Preparation of Photo-induced Refractive Index Pattern using Polysilane-Silica Hybrid Thin Films

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1. Introduction
Polysilanes are photo-functional polymers with σ-conjugation along the Si backbone and carbon-based side groups,[1-2] which have many attractive properties such as photo-electron conductivity, electro- or photo-luminescence, etc. Particularly, the photodecomposition of polysilanes provide the large refractive index change from the unexposed area. This is an important candidate material for some optical devices. Tsushima et al. have reported the fabrication of optical waveguide using polysilanes with their photobreaching properties.[3-4]

We have been studying about the organic-inorganic hybrid materials dispersing polysilane segments in inorganic oxides. The polysilane-silica hybrid thin films were prepared from polysilane-acrylic or -methacrylic block copolymers with alkoxysilyl or amide groups via sol-gel reaction using alkoxysilanes [5-10] Their refractive indices were also widely changed by the photobreaching process of polysilane segments under UV light irradiation. In this work, the fixation of refractive index change on polysilane-silica hybrid thin films was investigated.

2. Experimental
2.1 Synthesis of Polysilane-acrylic Block Copolymer
Polymethylphenylsilane (PMPS) (1.0 g), which was prepared by Wurtz coupling reaction of methylphenylidichlorosilane in THF, and 3-methacryloxypropyltriethoxysilane (MPTES) (1.0 g) were dissolved in toluene (10 ml) in a Pyrex tube, the mixture was sufficiently degassed by the freeze-thaw method. Photo-polymerization was carried out by irradiation of UV light (high pressure Hg lamp; 10 mW/cm²) for 6 min. Copolymers, P(MPS-co-MPTES), were obtained after reprecipitating from hexane.

Scheme 1

2.2 Preparation of Polysilane-silica Hybrid
As a typical procedure of preparation, to the THF solution of P(MPS-co-MPTES) and tetraethoxysilane (TEOS), di(ethylene glycol) mono-methyl ether and catalytic HCl were added. After mixing in dark at room temperature for 1 h, the thin films were prepared by spin-coating on substrates and heating at 120 °C for 1 h.

2.3 Preparation of Refractive Index Pattern
The UV light (high pressure Hg lamp) was irradiated to the hybrid thin films though a photo-mask. After UV irradiation, the photo-decomposed part of thin film was developed with hexane, followed by unmasked irradiation (1800 mJ/cm²) and heat treatment at 150 °C. The refractive index of each hybrid thin films was

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measured by the ellipsometry measurement with a He-Ne laser.

3. Results and Discussion

The polysilane-silica hybrid thin films were prepared from polysilane block copolymers, P(MPS-co-MPTES) (Mn = 10,000-15,000, Mw = 20,000-25,000 measured by GPC calibrated with polystyrene standards), with several feed ratios of TEOS via sol-gel reaction. The fabrication process of refractive index pattern using the polysilane-silica hybrid thin film was illustrated in Figure 1. Exposed part of the polysilane-silica hybrid thin film through a photomask was developed with hexane to remove the photodecomposed substances such as silanols and oligosilanes (step C). This procedure provided the nano-porous silica thin film with low refractive index (ca 1.40). Therefore, there is a large refractive index change between exposed and unexposed parts in the hybrid thin film.

However, the disadvantage is low durability of the unexposed polysilane segments for light, that is, a labile refractive index during the photodecomposition. In order to fix the refractive index change between two parts of the hybrid thin film, the succeeding unmasked irradiation and heat treatment were carried out toward the mask-irradiated polysilane-hybrid thin film (step D and E). The refractive index of polysilane-silica hybrid thin film on each steps were plotted, as shown in Figure 2. Although the refractive index slightly reduced after unmasked irradiation (step D), the sufficient difference of refractive index between the developed and secondly irradiated part still remains. The silanol derivatives with phenyl groups embedded in silica matrix are crosslinked by a condensation reaction at higher temperatures (step E). Therefore, it was found that the refractive index was stabilized by these processes.

![Figure 2. Refractive index change of each fabrication process (A to E) of P(MPS-co-MPTES)/TEOS = 1/5.](image)

The refractive index difference (Δn) was reduced with increasing TEOS content in the hybrid thin films. In the case of P(MPS-co-MPTES)/TEOS = 1/10 (weight ratio), Δn was about 3.5% and greater than that of fluorinated polyimides which was used as optical waveguides. The polysilane-silica hybrid thin films will be an applicable material with the large photo-induced refractive index change.

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References