

Photoinduced Low Refractive Index Patterning in a Photosensitive Hybrid Material

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ABSTRACT

Light illumination processing created photoinduced reduction of refractive index as well as volume contraction in an organic-inorganic hybrid material. Whereas both refractive index and film thickness are decreased significantly by the light exposure, transmittance and anti-soiling property of the hybrid film are not affected by the exposure. Direct patterning is possible upon light illumination using the photoinduced change in thickness without any developing process.

INTRODUCTION

Organic-inorganic hybrid materials appear as an appropriate response to new trends in optical field including optical waveguides, optical recording, and diffractive optical elements etc [1]. The hybrid materials promise a low-cost and low-temperature processing since they are based on the simple sol-gel method. Moreover, properties of the hybrid materials are easily controlled in the processing by structural modification between organic and inorganic components [2]. The most representative step to control properties of the hybrid materials is light illumination processing which induces organic cross-linking reaction generally [3]. Organic units of methacrylate, vinyl, etc, are cross-linkable with the addition of photo-initiators in the hybrid materials during light illumination. Thus, densities and refractive indices of hybrid materials generally increase, and film thicknesses decrease upon light irradiation [4]. However, the changes in properties using the photoinduced organic cross-linking reaction are not large. Also, the refractive index reduction required for various optical applications such as antireflective coatings is almost impossible [5]. In this study, a new process has been performed to control properties of an organic-inorganic hybrid material. While ultraviolet radiation step to induce organic cross-linking is used in previous hybrid materials, ultraviolet exposure step to lead the photoinduced decomposition of an organic unit is performed in this hybrid material. Refractive index reduces largely on ultraviolet radiation using the decomposition process. Also, film thickness decreases on the exposure so that direct patterning was carried out by the UV exposure without any further developing steps (wet etching, thermal curing, or UV fixing).

EXPERIMENT

The organic-inorganic hybrid material was obtained by sol-gel method. 3-trimethoxysilylpropyl methacrylate (MPTS, $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$, Aldrich) and heptadecafluorodecyl trimethoxysilane (PFAS, $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$, Toshiba) were used as precursors. The two precursors, MPTS and PFAS, were mixed with water in presence of 0.05N hydrochloric acid (HCl) as a catalyst for sol-gel reaction. After stirring the solution of MPTS(3), PFAS(1) and water(2) in the presence of 0.05N HCl (bracketed numbers indicate molar equivalents) for 9 hours 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 kept still for 30 minutes 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 2000 rpm for 30 seconds. Finally, the coated film was then cured thermally for 12 hours at 150°C. UV (200–260 nm) light irradiation was performed with Oriel 82511 Hg/Xg lamp, which gives a power density of 45 mJ/cm^2 . Refractive index was measured using a Metricon MODEL 2010 prism coupler at 632.8 nm and film thickness was measured by a Scanning electron microscope (SEM, Philips, XLSFEG) image of cross-section of the hybrid film. In order to remove a charging effect, gold was coated on samples for SEM measurement. Transmittance measurement was performed using UV/VIS/NIR spectrophotometer (Shimadzu UV3101PC) with scan interval of 2°. Here, fused silica glasses were used for the transmittance measurement.

RESULTS AND DISCUSSION

Fig. 1 shows the changes in refractive index and film thickness of this organic-inorganic hybrid material with the ultraviolet cumulated fluence. Here, initial refractive index (n_i) and film thickness (V_i) were 1.43 and 2 μm , respectively. The negative values of changes in refractive index and film thickness represent the reductions in the index and thickness on ultraviolet radiation. As shown in Fig. 1, the refractive index of the hybrid material decreases exponentially up to 0.045 with the ultraviolet fluence. Also, the film thickness decreases significantly by 0.4 (40 %) of the initial thickness with the ultraviolet fluence. Therefore, the refractive index and the film thickness can be largely tunable by this UV (200–260 nm) exposure step. Especially, the reduced refractive index value of 1.385 is very low, which is comparable to the indices of perfluorinated polymers (for example, the index of PTFE[®]: 1.38). The profile of refractive index across a film thickness can be found theoretically by the inverse WKB approximation. Fig. 2 shows the variation of refractive index profile across thickness of the hybrid film depending on cumulated UV fluence. Refractive indices which were measured with the prism coupler are

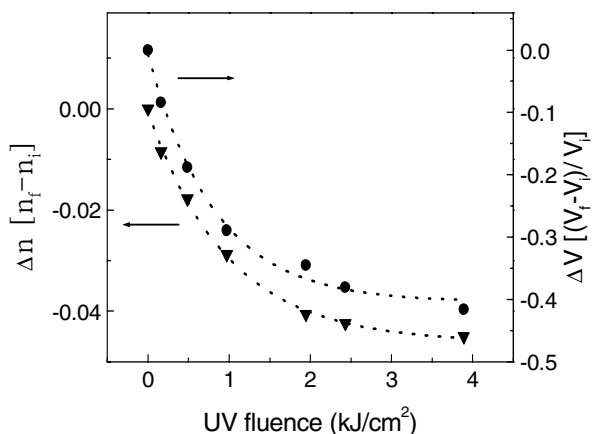


Fig. 1. Change in refractive index and film thickness of the organic-inorganic hybrid material with cumulated UV fluence from a 1000W Hg/Xe lamp.

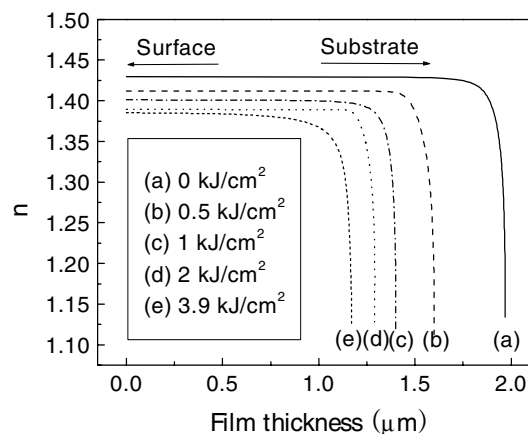


Fig. 2. Variation of refractive index profile across the hybrid film depth depending on cumulated UV fluence.

almost constant across film depths. The constant index profile across film depth is not affected significantly by UV irradiation. Therefore, the refractive index value in Fig. 1 can be an average refractive index for the whole film thickness. Methacryl organic unit in the hybrid material is responsible for the photoinduced change in properties. The methacryl unit decomposes on UV irradiation, as reported in polymethylmethacrylate (PMMA) [6]. Also, the decomposition effect of methacryl group in the hybrid material was already revealed in the previous report [7]. High index components including polar carbonyl group are removed due to the UV-induced decomposition, hence refractive index reduces largely upon UV radiation. Since bulky methacryl chains which hinder condensation reactions of remaining Si-OCH₃ and Si-OH sterically are removed upon UV radiation, further condensation reactions to form the Si-O-Si framework are enhanced concurrently with the decomposition of methacryl groups. Therefore film thickness decreases due to the shrinkage of the inorganic network via the photoinduced condensation reaction.

For the application of optical coatings such as antireflective coatings, high transmittance of films is essential. The processing to fabricate the optical coatings must not deteriorate the transmittance of materials. Fig. 3 shows the transmittance of the organic-inorganic hybrid films which were not irradiated and irradiated with ultraviolet of 4 kJ/cm^2 . As shown in Fig. 3, the hybrid film is very transparent. And transmittance does not change in the wavelength region of visible ray on UV irradiation, which means UV exposure step does not affect transmittance of the film in the visible ray region. Therefore, this UV exposure step can control refractive index and film thickness largely without any deterioration in transmittance for various designs of

optical coatings.

Contact angle between a water drop and the hybrid film (flat film surface) were measured with a contact anglemeter (Krüss GmbH) at room temperature, as shown in Fig. 4. The theoretical maximum contact angle of a flat surface is 115° when the film surface consists of only CF_3 pendent group [8]. The measured contact angles are about 111° , similar to the theoretical maximum value. Thus, surface of the hybrid film is very hydrophobic. Moreover, the contact angles do not change with UV fluence. It was reported that the surface layer where the fluoroalkyl group of $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2$ is self-assembled has contact angle of 112° , which is close to the value of the hybrid film. It seems accordingly that the fluoroalkyl group in the hybrid film forms dominantly the surface area and the fluoroalkyl chain does not decompose on UV radiation, maintaining hydrophobicity of the film surface. Since organic molecules or dusts are adsorbed usually on the hydrophilic surface of silica to reduce surface energy so that films become dirty and transparencies are lowered, hydrophobic surfaces are necessary for application in optical coatings or electronic packagings. The hybrid film has good hydrophobicity and the UV exposure step maintains the hydrophobicity of the surface for the applications.

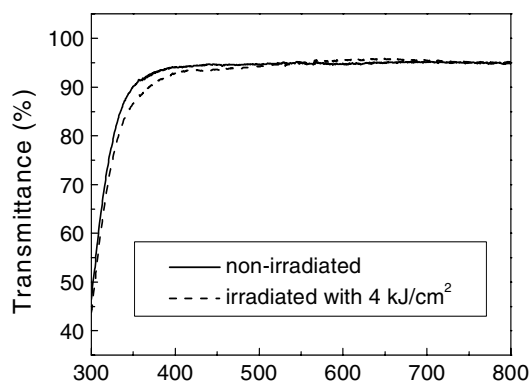


Fig. 3. Transmittance of the hybrid films which were non-irradiated and irradiated with UV (4 kJ/cm^2).

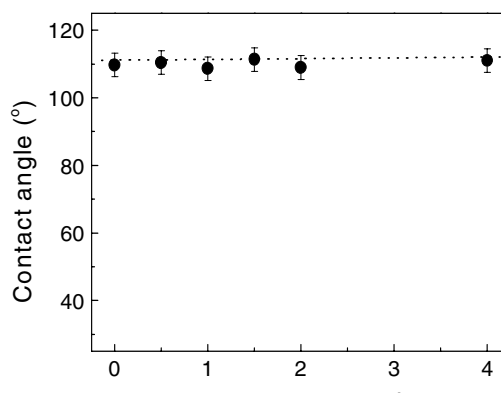


Fig. 4. Change in contact angle between water drop and the hybrid film surface with cumulated UV fluence.

Direct patterning of the hybrid material was carried out by UV fluence of 2 kJ/cm^2 through a quartz contact mask of $6 \mu\text{m}$ period pattern. No further developing steps (wet etching, thermal curing, or UV fixing) were necessary to reveal the surface relief due to the photoinduced thickness change. Fig. 5 (a) shows an atomic force microscope (AFM) image of the lined pattern inscribed on the surface of the hybrid material and Fig. 5 (b) shows a magnified view ($\times 400$) of the illustrated pattern written in the hybrid material as seen through the optical microscope. The three-dimensional view of AFM revealed that a periodic pattern of a sinusoid 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.

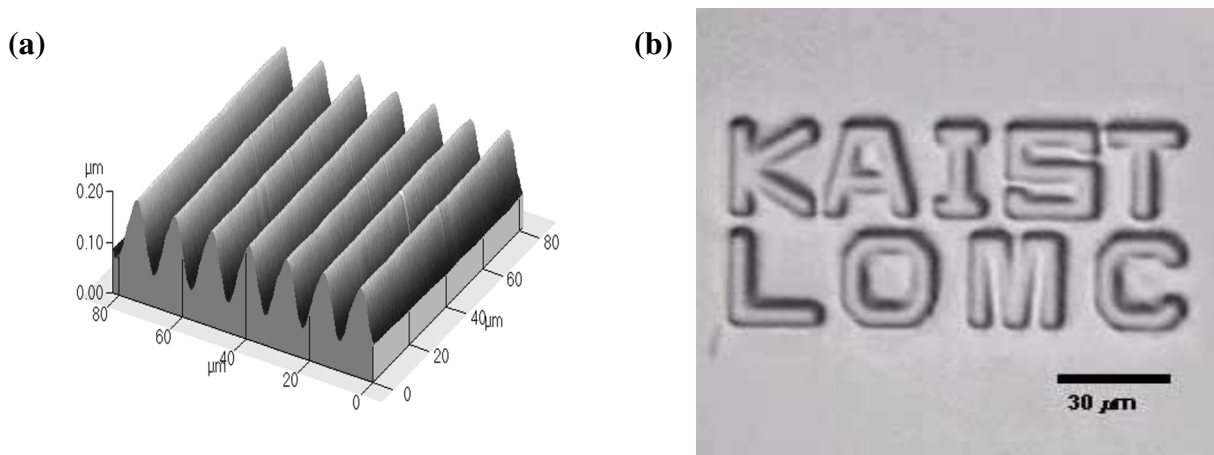


Fig. 5. Atomic force and optical micrographs of the hybrid films which were exposed through a quartz contact mask to ultraviolet fluence of 2 kJ/cm^2 . (a) An atomic force microscope image of the surface relief pattern inscribed into the hybrid material. A periodic pattern period is $12 \mu\text{m}$ and a change in depth from the original surface is 141 nm . (b) Optical microscope image of the illustrated photoinduced printing using its volume change.

CONCLUSIONS

UV (200–260 nm) irradiation created large reduction in refractive index via the photoinduced decomposition of methacryl group in the organic-inorganic hybrid material. Also, the UV exposure led to film thickness reduction in the hybrid material. Since film thickness reduces on UV illumination, direct patterning was possible without any developing steps. Whereas UV exposure step to decompose the methacryl unit affects refractive index and thickness significantly, the exposure does not affect transmittance of the hybrid film in visible region of ray. Moreover, the hybrid film surface is very hydrophobic and the hydrophobicity of the film maintains well upon UV irradiation because the fluoroalkyl group still remains without any decomposition. Therefore, the UV exposure step to decompose the specific organic unit selectively can control refractive index and film thickness largely without any deterioration in hydrophobicity as well as transmittance for various designs of optical coatings.

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