Wavelength-Dependent Photosensitivity in a Germanium-Doped Sol–Gel Hybrid Material for Direct Photopatterning**

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Photosensitivity, as evident in permanent changes in refractive index and volume upon light exposure, is observed in a germanium-doped methacrylate hybrid material (hybrimer) and found to depend on the wavelength of the UV light. Exposure to short-wavelength UV illumination (220–260 nm) results in very high photosensitivity with changes in refractive index ($\Delta n \approx 0.0164$) and film thickness ($\Delta t \approx 40\%$) that are mainly a result of photopolymerization and Ge-related densification. In contrast, the hybrimer is hardly photosensitive to light in the long UV-wavelength range (350–390 nm). Direct photopatterning of a single circle on the hybrimer film creates a concave lens-like topography upon illumination with UV light of short wavelength and a convex lens-like one upon illumination with UV light of long wavelength.

1. Introduction

Micro-optical structures have been studied widely owing to their increased use in compact optoelectronics, optical computing, and optical communication devices. Conventional microfabrication is carried out via a multi-step process that includes an etching or developing stage. The process could be simplified by using photosensitive materials that can undergo permanent changes to their refractive index and volume simply by exposure to light. This would allow the fabrication of micro-optical structures without an etching or developing step. It has been known that Ge-doped silica glasses,[3] photopolymers,[4] and azo polymers[5] are typical photosensitive materials that can have their refractive index modulated or have surface relief micro-optical structures created in them, just by exposure to UV light. However, these materials possess comparatively little photosensitivity, are sensitive to heat, and are often not transparent enough to be used in the fabrication of micro-optical devices.

Recently, it has been reported that sol–gel-derived inorganic–organic hybrid materials (hybrimers) also exhibit high photosensitivity upon illumination with UV light and can be used in the fabrication of many micro-optical devices such as waveguides,[6] microlenses,[7] and gratings.[8,9] In the photosensitive hybrimers, various photosensitivity mechanisms, such as photopolymerization,[10,11] photobleaching,[12–15] photomigration,[16] photodecomposition,[17,18] and photodensification,[19,20] have been proposed to explain the different types of change in the refractive index and volume. It would seem that the photosensitivity of the hybrimer can be maximized by optimizing both of the photosensitive mechanisms of the inorganic and organic components. In fact, it has been found that Ge-doped methacrylate hybrimer consisting of methacrylate and Ge-doped silica in the molecular structure shows high photosensitivity in the form of a refractive-index increase and accompanying volume compaction. Both the Ge-related densification in the silica network and the photopolymerization of methacrylate induced by illumination with UV light contribute to the photosensitivity. It is known that the photoinduced densification of Ge-doped silica glass occurs only for light in the deep UV region of the spectrum.[21] Also, it has been reported that the photopolymerization of acrylates is likewise dependent on the wavelength of the UV light employed.[22] Thus, it is expected that the photosensitivity of the Ge-doped methacrylate hybrimer will be highly sensitive to the wavelength of the UV light used, as the photosensitivity mechanisms will vary depending on the wavelength of the illuminating light.

In this study, we first examined the photosensitivity mechanisms of the Ge-doped methacrylate hybrimer as a function of the wavelength of the illuminating light. Then, the change in the refractive index ($\Delta n$) and the film thickness ($\Delta t$) induced by irradiation with two UV lamps yielding light of different wavelengths were investigated. It was found that the photosensitivity mechanism relied on the wavelength of the illuminating light. Finally, we demonstrated the fabrication of lens-like shapes by photopatterning of the hybrimer using the two different UV lamps.

2. Results and Discussion

The Ge-doped methacrylate hybrimer films were irradiated with a Hg/Xe lamp and a Hg lamp which possess different UV spectral ranges of 220–260 nm and 350–390 nm, respectively. Figure 1 shows the change in the refractive index and the thickness of the films as a function of UV-light fluence for both the UV lamps. Irradiating with the Hg/Xe lamp caused an initial drastic change in both the refractive index and the film thickness. These effects were seen to saturate after exposure for

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long times. On the other hand, the Hg-lamp illumination barely changed the refractive index and the film thickness, with the initial increase being small.

To summarize, using the Hg/Xe lamp resulted in high photosensitivity, and using the Hg lamp resulted in low photosensitivity. This implies that the photosensitivity of the Ge-doped methacrylate bybrimer depends heavily on the wavelength of the UV light. The different photosensitivity mechanisms of the Ge-doped methacrylate bybrimer were examined as a function of the wavelength of the irradiating light.

2.1. Photopolymerization with a Photoinitiator

Figure 2a shows the evolution of the Fourier-transform infrared (FT-IR) spectra of the Ge-doped methacrylate bybrimer as a function of fluence using the Hg/Xe lamp. Exposure to the short-wavelength radiation of the Hg/Xe lamp reduces the intensity of the ν(C=O) peak at 1638 cm⁻¹ and shifts the ν(C=O) peak at 1718 cm⁻¹ to longer wavenumbers. This represents the consumption of C=O bonds and the loss of conjugation with the C=C bond in the methacrylate bybrimer owing to photopolymerization in the initial stages of UV illumination. However, it may be seen that the integrated area of the ν(C=O) band at 1718 cm⁻¹ remains constant. The degree of conversion of the C=C bond was calculated by the ratio of the integrated area of the ν(C=O) peak to the integrated area of the ν(C=O) peak. We calculated and plotted this as a function of UV fluence (Fig. 2b). The degree of conversion of the C=C bond increases up to 90% with growing UV fluence. This indicates that photopolymerization occurs efficiently in the bybrimer under illumination with light of short UV wavelength. In addition, the intensities of the ν(Si–O (H)) peak and the ν(–OH stretching mode) band at around 944 and at 3400 cm⁻¹, respectively, and the ν(–CH₃) peak at 1166 cm⁻¹ gradually decrease.

**Figure 1.** Change in refractive index and film thickness of the Ge-doped methacrylate bybrimer as a function of UV-light fluence when illuminated by a) a Hg/Xe lamp (220–260 nm) and b) a Hg lamp (350–390 nm).

**Figure 2.** Photopolymerization behavior of a Ge-doped methacrylate bybrimer with a photoinitiator under the illumination of a Hg/Xe lamp (220–260 nm): a) FT-IR spectra and b) calculated degree of conversion of the C=C bond as a function of UV-light fluence in air and under a N₂ atmosphere.
with fluence. This indicates that a concurrent photoinduced condensation between silanol and alkoxy in the metastable siloxane network occurs during illumination with UV light. Therefore, sharp changes in the refractive index and the film thickness in the initial stage of exposure to UV light (Fig. 1a) are attributed to structural densification caused by the photopolymerization of methacrylates and the photoinduced condensation of siloxane. Figure 3 shows the FT-IR spectra of the films and the degree conversion of the C=O bond as a function of fluence, this time under illumination from the Hg lamp. The intensity of the ν(C=O) peak at 1638 cm⁻¹ barely decreases, resulting in a low degree of conversion (less than 10%). This indicates that the photopolymerization is not induced by irradiation with light from the long UV-wavelength part of the spectrum. Also, no significant change in the intensities of the ν(Si–O(H)) peak, the ν(–OH stretching mode) band, or the ν(–CH₃) peak is seen during the illumination. This indicates that light with a long UV wavelength does not induce the condensation reaction. Thus, almost no photosensitivity is observed under illumination with the Hg lamp except a very small change in the first stage of irradiation as shown in Figure 1b.

Oxygen inhibition has always been a problem in the free-radical photopolymerization of acrylates. The presence of molecular oxygen strongly influences free-radical polymerization, because the free radicals formed by the photolysis of the initiator are rapidly consumed by O₂ molecules to yield peroxy radicals. These species are not reactive towards the remaining unreacted monomer and can therefore not initiate or participate in any polymerization reaction. This detrimental effect of oxygen is also suspected to have a pronounced influence on the free-radical photopolymerization of the Ge-doped methacrylate hybrimer. To investigate this, the films were irradiated using the Hg/Xe lamp and the Hg lamp under a N₂ atmosphere. Figure 2b shows the results of the degree conversion of the acrylic double bond as a function of UV fluence for irradiations performed in N₂ and in air. The variation of the degree of conversion with increasing fluence in the case of the Hg/Xe lamp is almost identical in air and under a N₂ atmosphere. On the other hand, exposure to the Hg lamp under a N₂ atmosphere raises the maximum value of the degree of conversion compared to that in air, as shown in Figure 3b. Therefore, the illumination with long-wavelength UV light in an N₂ atmosphere can enhance the photopolymerization, but its effect is small compared with that of employing radiation with a short UV wavelength.

2.2. Photopolymerization Without a Photoinitiator

Recently, it was reported that the acrylates, like many other organic compounds, can be photopolymerized by irradiation with light of short UV wavelength, that is, below 260 nm. This result is explained by the large absorption at short wavelength and also the high photon energy. Thus, it is expected that the Ge-doped methacrylate hybrimer can be also photopolymerized to create photosensitivity without adding a photoinitiator. Figure 4 shows the photopolymerization behavior of the hybrimer without a photoinitiator as a function of the UV wavelength. In the short-wavelength region in Figure 4a, the intensity of the ν(C=O) peak gradually diminishes with an increasing fluence of up to 80 J cm⁻². This clearly confirms that the excitation of the C=O bonds is caused not by a photoinitiator, instead, the high-energy photon itself directly initiates the photopolymerization of the acrylates in the hybrimer. In other words, the high photon energy can induce photopolymerization without using a photoinitiator. Thus, light from the short-wavelength UV spectrum can photopolymerize the methacrylate group in the hybrimer even without the addition of a photoinitiator. As a result, the degrees of conversion in Figure 2b are almost the same, even though the illumination is made in an air atmosphere. In contrast, when employing long-wavelength light the intensity of the ν(C=O) peak in the spectrum from the hybrimer is not changed at all, indicating a very small degree of conversion, as shown in Figure 4b. This explains the reason why the degree of conversion is low at this wavelength.

Figure 3. Photopolymerization behavior of a Ge-doped methacrylate hybrimer with a photoinitiator under the illumination of a Hg lamp (350–390 nm): a) FT-IR spectra and b) calculated degree of conversion of the C=O bond as a function of UV-light fluence in air and under a N₂ atmosphere.
even with long exposures, as seen in Figure 3b. This shows that photopolymerization cannot occur without adding a photoinitiator as expected when using light of this wavelength. The methacrylate has no absorption at this wavelength, and the energy of the photon is too low to induce direct excitation of the C=C bond for the photopolymerization. An almost constant difference in the degree of conversion of the C=C bond is seen between the results in air and in N₂. The consistently lower value in air is a result of the detrimental effect of oxygen. This effect is not seen in the data obtained when using the shorter-wavelength illumination, as the effect of oxygen is compensated for in this case.

2.3. Germanium-Related Densification

Based on the idea of the photosensitive Ge-doped silica glass, a sol–gel-derived Ge-doped methyl hybrimer was examined and showed high photosensitivity, consisting of large changes in its refractive index and an accompanying volume compaction.[19,20] This results from the Ge-related densification of the silica network, which was found only in the Ge-doped hybrimer. The Ge-related densification consists of the compaction of the matrix by the breakage of the Ge–O bond. It was produced in the hybrimer by illumination with light of short wavelength as in the silica glass. It was also found that the photosensitivity was enhanced in the Ge-doped methacrylate hybrimer by the photopolymerization of methacrylate.[20,27] Ge precursor (germanium isopropoxide, GI) or tetramethyloxysilicate (TMOS) are used to prepare Ge-doped or undoped films, respectively, and then the photosensitivity of the hybrimer films, Ge-doped or undoped methacrylate hybrimer, was investigated to examine the role of Ge-related densification. The changes in refractive index and film thickness upon exposure to UV light are presented in Figure 5. In the case of Hg/Xe-lamp exposure, the photosensitivity of the undoped meth-

Figure 4. Degree of conversion of the C=C bond in a Ge-doped methacrylate hybrimer without a photoinitiator under illumination of a) a Hg/Xe lamp (220–260 nm) and b) a Hg lamp (350–390 nm).

Figure 5. Changes in refractive index and film thickness of a Ge-doped and undoped methacrylate hybrimer illuminated by a) a Hg/Xe lamp (220–260 nm) and b) a Hg lamp (350–390 nm) as a function of UV-light fluence.
acrylate hybrimer, synthesized using TMOS instead of GI, is lower than that of the Ge-doped methacrylate hybrimer (Fig. 5a). The distinct difference in photosensitivity between the Ge-doped and undoped methacrylate hybrimers is attributed to the Ge-related densification. In contrast, illumination with the Hg lamp does not change the refractive index or the film thickness in either the doped methacrylate hybrimer or the undoped methacrylate hybrimer (Fig. 5b). Thus, it is confirmed that the Ge-related densification in the hybrimer is activated by light from the short-wavelength region of the spectrum. Therefore, a large increase in refractive index and concomitant volume compaction can be made by combining photopolymerization and Ge-related densification by illuminating with light from the short UV-wavelength region of the spectrum.

2.4. Photodecomposition of Methacrylate

Typically, organic polymers are liable to decompose upon UV illumination. For example, poly(methyl methacrylate) decomposes on long exposure to UV radiation of short wavelength since the carbonyl group absorbs UV light in the 190–280 nm wavelength region.\(^{[2]}\) Also, the decomposition of the methacrylate group in the hybrimer, which results in a reduction in the refractive index and the film thickness, has already been noted.\(^{[1]}\) Thus, the Ge-doped methacrylate hybrimer, mainly composed of a Si–O–Si network with methacryl groups, should also be susceptible to the photodecomposition reaction when subjected to long exposures of UV radiation, leading to decreases in refractive index and film thickness. This behavior is consistent with our observations, such as the refractive-index decrease that occurs eventually after a very long Hg/Xe lamp irradiation (Fig. 1a). The photodecomposition of methacrylate seems only to be active when illuminating with short-wavelength UV radiation. Figure 6 presents FT-IR spectra that show the change in the carbonyl group in the Ge-doped methacrylate hybrimer irradiated with light from the Hg/Xe lamp and the Hg lamp. A large fluence (over 810 J cm\(^{-2}\)) of light from the Hg/Xe lamp diminishes the carbonyl ν(C=O) stretching mode peak at 1718 cm\(^{-1}\) continuously as the fluence increases. This confirms the occurrence of the photodecomposition of the methacrylate in the Ge-doped methacrylate hybrimer (Fig. 6a). During the photodecomposition of the methacrylate, high-index molecular species including polar carbonyl groups are evaporated off as gaseous products, decreasing both of the refractive index and the film thickness of the Ge-doped methacrylate hybrimer. In addition, the intensity of the Si–O–Si peak at 1108 cm\(^{-1}\) shifts to lower wavenumbers, indicating a decrease in the Si–O–Si bond angle upon UV-light irradiation using the Hg/Xe lamp. This shows that a further densification reaction of the silica network proceeds as the bulky methacrylate chains are removed by the photodecomposition. The densification can also contribute to the reduction of the film thickness. On the other hand, the carbonyl stretching-mode peak is unchanged with Hg-lamp irradiation, as seen in Figure 6b. This indicates that the methacrylate does not decompose upon long UV-wavelength radiation, as is expected for polymers. Also, no change in the Si–O–Si peak is found for the hybrimer illuminated by the Hg lamp as shown in Figure 6b, and that is because the methacrylate groups stick to the matrix even after a lengthy exposure to UV light.

2.5. Direct Photopatterning

The Ge-doped methacrylate hybrimer is directly photopatterning without the need for any developing step because of simultaneous changes in both the refractive index and the thickness upon exposure to UV light. As shown and discussed...
above, the hybrimer is photosensitive only with the Hg/Xe lamp, which has short-wavelength light. The hybrimer is shrunk by photopolymerization and photocondensation during the initial stage of UV irradiation (low fluence), and Ge-related densification, photodecomposition, and silica densification at a later stage of UV irradiation (high fluence). In contrast, only a small amount of photopolymerization occurs in hybrimers during the initial stages of illumination with an Hg lamp. Thus, it is expected that the shape patterned by direct UV exposure can vary depending on the UV lamps used. Direct photopatterning was carried out using a UV fluence of 1800 J cm\(^{-2}\) through a quartz contact mask consisting of a single 5 µm circle using both a Hg/Xe lamp and a Hg lamp. The pre-drying process was employed as is necessary in the use of a contact mask, as reported previously.\(^{[13]}\) Figure 7 shows a three-dimensional atomic force microscopy (AFM) image of the single-circle pattern on the Ge-doped methacrylate films after illumination with the different UV lamps. Lens-like shapes may be detected that possess different shapes depending on which lamp was employed. The Hg/Xe-lamp exposure makes concave lens-like shapes induced by volume compaction that is mainly a result of photopolymerization and Ge-related densification (Fig. 7a), as expected. Surprisingly, a convex-lens-like shape is seen after direct photopatterning using the Hg lamp (Fig. 7b), even though little photoinduced reduction of the film thickness was found (Fig. 1b). It was found that selective UV-light exposure using a photo-mask can be accompanied by mass transport of material via a diffusion process of the monomer and/or small-molecular oligomers in the hybrid film.\(^{[16]}\) When UV light was irradiated onto a specific area, the photoinitiator was decomposed and reacted with a polymerizable group. The photopolymerization takes place only in the illuminated areas, leading to the formation of concentration gradients in the films. Consequently, diffusion of the constituents occurs from the non-irradiated regions to the irradiated regions of the hybrid films, which results in the creation of volume expansion in the exposed area. This photosensitivity mechanism in the hybrimer is called photomigration. Thus, the shape resulting from direct photopatterning by Hg-lamp exposure can be convex-lens-like owing to volume expansion from photomigration. On the other hand, for the illumination with the Hg/Xe lamp, photomigration is dominated by the other major photosensitive mechanisms revealed in this study. This results in direct photopatterning of a concave-lens-like shape. However, the bulges at the edge of the shape (see Fig. 7a) are a result of the occurrence of photomigration from the Hg/Xe-lamp exposure. Therefore, the Ge-doped methacrylate hybrimer is a potential photosensitive material to be used in the fabrication of various shapes for micro-optical devices. The appearance of the micro-optical structures can be controlled by changing the wavelength of the UV light and its fluence.

3. Conclusions

The Ge-doped methacrylate hybrimer showed different photosensitivity depending on the wavelength of the illuminating light. Under illumination with 220–260 nm wavelength light, the hybrimer undergoes photopolymerization, photocondensation, germanium-related densification, methacrylate decomposition, and silica-network densification. Specifically, regarding photopolymerization, the hybrimer is photopolymerized by the energetic photon without a photoinitiator being necessary. As a result, short-wavelength illumination creates high photosensitivity, resulting in large changes in refractive index and film thickness. On the other hand, under illumination with light of 350–390 nm, the hybrimer exhibits negligible photosensitivity, and photopolymerization occurs only with a photoinitiator. Photosensitivity to long-wavelength UV light can be enhanced by irradiation in a N\(_2\) atmosphere, but the response is much lower than to UV light with a short wavelength.

The shapes obtained from the direct photopatterning on the Ge-doped methacrylate hybrimer were also dependent on

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**Figure 7.** AFM images of the direct photopatterning of a single circle in a Ge-doped methacrylate hybrimer illuminated by a) a Hg/Xe lamp (220–260 nm) and b) a Hg lamp (350–390 nm).
the wavelength of the UV light. The short-wavelength light produced concave shapes, mainly owing to the photopolymerization and the Ge-related densification. On the other hand, the convex shape is fabricated under long-wavelength UV light irradiation, as only photomigration occurs from unexposed areas to exposed areas, without any densification.

4. Experimental

Ge-doped methacrylate hybrimer was prepared from 3-trimethoxysilylpropyl methacrylate (MPTS, Aldrich) and germanium isoproxide (GI, Aldrich) in a 9:1 molar ratio. Since the hydrolysis reaction of GI was very fast compared with that of MPTS, MPTS was first hydrolyzed with 0.75 equivalents of water in the presence of 0.01 N hydrochloric acid as a catalyst. After that, GI was added to the pre-hydrolyzed solution and stirred for 1 h to advance the hydrolysis and the condensation. The mixed solution was reacted with additional water for 24 h to complete the hydrolysis and the condensation. The total amount of water used was 2.625 mol-% over total silane in the solution. The obtained solution was totally transparent. 2-Benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-11 (Irgacure 369, Aldrich) was added to the transparent solution as a photoinitiator of the methacrylate. Subsequently, the transparent solution was filtered through a 0.22 μm filter to remove impurities and bubbles. The solution was then coated onto a p-type Si(100) wafer by spin-coating at 4000 rpm (rpm: revolutions per minute) for 30 s. Single coating yields an approximate film thickness of 5–6 μm. The films were illuminated by a Hg/Xe lamp (Oriel 82511, power density of 70 mW cm⁻² with a spectral range of around 220–260 nm) and a Hg lamp (Oriel 97435, power density of 70 mW cm⁻² with a spectral range of around 350–390 nm) [29].

The molecular structural change of the films upon UV-light illumination was investigated using Fourier-transform infrared (FT-IR, JASCO 680 Plus) spectroscopy. The refractive index and thickness of the films were measured at 632.8 nm with a prism coupler (Metricon 2010). Direct-patterning of the Ge-doped methacrylate hybrimer was carried out using a UV-light fluence of 1800 J cm⁻² through a quartz contact mask. Finally, the patterned microimages were observed by using atomic force microscopy (AFM, Park Scientific Instruments, Auto probe 5 M).

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