraction on light irradiation.

Experimental

Preparation of the hybrid film

3-Trimethoxysilylpropyl methacrylate (MPTS, Aldrich) and (heptadecafluorodecyl)trimethoxysilane (PFAS, Toshiba) were used as precursors without further purification. The two precursors, MPTS and PFAS, were mixed with distilled water in the presence of 0.05 N hydrochloric acid (HCl) as a catalyst for sol–gel reaction.¹³ After stirring the solution of MPTS–PFAS–water (3 : 1 : 2 mol. equiv.) in the presence of 0.05 N HCl for 9 h at 60 °C, a totally transparent solution was obtained. Subsequently, the transparent solution was filtered through a 0.22 μm -size filter to remove impurities and gas bubbles. The filtered solution was left to stand for 30 min to remove gas bubbles resulting from the stirring and filtering. The solution was then coated onto a p-doped Si(100) wafer by spin-coating at 3000 rpm for 30 s. The coated film was pre-baked for 1 min at 70 °C in order to improve the adhesion between the film and a native SiO₂ layer on a Si wafer. After pre-baking, the coated film was then cured thermally for 12 h at 150 °C. Finally, ultraviolet light (200–260 nm) irradiation was performed with an Oriel 82511 Hg/Xg lamp, which gives a power density of 45 mJ cm⁻². Here, the temperature around the film is about 30 °C upon UV irradiation.

Preparation of the hybrid bulk

The prepared sol solution was gelled in a closed Petri dish at 90 °C in air for 1 week. After thermal curing for 12 h at 150 °C, a transparent hybrid bulk was obtained. Finally, UV light (200–260 nm) irradiation was performed under the same conditions as above.

Characterization

Refractive index was measured using a Metricon MODEL 2010 prism coupler at 632.8 nm and film thickness was

measured obtaining a scanning electron microscope (SEM, Philips, XLSFEG) image of a cross-section of the hybrid film. In order to remove a charging effect, gold was coated on samples for SEM measurement. Infrared spectra were collected on a Bruker EQUINOX55 Fourier transform infrared spectrometer in the range of 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} . Quantitative analysis of the hybrid material film was investigated by energy dispersive X-ray spectroscopy (EDS) at 15 kV. Thermal analyses using thermogravimetric analysis (TGA) were performed under a nitrogen flow using a Dupont Model 951 thermogravimetric analyzer at a heating rate of 5 $^{\circ}\text{C min}^{-1}$ in the temperature range of 30 to 700 $^{\circ}\text{C}$. Powder hybrid materials were prepared for the TGA by grinding the hybrid material. The density of the hybrid bulk was measured by the Archimedes method using a Sartorius LA120S balance. The surface morphology of the patterned hybrid film was observed by atomic force microscopy (AFM, Park Scientific Instrument, Autoprobe 5M) in a cyclic contact mode. The scanned area was 80 \times 80 μm . A magnified (\times 400) top-view image of the illustrated pattern written in the hybrid material was taken using an optical microscope (Leica, Metallux 3).

Results and discussion

This organic–inorganic hybrid material is composed of an inorganic Si–O–Si main chain and functional organic perfluoroalkyl and methacryl side-groups, as shown in Fig. 1. These functional organic groups are covalently bonded to the inorganic Si–O–Si network, where the organic components fill the vacant spaces in the inorganic silica framework and modify the silica network.¹⁰ Perfluoroalkyl groups reduce the refractive index in solution¹² while methacryl groups undergo photo-induced decomposition upon UV absorption of the carbonyl group. The UV-induced decomposition of methacrylate is well known in poly(methyl methacrylate).^{14,15} Carbonyl groups of poly(methyl methacrylate) absorb UV light in the 190–280 nm wavelength region. The resulting excitation of these carbonyl

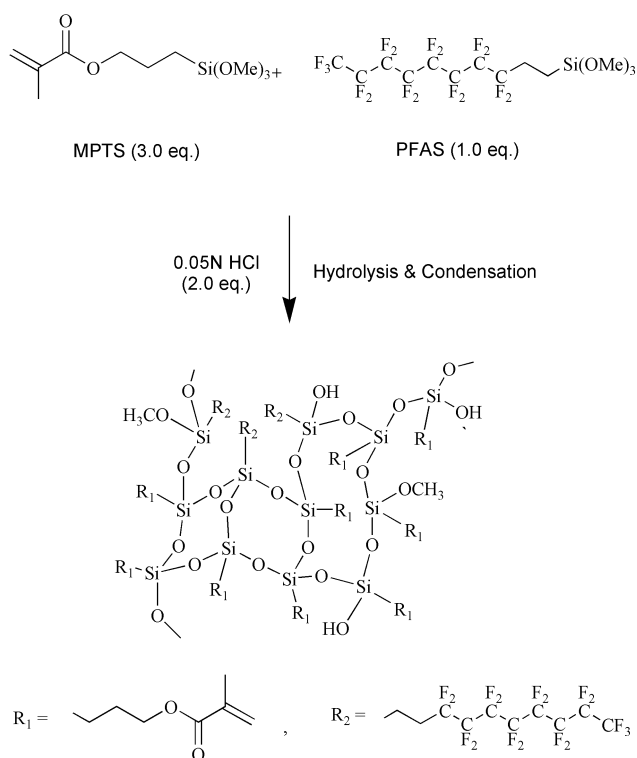


Fig. 1 Chemical structure of the sol–gel precursors and the idealized structure of the hybrid solution. The precursors comprise inorganic networks modified by organic functional methacrylate (R_1) and fluoroalkyl groups (R_2) via hydrolysis and condensation reactions.

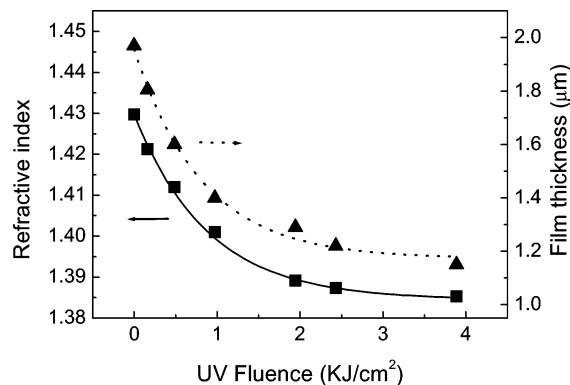


Fig. 2 Change in refractive index and thickness of the hybrid material film with ultraviolet fluence from a 1000 W Hg/Xe lamp (200–260 nm, 45 mJ cm^{-2}).

groups leads to the removal of ester groups and scission of the main chain. The polymeric fragments removed from the polymer are normally observed as gases such as CO_2 , CH_4 , etc. These small gas molecules diffuse out from the matrix so that the density of poly(methyl methacrylate) decreases as the exposure time to deep UV light increases.

Fig. 2 shows the changes in refractive index and the thickness of this organic–inorganic hybrid film with the ultraviolet cumulated fluence. The refractive index measured with a prism coupler method is an average value for the whole film thickness. The refractive index decreases exponentially from 1.4298 down to 1.3853 with the ultraviolet fluence. Also, the film thickness decreases exponentially from 1.97 to 1.15 μm with the UV cumulated fluence. Therefore, this hybrid material is photosensitive and shows large photoinduced changes. Especially, the reduced refractive index value of 1.3853 is very low, and is comparable to the indices of perfluorinated polymers (e.g. PTFE[®]: 1.38¹²).

Photoinduced structural changes in the hybrid material were investigated by Fourier transform infrared (FT-IR) spectroscopy. The absorption spectra of the hybrid material films exposed to different UV energies are compared in Fig. 3. As shown in spectrum A (non-irradiated), there is no peak for the vinyl group $\nu(\text{C}=\text{C})$ mode at 1637 cm^{-1} (α).¹⁶ This suggests that most of the C=C bonds of MPTS are opened during the thermal curing at 150 $^{\circ}\text{C}$ for 12 h before UV radiation, indicative of the fact that most vinyl groups start to thermally decompose at about 100 $^{\circ}\text{C}$.¹⁷ The decomposition of the methacryl chains on irradiation is evidenced by the fact that the intensity of the carbonyl $\nu(\text{C}=\text{O})$ stretching mode at 1736 cm^{-1} (β) decreases significantly as the UV fluence increases.¹⁴

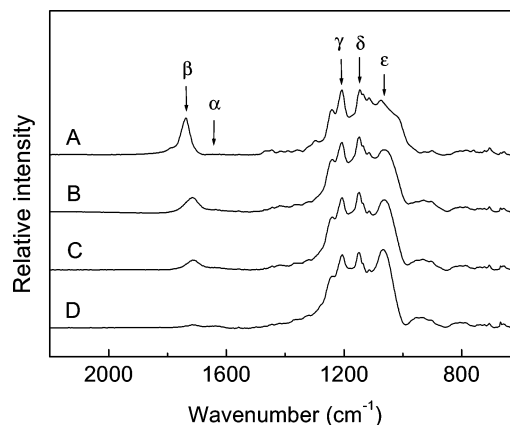


Fig. 3 FT-IR Absorption spectra of the organic–inorganic hybrid film. The y-axis shows the relative intensities of the absorption coefficient. Spectra A–D correspond to the non-irradiated, 0.5, 1.0 and 1.9 kJ cm^{-2} irradiated samples, respectively.

Perfluoroalkyl groups seem to be stable to degradation on irradiation, as shown by little change in the intensities at 1206 and 1146 cm^{-1} , assigned to C–F stretching and C–H bending modes in the perfluoroalkyl chains (γ and δ).¹⁸ Also, photoinduced condensation reactions in the inorganic Si–O–Si network are evidenced by the increase of the intensity of $\nu_{\text{as}}(\text{Si–O–Si})$ mode at 1060 cm^{-1} (ϵ).^{11,19} A decrease in the distribution of the siloxane bond angles is indicated by the sharpening of the $\nu_{\text{as}}(\text{Si–O–Si})$ band (ϵ), which is opposite to the result that the distribution of the bond angles increases when methacrylate is organically cross-linked in other hybrid materials.¹¹

The changes in the relative atomic ratios of the hybrid material due to UV irradiation were investigated by energy dispersive X-ray spectroscopy (EDS) as shown in Fig. 4. As the UV fluence increases, the atomic ratios of carbon to silicon and oxygen to silicon decrease exponentially. The decreases in the relative amounts of carbon and oxygen are related to the decomposition of the organic methacryl group. By reference to the decomposition pattern of poly(methyl methacrylate) upon UV irradiation,^{14,15} the carbonyl groups of the organic methacryl species in the hybrid material absorbs UV light in the 190–280 nm wavelength region. The excitation of the carbonyl groups leads to the decomposition of the organic methacryl chains, with the organic fragments removed from the hybrid material decomposed to gaseous products containing carbon and oxygen. While the methacryl chains decompose on irradiation, the perfluoroalkyl groups do not decompose. Thus, the atomic ratio of carbon to fluorine decreases exponentially with ultraviolet fluence in Fig. 4.

Fig. 5 illustrates TGA curves of two hybrid samples which were non-irradiated and irradiated (2 kJ cm^{-2}). The two samples show significant weight losses between 300 and 550 $^{\circ}\text{C}$ with a plateau at 600 $^{\circ}\text{C}$, due to the decomposition of the organic groups (methacryl and perfluoroalkyl chains). Most

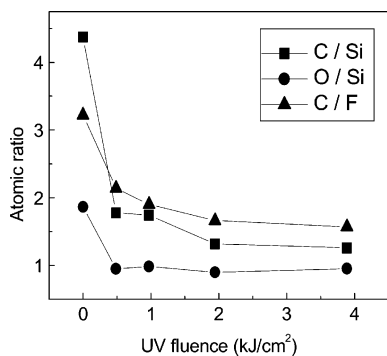


Fig. 4 Energy dispersive X-ray spectroscopy (EDS) of the hybrid film monitoring the change of relative atomic ratios upon UV irradiation.

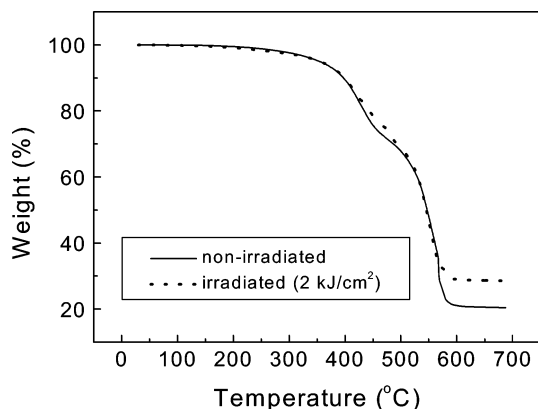


Fig. 5 TGA curves of non-irradiated and irradiated (2 kJ cm^{-2}) hybrid materials at 5 $^{\circ}\text{C min}^{-1}$.

inorganic groups remain at 600 $^{\circ}\text{C}$. The char yield (inorganic residues) of the UV-irradiated sample at 600 $^{\circ}\text{C}$ is larger than that of the non-irradiated sample. This suggests that the proportion of organic groups in the hybrid material is lowered on UV irradiation because methacryl units decompose and are removed as volatile gas molecules, and thus the relative proportion of inorganic groups increases after UV irradiation.

The organic methacryl groups fill the vacant spaces in the Si–O–Si framework before UV exposure. On UV irradiation, the methacryl units decompose and are removed from the framework as gaseous products. Since bulky methacryl chains which sterically hinder condensation reactions are removed upon UV irradiation, further condensation reactions to extend the Si–O–Si frameworks are enhanced concurrently with the decomposition of methacryl groups. Therefore the film thickness decreases, as shown in Fig. 2, due to the shrinkage of the inorganic network *via* photoinduced condensation reactions.

A refractive index change Δn of a material is given by the differential form of the Lorenz–Lorentz equation [eqn. (1)]:²⁰

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

where $\Delta \alpha/\alpha$ and $\Delta \rho/\rho$ are the relative changes in polarizability and density, respectively. From eqn. (1) above, the two effects of the polarizability change and the density change determine the refractive index change. Assuming that a change in polarizability of a material is zero upon UV irradiation, the refractive index change can be expressed by eqn. (2).

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

Fig. 6 shows the changes in refractive index and density of the bulk hybrid material with the cumulated UV fluence. The refractive index and density of the hybrid bulk were measured by a prism coupler method and by the Archimedes method, respectively. Whereas the refractive index of the bulk sample decreases significantly up to 0.044 with cumulated UV fluence, the density of the bulk is reduced slightly up to 0.02 g cm^{-3} . The refractive index reduction calculated from eqn. (2) with the measured density change is about 0.005, which is much smaller than the measured value of the refractive index change in Fig. 6. Therefore, the contribution of density change to the refractive index change is not dominant in this hybrid material. The other effect for the refractive index change is the polarizability change [eqn. (1)]. Generally, carbonyl groups are very polar and hence result in high refractive indices of materials.²¹ These carbonyl groups are removed on UV irradiation by the decomposition of methacryl chains in the hybrid material, as shown in Fig. 3. Thus, it is considered that the polarizability reduction by the removal of carbonyl groups

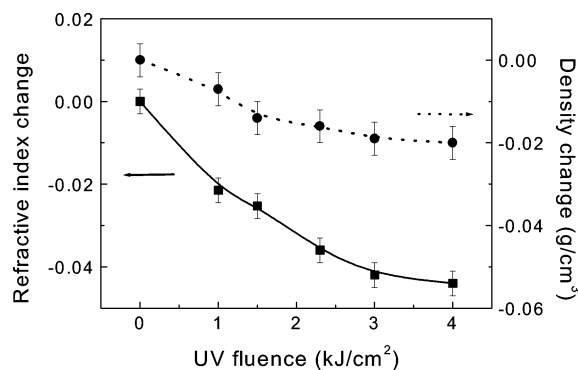


Fig. 6 Change in refractive index and density of the bulk hybrid material with ultraviolet fluence from a 1000 W Hg/Xe lamp (200–260 nm, 45 mJ cm^{-2}).

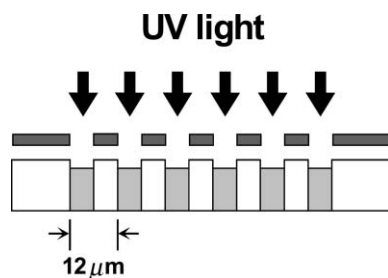


Fig. 7 Schematic representation of UV direct patterning using a contact mask. The refractive index is reduced and the film shrinks in the UV-illuminated regions upon decomposition of the methacrylate groups.

contributes dominantly to the decrease in refractive index on UV irradiation.

Imprinting the organic–inorganic hybrid material was carried out using a UV fluence of 1.9 kJ cm^{-2} through a quartz contact mask, as shown in Fig. 7. No further steps (wet etching, thermal curing, or UV fixing) were necessary to reveal and stabilize the surface relief due to the photoinduced contraction in the volume. Fig. 8(a) shows an atomic force microscope (AFM) image of the lined pattern inscribed on the surface of the hybrid material and Fig. 8(b) shows a magnified view ($\times 400$) of the illustrated pattern written in the hybrid material as seen through an optical microscope. The three-dimensional view by AFM revealed that a periodic pattern of a sinusoidal wave was formed upon the hybrid material with a $12 \mu\text{m}$ period spacing and 141 nm changes in depth from the original surface. Compared to the thickness change shown in Fig. 1 (680 nm thickness change at the same UV fluence), the

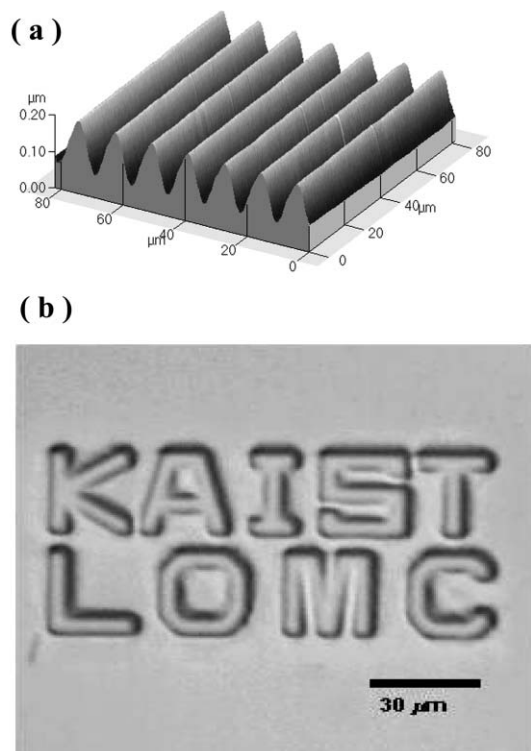


Fig. 8 Atomic force and optical micrographs of hybrid films exposed through a quartz contact mask at a UV fluence of 1.9 kJ cm^{-2} . (a) An atomic force microscope image of the surface relief pattern inscribed into the hybrid material. The periodic pattern period is $12 \mu\text{m}$ and the change in depth from the original surface is 141 nm . (b) Optical microscope image of the illustrated photoinduced printing *via* volume change.

smaller thickness change between the exposed and unexposed regions through a contact mask is due to scattering of light at the mask and back reflections from the Si wafer.

Conclusion

Reduction in refractive index and thickness occurred upon UV irradiation in the photosensitive organic–inorganic hybrid material derived from a methacrylate-modified silica compound. The refractive index decreased from 1.4298 to 1.3853 at a wavelength of 632.8 nm and the film thickness changed from 1.97 to $1.15 \mu\text{m}$ upon UV illumination. It is considered that the decomposition of methacryl groups causes the large reduction of refractive index on UV irradiation while photoinduced densification in the inorganic framework causes the concurrent decrease of film thickness. Whereas organic methacryl groups largely decompose, rigid inorganic frameworks maintain inorganic bonding without scission on UV irradiation. Thus, a low refractive index with volume contraction in the hybrid material can be obtained by UV irradiation. This photosensitive hybrid material, therefore, can be applied in the fields of antireflective coatings and integrated optical devices using Bragg gratings, and in the production of low dielectric materials.

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