

Photochemical reactions in fluorinated sol–gel hybrid materials doped with a photolocking agent for direct micropatterning

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We report on photochemical reactions in the fluorinated sol–gel hybrid materials doped with a photolocking agent consisting of 3-trimethoxysilylpropyl methacrylate (MPTS), heptadecafluorodecyltrimethoxysilane (PFAS), zirconium n-propoxide (ZPO), and methacrylic acid (MAA). We investigated the effect of the types and density of the photoinitiator, UV fluence, and the illuminating wavelength region on the microstructures and optical properties. The changes in refractive index and thickness during the photolocking process rely heavily on the remaining high index molecules from the photoinitiator. Finally, we fabricated a planar optical waveguide and microlens array using a binary contact mask through the photochemical self-developing process. The fluorinated sol–gel hybrid materials doped with a photolocking agent are promising for applications in planar optical waveguides and microlens array owing to the ease of their process.

Introduction

Planar optical waveguides have been of much interest in integrated optical circuit device applications. There have been many efforts to develop the planar waveguides using optically transparent materials such as silica and polymers.^{1,2} Especially, polymers have a great advantage in defining waveguide patterns easily in the film using a photolithographic etching technique.³ Also, an etching-free process has been proposed as a simpler technique to fabricate channel waveguides in polymers by using the photolocking of dopants inside the matrix.^{4,5} Sol–gel-derived inorganic–organic hybrid materials (HYBRIMERS) composed of both organic and inorganic components have also been applied to fabricate the channel waveguides due to their superior optical properties and relatively high thermal stability compared with general optical polymers.^{6–8}

Recently, we have reported on the photolocking of photoinitiators in the HYBRIMER films.^{9–11} The channel waveguide was successfully fabricated through selective UV exposure without any etching or a developing process called photochemical self-developing (PSD). However, the molecular structural changes during the photolocking process in the HYBRIMER are still unclear. And also, the used HYBRIMER consisting of methacrylate and silica/zirconia networks has relatively a high refractive index compared with pure silica, which can cause a high coupling loss when the planar optical devices are connected with a general silica fiber. To reduce the refractive index of a HYBRIMER, we incorporated a fluorine into the HYBRIMER by using heptadecafluorodecyl trimethoxysilane (PFAS). It was also expected that the fluorine incorporation into the HYBRIMER would lower its absorption loss.¹² However, in the fluorine-incorporated HYBRIMER, the methacryl groups in the HYBRIMER could be photodecomposed under UV exposure, which caused a decrease in the film thickness as well as in the refractive index.¹³ Thus, it is necessary to understand the photochemical reactions in the fluorinated HYBRIMER with UV exposure to control its optical properties.

Therefore, in this study, we first prepared the transparent fluorinated HYBRIMER film doped with a photolocking agent using a sol–gel method, confirming the structural changes

during the photolocking process in the HYBRIMER. We investigated the effect of the type and density of the photoinitiator, UV fluence, and the illuminating wavelength region on the microstructures and optical properties. Finally, we demonstrated a linear channel waveguide and microlens array pattern using the PSD process.

Experimental

3-Trimethoxysilylpropyl methacrylate (MPTS, Aldrich), heptadecafluorodecyltrimethoxysilane (PFAS, Toshiba), zirconium n-propoxide [ZPO, $Zr(OC_3H_7)_4$], and methacrylic acid [MAA, $H_2C=CHCO_2H$] were used as starting precursors. MPTS and PFAS were first hydrolyzed with 0.75 equivalents of water in the presence of 0.05 M hydrochloric acid (HCl) as a catalyst. ZPO was reacted with MAA in a molar ratio of 1:1 to avoid undesired precipitation of ZrO_2 particles by chelating complex formation. After that, the chelated ZPO solution was added to the prehydrolyzed MPTS and PFAS solution and stirred for 1 hour to advance hydrolysis and condensation. The mixed solution was reacted with additional water for 20 h to complete the hydrolysis and condensation. The total amount of water was 1.5 equivalents of total alkoxides in the solution. The obtained solution was totally transparent. The photolocking agents were added to the transparent solution. Benzylidimethylketone [BDK, $C_6H_5COC(OCH_3)_2C_6H_5$] and 1-hydroxycyclohexylphenylketone [HCPK, $OHC_6H_{11}COC_6H_5$] were used as photoinitiators as well as photolocking agents.

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 3000 rpm for 30 s. Single coating yielded an approximate 6–7 μm thickness of the films. For the photolocking reaction, the films were illuminated by a 1 kW Hg–Xe UV lamp (ca. 220–260 nm, Oriol82521, power density of 28 $mW cm^{-2}$) and a 500 W Hg UV lamp (ca. 350–390 nm, Oriol97435, power density of 100 $mW cm^{-2}$) with a wavelength filtering mirror for different UV doses to examine the photochemical reactions in the fluorinated HYBRIMER film, respectively. The UV illuminated films were characterized directly or after baking at 150 °C for 5 h.

The refractive index of the film was determined by using a prism coupler (Metricon 2010) at a wavelength of 1550 nm. Thickness was measured by obtaining a cross-sectional scanning electron microscope (SEM) image of the hybrid films. To remove a charging effect, gold was coated onto samples for SEM measurement. The structure change of the dopant during the photolocking process was investigated by Fourier transform infrared (FT-IR, Bruker EQUINOX55) spectroscopy. Finally, the patterned images of the sol-gel hybrid materials were investigated by optical microscopy and atomic force microscope (AFM, Park Scientific Instruments, Autoprobe 5 M).

Results and discussion

Change in refractive index and thickness

Fig. 1 shows the refractive index changes in the fluorinated HYBRIMER films doped with a photoinitiator as a function of UV light of *ca.* 220–260-nm wavelength. The refractive index of the fluorinated HYBRIMER film without a photoinitiator is 1.440 at 1550 nm, which is almost the same as that of pure silica. Even when the photoinitiator was doped into the fluorinated HYBRIMER film, its refractive index was still same as that of the undoped HYBRIMER film if the final film was heat-treated at 150 °C for 5 h without UV exposure. This probably indicates the evaporation of unreacted photoinitiators out of the film. The refractive index of the fluorinated HYBRIMER film increased abruptly with UV fluence at the early stage. This stiff increase was expected because of the structural densification caused by polymerization of the

methacryl groups in MPTS and MAA. When the UV fluence increased, the index change behaviors became quite different as the photoinitiator concentration increased or decreased. At low doping levels, the refractive index slightly increased and then decreased with UV fluence, which was not observed in the HYBRIMER that consisted of MPTS and ZPO without fluorine. It was reported that the photodecomposition of the methacryl groups in the HYBRIMER is accelerated with the introduction of fluorine into the HYBRIMER.¹³ On the other hand, the refractive index continued to increase and then was saturated at high doping levels of the photoinitiator. In the case of polymethylmethacrylate (PMMA), the UV-induced decomposition of the methacryl group generally begins with the formation of radicals by ester group breakage.¹⁴ It is considered that the photoinduced free radicals from the photoinitiators restrain the removal of decomposed organic groups out of the film by blocking the radicals from the dissociated carbonyl groups. Thus, we expect that the photodecomposed organic parts remain in the film, which lead to the saturation of its refractive index.

Fig. 2 shows the refractive index changes in the fluorinated HYBRIMER doped with a photoinitiator with *ca.* 350–390-nm UV exposure. In this wavelength region, the index decrease was not observed regardless of photoinitiator concentration. It is well known that carbonyl groups of PMMA absorb UV light in the *ca.* 190–280-nm wavelength region.^{14,15} Thus, the photodecomposition reaction does not occur by illuminating *ca.* 350–390-nm wavelength light. Therefore, it is highly recommended to use UV light in this wavelength region to avoid undesired photodecomposition reactions, especially in the case of the fluorinated systems.

To investigate the photosensitivity of the fluorinated

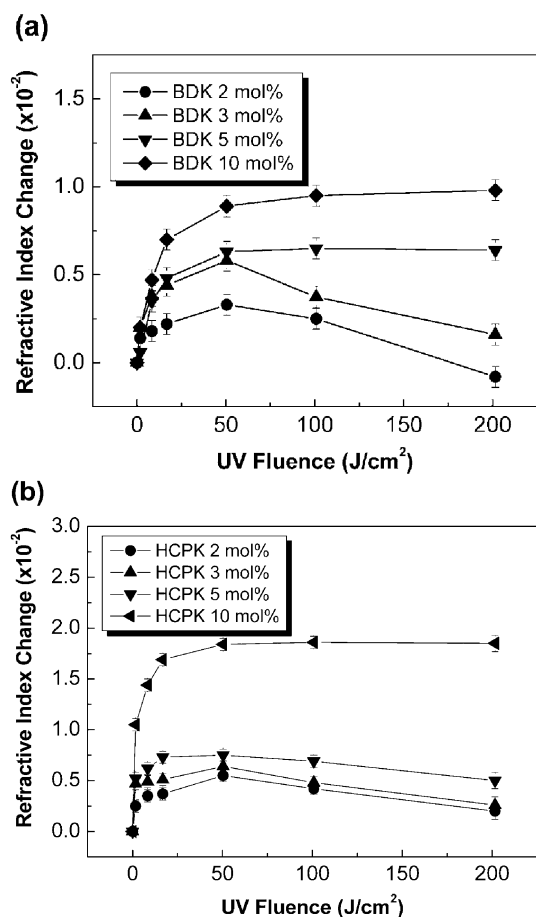


Fig. 1 Refractive index changes in the fluorinated HYBRIMER doped with (a) BDK and (b) HCPK, as a function of *ca.* 220–260-nm UV fluence.

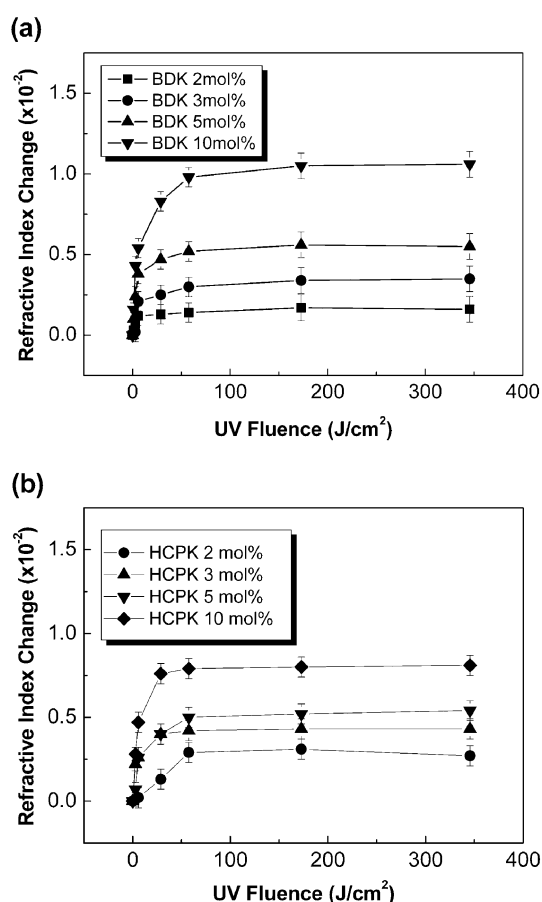


Fig. 2 Refractive index changes in the fluorinated HYBRIMER doped with (a) BDK and (b) HCPK, as a function of *ca.* 350–390-nm UV fluence.

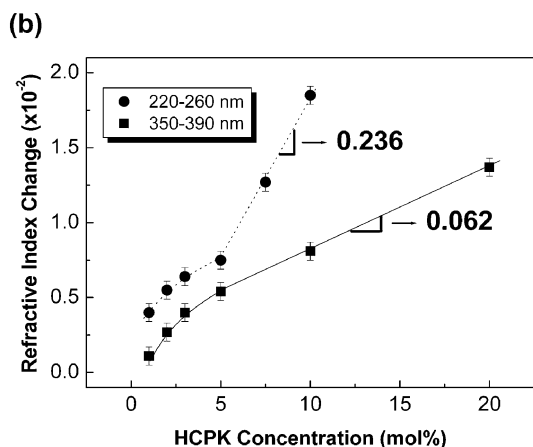
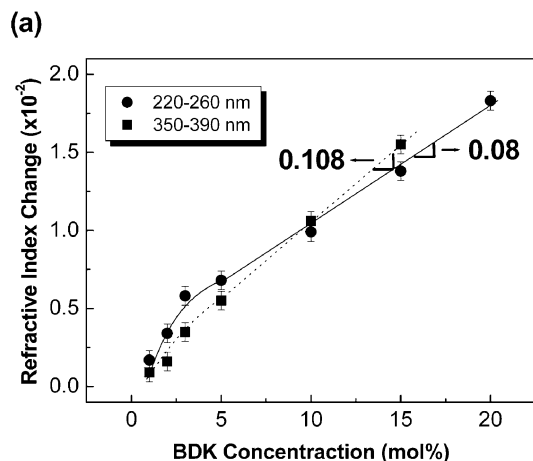


Fig. 3 Refractive index changes in the fluorinated HYBRIMER depending on (a) BDK and (b) HCPK concentrations.

HYBRIMER doped with two different photoinitiators, the refractive index changes were plotted as a function of photoinitiator concentration with illuminating UV light in two different wavelength regions, respectively. The refractive index difference was calculated by subtracting the index of the unirradiated film from the maximum value with UV exposure. As shown in Fig. 3, the refractive index of the film increased slowly, and then linearly increased with photoinitiator concentration. In the case of BDK, the index increase behaviors were similar regardless of the illuminating wavelength region. On the other hand, in the case of HCPK, the index increase was much stiffer when the UV light in the *ca.* 220–260-nm wavelength region was used. This difference in the index increases resulted from the photodecomposition efficiency of BDK and HCPK. BDK has absorption in both the *ca.* 250–260 and the *ca.* 325–355-nm wavelength regions, but HCPK has absorptions at *ca.* 200–210 and *ca.* 240–250 nm. Even if the index increase was most effective when HCPK was used as a photoinitiator with *ca.* 220–260-nm wavelength UV exposure, it was not desirable to use HCPK for the optical application because of the hydroxyl group in its molecular structure.

Fig. 4 shows the thickness change in the fluorinated HYBRIMER film with *ca.* 350–390-nm wavelength UV exposure. The thickness of the fluorinated HYBRIMER lightly doped with the photoinitiator slightly decreased because of the volume shrinkage by the polymerization of organic groups and the consequent further condensation of unreacted Si–OH groups. However, the thickness of the HYBRIMER film heavily doped with the photoinitiator increased as the UV fluence increased because the photoinitiators lost their mobility and volatility, and they were finally locked in the HYBRIMER matrix by UV light. These results of the refractive index and

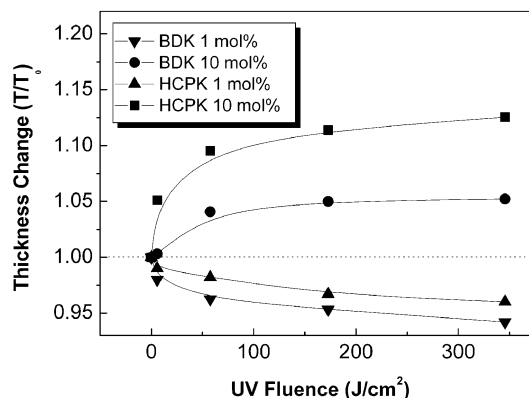


Fig. 4 Thickness change in the fluorinated HYBRIMER doped with BDK and HCPK.

thickness changes showed that the refractive index increase was obtained largely by the densification and photolocking reaction at low and high doping levels of photoinitiators, respectively.

Microstructural change

As discussed earlier, several photochemical reactions took place such as polymerization, silica condensation, photodecomposition, and photolocking in the fluorinated HYBRIMER with UV exposure. Among these reactions the photolocking reaction was expected to be highly related with the refractive index and thickness change. Thus, it was necessary to investigate the microstructural changes during the photolocking reaction. Therefore, photoinduced microstructural changes during UV exposure in the fluorinated HYBRIMER doped with HCPK were investigated *via* Fourier transform infrared (FT-IR) spectroscopy. There was a band at 1670 cm^{-1} for the C=O vibrational stretching mode of HCPK, but it overlapped with that of MPTS in the used HYBRIMER. To discern changes of HCPK in the HYBRIMER with UV exposure, we fabricated a new hybrid matrix (VF) without carbonyl groups consisting of vinyltrimethoxysilane (VTMS) and PFAS. To confirm the structural change during the photolocking process, the residual carbonyl groups from the HCPK were investigated with UV exposure. Fig. 5(a) shows the change of the C=O band of HCPK in the carbonyl-free HYBRIMER film with UV fluence before baking. The C=O band of HCPK shifts from 1670 to 1730 cm^{-1} and becomes broad as the UV fluence increases, which indicates that the carbonyl groups lose their conjugation due to the photoinduced dissociation and the attachment on the carbon double bonds. Fig. 5(b) shows the structural change with and without UV exposure after heat-treatment at $150\text{ }^{\circ}\text{C}$ for 5 h. The C=O band of HCPK in the unexposed film was totally removed after baking whereas that in the exposed film was still detected at 1730 cm^{-1} . Thus, it has been considered that the doped HCPK can be removed by heat-treatment without UV exposure. However, it is locked into the HYBRIMER matrix and then remains there through UV exposure even after final heat-treatment. These results enabled us to explain the refractive index change in the fluorinated HYBRIMER film doped with a photoinitiator as follows. As shown in Figs. 1 and 2, the refractive index is the same as that of the undoped HYBRIMER film regardless of the photoinitiator concentrations if the final film is heat-treated at $150\text{ }^{\circ}\text{C}$ for 5 h without UV exposure. The invariance of the refractive index is attributed to the evaporation of the photoinitiators out of the film by heat-treatment without UV exposure. Thus, we found that the refractive index change in the photolocking process relies heavily on the remaining high index molecules from the photoinitiator.

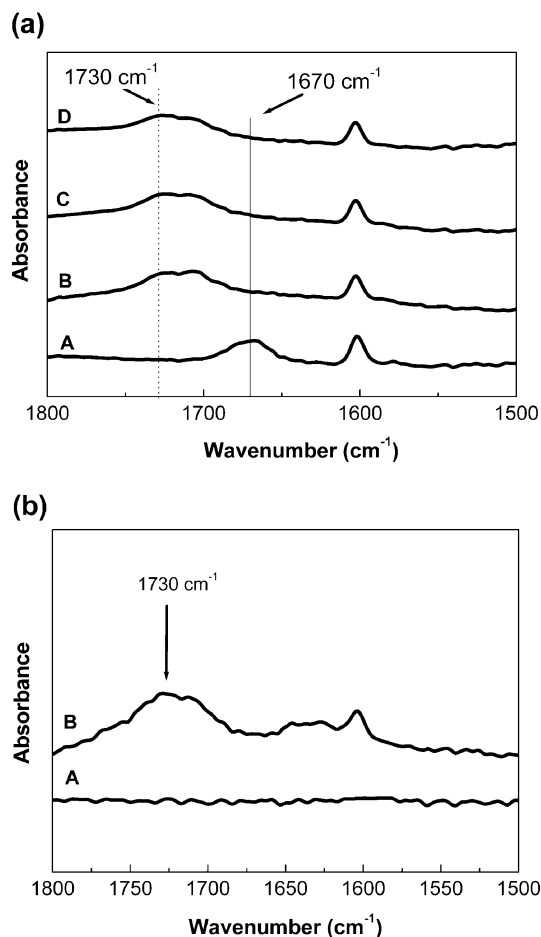


Fig. 5 (a) FT-IR spectra of the VF system doped with HCPK and irradiated by A) 0, B) 8.4, C) 16.8, and D) 100.8 J cm⁻² of ca. 220–260-nm UV fluence before baking; (b) FT-IR spectra of the VF system doped with HCPK and irradiated by A) 0 and B) 100.8 J cm⁻² of ca. 220–260-nm UV light after baking at 150 °C for 5 h.

Fig. 6 presents the photolocking of HCPK in the fluorinated HYBRIMER consisting of MPTS, PFAS and chelated ZPO. The change in the C=O vibrational stretching mode was investigated by using the FT-IR spectra of a 10 mol% HCPK-doped film with and without UV exposure after baking as shown in Fig. 6(a). Since the used HYBRIMER also has carbonyl groups as mentioned above, it was difficult to distinguish the C=O stretching modes from MPTS and HCPK. To obtain the difference between these two FT-IR spectra, we subtracted the spectra of the unexposed film from those of the exposed one. Fig. 6(b) shows the difference between the spectra of the UV-exposed and -unexposed films after baking. There is a peak at 1730 cm⁻¹ that coincides with the previous result in Fig. 5. Thus, it can also be considered that the doped HCPK can be diffused out from the fluorinated HYBRIMER by heat-treatment without UV exposure.

Applications

The fluorinated HYBRIMER is patternable *via* the PSD process since both the refractive index and thickness of the irradiated area increase through selective UV exposure without the etching step. The fluorinated HYBRIMER film doped with 15 mol% BDK was used for the direct photo-patterning. The pre-drying process was used for a use of contact mask, which was reported elsewhere.¹¹ Selective UV exposure accompanied not only the photolocking of the high index molecules but also the mass transport *via* the diffusion process. When UV was irradiated onto a specific area, the photoinitiator was

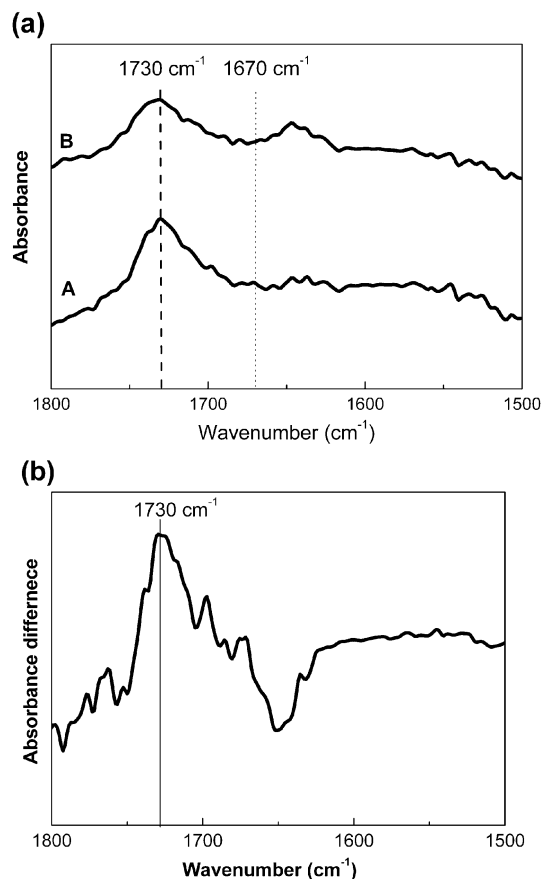


Fig. 6 (a) FT-IR spectra of the fluorinated HYBRIMER doped with HCPK irradiated by A) 0 and B) 100.8 J cm⁻² of ca. 220–260-nm UV light after baking at 150 °C for 5 h; (b) the difference between the FT-IR spectra from (a) A and (a) B.

decomposed and reacted with a polymerizable group. Thus, the concentration of photoinitiators and polymerizable monomers in the exposed area was lower than those in the unexposed area, which causes the diffusion of these molecules from the unexposed area to the exposed one. Fig. 7 shows the atomic force microscopy (AFM) images of the direct photo-imprinted waveguide pattern in the fluorinated HYBRIMER doped with BDK with UV fluence. The irradiated surface inflates continuously from the irradiated area with its width of 2 μm. The height increase rate changed from 6 to 9% as the UV fluence increased from 172.8 to 345.6 J cm⁻². Finally, the inflation is saturated at a UV fluence of 345.6 J cm⁻². Thus, we found that the photoinduced mass transport is established by the diffusion of the reactive molecules in the fluorinated HYBRIMER matrix.

Using the PSD process, we also fabricated microlens arrays. It is generally required to use a gray scale mask to make the lens shape. However, the lens shape may be obtained just by using a general binary mask in the PSD process. Fig. 8 shows an array of microlenses, each with a diameter of 30 μm, inscribed on the fluorinated HYBRIMER doped with BDK. The thickness change from the original surface is around 1.45 μm. As shown in Fig. 8, smooth surface deformation gives a convex surface shape without a gray scale mask. Not only a physical shape but also a refractive index gradient can play an important role in the focusing of light such as a graded refractive index lens. Owing to the intrinsic characteristics of the PSD process, there exists the index gradient from the center to the edge of the lens pattern. Thus, it is expected that it should have a shorter focal length than a step-index lens. More experiments are still needed to understand more about this effect in the sol-gel HYBRIMER that uses the PSD process.

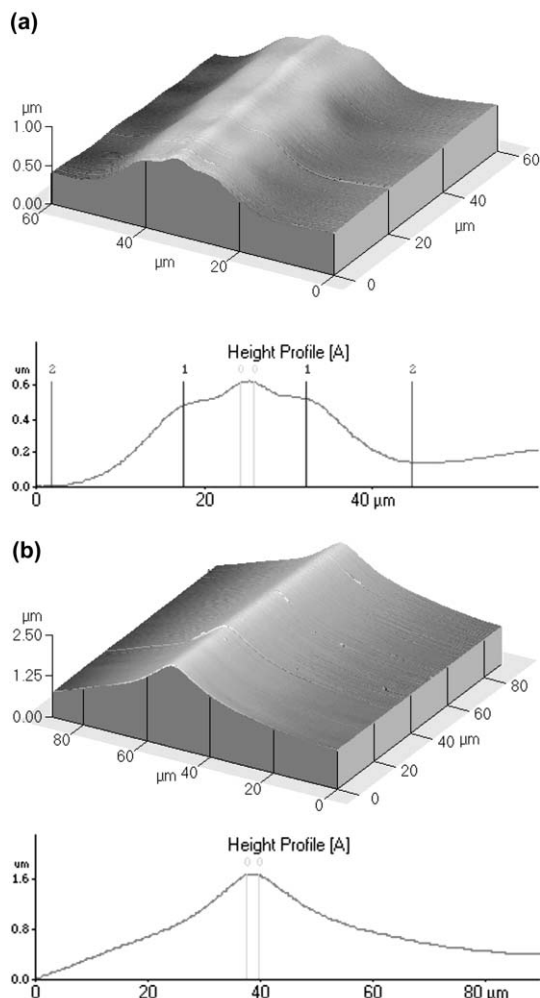


Fig. 7 AFM images of the fluorinated HYBRIMER doped with 15 mol% BDK irradiated by (a) 172.8 and (b) 345.6 J cm⁻² during direct photo-patterning using a binary mask with 2- μ m width.

Conclusion

The photoinitiator-doped HYBRIMER film was successfully prepared using MPTS, PFAS, and ZPO. The refractive index increased with UV fluence and photoinitiator concentration. At low doping levels of the photoinitiator, the refractive index decrease was found to be due to the photodecomposition of methacryl groups when UV light in the *ca.* 220–260-nm wavelength region was used. The doped photoinitiator was locked or fixed in the fluorinated HYBRIMER matrix by UV exposure, which led to the increase of both the refractive index and thickness. Otherwise, it is diffused out from the matrix by heat-treatment. The changes in the refractive index and thickness during the photolocking process rely heavily on the remaining high index molecules from the photoinitiator. Selective UV exposure accompanies not only the photolocking of the high index molecules but also the mass transport *via* the diffusion process. Finally, we fabricated a planar optical waveguide and microlens array using a binary contact mask through the photochemical self-developing (PSD) process.

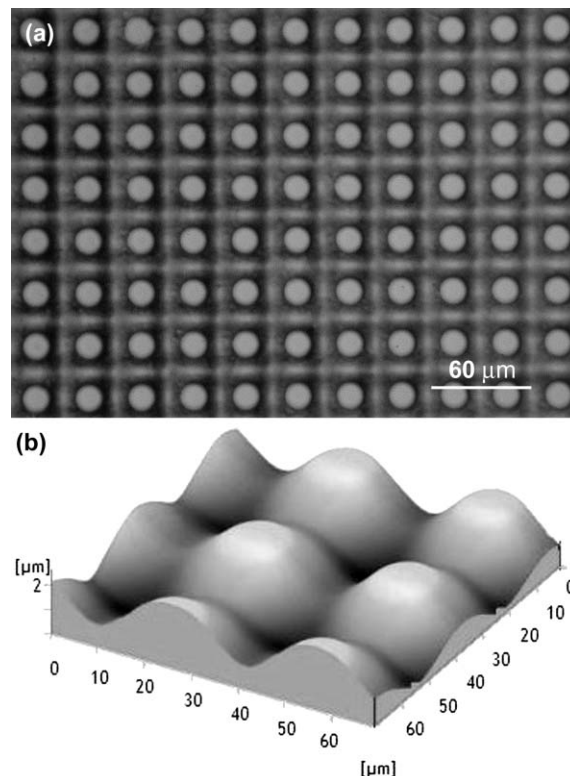


Fig. 8 (a) Optical microscope and (b) AFM images of the microlens array inscribed on the fluorinated HYBRIMER.

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