Refractive Index Modification of Polysilane Films by UV-Light Irradiation

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The refractive index modification of polysilane films by the Ultra-Violet (UV) light irradiation was investigated. Poly(methylphenylsilane) (PMPS) and other polysilanes involving phenyl group attached directly to a silicone atom showed high refractive index (n_em ~ 1.70) and very large refractive index reduction (Δn = -0.14) at λ = 633 nm compared with alkyl substituted polysilanes. The effective reduction in these polysilanes was found to be caused by the elimination of phenyl substituents in addition to the shortening of the σ-conjugation due to the photo-oxidation of silicon backbone for shorter wavelength UV light exposure. Thus, UV-exposed polysilanes turned to almost the same siloxane-like structure consisting of Si-O-Si backbone with alkyl substituents, and their refractive indices converged to a lower value of about 1.55. These results indicate that the molecular design of the side groups to enhance the initial refractive index can expand the dynamic range (Δn) in the refractive index modification of the polysilane film.

Keywords: Polysilane, UV photodecomposition, Refractive index modification

1. Introduction

Photo-induced refractive index change in organic compounds is a very important property for an application to various optical components such as switchable waveguide and optical data storage. Recently, several photochemical compounds have been reported to obtain both large refractive index changes and transparency in wide wavelength band. Chauvin et al. obtained the refractive index change of 0.05 using photochromism of amorphous diarylethenes [1], Freiberg et al. also reported large refractive index change by isomerization of azo-benzene pendant liquid crystalline polymer [2]. However, these compounds showed absorption band in the visible wavelength region. Murase and Horie achieved transparency in entire visible wavelength with diazo and azido groups doped PMMA film [3]. In these systems, the decrease of π-conjugation due to photo-irradiation was used for refractive index changes. On the other hand, polysilanes consisting of a silicon backbone and two organic side-groups attached to each Si atom have attracted considerable attention because of their unique chemical and physical properties characterized by σ-conjugation expanding along the silicon backbone [4]. One of the well-known chemical properties of these polymers is the photo-oxidation of silicon backbone by irradiating ultra-violet (UV) light in air [5,6,7]. The incorporation of O atoms into the silicon backbone brings about the disconnection of the σ-conjugation on the Si backbone to reduce the refractive index effectively in the irreversible manner. Moreover, polysilanes have high transparency in entire visible wavelength region. These unique properties have been attempted to apply to several interesting optical components, e.g., etching-less waveguide [8], optical phase shift mask [9], polarization-recording medium [10], tunable micro-ring resonator [11], and so on. However, the details of the refractive index reduction due to the UV irradiation, i.e., the range of reduction and its dependence of chemical structures, have not been fully discussed. It must be important to know the fundamental knowledge
Table 1. The substituents of the polysilanes and their structures used in this study.

<table>
<thead>
<tr>
<th>R₁</th>
<th>R₂</th>
<th>Abbreviation</th>
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<tbody>
<tr>
<td>Methyl</td>
<td>Phenyl</td>
<td>PMPS</td>
</tr>
<tr>
<td>Methyl</td>
<td>cyclo-Hexyl</td>
<td>PMcHS</td>
</tr>
<tr>
<td>Methyl</td>
<td>n-Propyl</td>
<td>PMnPS</td>
</tr>
<tr>
<td>Methyl</td>
<td>β-Phenethyl</td>
<td>PMβPS</td>
</tr>
<tr>
<td>Methyl</td>
<td>p-Tolyl</td>
<td>PMTS</td>
</tr>
<tr>
<td>Methyl, Phenyl (1:1)</td>
<td>Phenyl</td>
<td>DPPMPS *</td>
</tr>
</tbody>
</table>

R₁ and R₂ denote two substituents of each Si atom. * Copolymer of PMPS and poly(di-phenylsilane).

for an application of polysilanes as optical materials.

In this paper, we focused on the relationship between the chemical structure of substituents and the refractive indices in several polysilanes as well as their changes by UV photo-irradiation. Polysilanes having phenyl side-group showed higher refractive index due to the σ-π conjugation between silicon backbone and phenyl substituent. The shorter wavelength UV light exposure was found to cause effective reduction of the refractive index and to give a large dynamic range of the photo-modulation.

2. Experimental

The substituents of the several polysilanes used in this study and their abbreviation were listed in Table 1. The substituent R₁ was kept to methyl group, and R₂ was changed to several varieties of organic substituents. PMPS is a prototypical polysilane, which is characterized by σ-π conjugation between silicon backbone and phenyl group. Two alkyl polysilanes, PMcHS and PMnPS were selected for examining the effect of the π-conjugation. In order to examine the σ-π conjugation effect, PMβPS was employed as the one that has an alkyl linkage between silicon backbone and phenyl substituent, which interrupts the σ-π conjugation. PMTS was a trial polysilane to control the σ-π interaction with tolyl group. A last polysilane, DPPMPS was also trial polysilane to enhance the refractive index with increasing π-conjugation content.

All polysilanes used in this study were prepared by Wurtz-coupling of the corresponding dichloro monomers (or monomer mixture for copolymer) with sodium metal in toluene according to the literature procedure [12]. Molecular weight of the polysilanes was measured using GPC with a polystyrene calibrant. Polysilane films of a thickness about 0.3 μm were prepared on glass plates or silicon wafers by a spin coating technique, and then dried at room temperature. The refractive index and the thickness of the films on silicon substrates were measured using an ellipsometer (DHA-XAIR/S3, Mizojiri Optical Co., Ltd.) employing λ = 633 nm radiation from a He-Ne laser. The photodecomposition process was traced from the UV absorption spectra of films on glass substrates, and IR spectra of cast film on thallium bromo-iodine (KRS-5) plate under the same conditions as mentioned above.

3. Results and Discussion

Figure 1 shows typical changes in the refractive index of a PMPS film with the UV light exposure dose. Two different UV light sources were used in this measurement, a mercury-arc lamp (λ = 185, 254, 313 nm, TOSCURE401, Toshiba Lightech Inc.), and an excimer lamp (λ = 308 nm, UER20-308 (V), Ushio Electric, Inc.). PMPS having σ-conjugation in the backbone and π-electron system of phenyl substituent showed very high initial refractive index (n₀) of about 1.70, and reduced continuously to 1.63 (Δn = -0.07) with the amount of excimer lamp exposure. When the PMPS films were, however, exposed to shorter wavelength UV light (< 280 nm) from a mercury-arc lamp, the refractive index was reduced more effectively to 1.58 (Δn = -0.12). The decrescence curve with the
mercury-arc lamp exposure has an inflection point around 600 mJ/cm². At this point, the refractive index was almost the same to the saturation value with the excimer lamp exposure. This wavelength dependence implies that two different reactions participated in the reduction of its refractive index, i.e., 1.70-1.63 and 1.63-1.58. Figure 2 shows the changes of UV absorption spectra of a PMPS film with UV light exposure, respectively. The PMPS film shows two absorption bands, at around 330 nm attributable to σ-conjugation on silicon backbone, and at around 280 nm attributable to phenyl substituent. Under the excimer lamp exposure, decrease of the σ-conjugation with UV light exposure was clearly observed. This is caused by an incorporation of O atoms into the silicon backbone. In contrast, under the mercury-arc lamp exposure containing shorter wavelength light, the photodecomposition process accompanied with disappearance of the phenyl group. The FT-IR spectra showed the decrease of absorbance around 1428 cm⁻¹ attributed to Si-phenyl bond, indicating that phenyl substituent was eliminated during photo-oxidation with shorter wavelength UV light exposure, to yield large refractive index reduction due to disappearance of the π-conjugation. We confirmed the vaporization of benzene during thermal decomposition of an UV-exposed PMPS, by a peak at mW. = 78 in GC-MASS spectra. The heat form mercury-arc lamp is very important to achieve effective elimination of phenyl substituents upon UV-photodecomposition.

The molecular weight dependence was also investigated with PMPS. Commonly, the σ-conjugation length on the polysilane backbone was increased with its molecular weight [12,13]. PMPS having molecular weight of 6.4×10⁴, 1.6×10⁵, and 2×10⁵ was used in this study. The refractive indices of these polysilanes were summarized in Table 2. Interestingly, the initial refractive index was slightly decreased with increasing molecular weight. The backbones of these polysilanes were terminated with methoxy groups formed in quenching of wurtz-coupling reaction. Alkox group may act to increase the refractive index, since trimethylsilanol has higher refractive index than tetramethyilsilane (Δn = 0.029) [14]. Hence, these slight differences of refractive index depending on its molecular weight might be derived from content of methoxy terminal group. This result means that the molecular weight of the polymer was less effective on its refractive index.

The refractive indices and its reduction of other polysilanes are summarized in Table 3. The mercury-arc lamp was employed as a UV light...
source for the sake of elimination of side substituents. PMPS and DPPMPS showed the highest refractive index in these polysilanes. The alkyl substituted polysilanes, PMcHS and PMPnPS, showed a lower refractive index ($n_{\text{ref}}$) than that of PMPS, indicating that the $\pi$-conjugation of the side group largely affected on high refractive index of polysilanes. Another characteristic electronic structure of PMPS is $\sigma-\pi$ conjugation between silicon backbone and phenyl substitution, that is, a charge-transfer between $\sigma$ orbital and $\pi^*$ orbital [15]. The PMBPS has alkyl chain between the silicon backbone and phenyl group which interrupt $\sigma-\pi$ interaction [16]. The refractive index of PMBPS was a little higher than alkyl polysilanes. This is due to $\pi$-conjugation on phenyl group, but apparently lower than PMPS. These results indicate that $\sigma-\pi$ interaction also contribute to high refractive index of PMPS.

It is noted that all the saturated value ($n_{\text{sat}}$) of the refractive index reduction converged to about 1.55. Since, mentioned above, UV light exposure causes the scission of silicon backbone and elimination of phenyl substituents, polysilanes were turned to almost the similar siloxane-like structure consisting of Si-O-Si backbone and alkyl substituents, to give lower refractive index of around 1.55. The plausible molecular structures are illustrated in Fig. 3.

These results lead to the possibility of expanding the dynamic range of refractive index modification by setting initial refractive index higher. We tried to control the $\Delta n$ with the chemical structure. First, we attempted to enhance the $\sigma-\pi$ interaction by introduction of electron-donating para-substitution on phenyl group [17]. We employed PMTS which has methyl group as an electron-donating moiety.

![Molecular structure of PMPS and PMBPS](image)

**Table 2. Molecular weight dependence of the refractive index in PMPS film.**

<table>
<thead>
<tr>
<th>Mw</th>
<th>$n_{\text{ref}}$</th>
<th>$\Delta n$</th>
<th>Error ($\Delta n$)</th>
</tr>
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<tbody>
<tr>
<td>200,000</td>
<td>1.68</td>
<td>-0.11</td>
<td>$\pm 0.002$</td>
</tr>
<tr>
<td>16,000</td>
<td>1.69</td>
<td>-0.14</td>
<td>$\pm 0.002$</td>
</tr>
<tr>
<td>6,400</td>
<td>1.70</td>
<td>-0.12</td>
<td>$\pm 0.004$</td>
</tr>
</tbody>
</table>

*Refractive index before UV exposure. *b Changes in refractive index.

**Table 3. Optical properties of the polysilanes used in this study.**

<table>
<thead>
<tr>
<th>Polysilane</th>
<th>$n_{\text{ref}}$</th>
<th>$n_{\text{sat}}$</th>
<th>$\Delta n$</th>
<th>Error ($\Delta n$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPS</td>
<td>1.69</td>
<td>1.55</td>
<td>-0.14</td>
<td>$\pm 0.002$</td>
</tr>
<tr>
<td>PMcHS</td>
<td>1.63</td>
<td>1.54</td>
<td>-0.09</td>
<td>$\pm 0.002$</td>
</tr>
<tr>
<td>PMPnPS</td>
<td>1.60</td>
<td>1.55</td>
<td>-0.05</td>
<td>$\pm 0.003$</td>
</tr>
<tr>
<td>PMBPS</td>
<td>1.65</td>
<td>1.57</td>
<td>-0.08</td>
<td>$\pm 0.002$</td>
</tr>
<tr>
<td>PMTS</td>
<td>1.66</td>
<td>1.55</td>
<td>-0.11</td>
<td>$\pm 0.002$</td>
</tr>
<tr>
<td>DPPMPS</td>
<td>1.70</td>
<td>1.57</td>
<td>-0.13</td>
<td>$\pm 0.003$</td>
</tr>
</tbody>
</table>

*Refractive index before UV exposure. *b Refractive index after UV photodecomposition saturation. *c Changes in refractive index.

Fig. 3. The plausible molecular structure modification of polysilanes with UV light exposure.
Contrary to expectation, however, PMTS showed lower refractive index than that of PMPS. Since UV absorption intensity of PMTS around at 340 nm attributed to σ-conjugation was weakened compared with PMPS, the para-substitution of methyl lowered the charge-transfer between σ and π* orbital, and resulted in lower refractive index. Since, however para-substitution of electron-donating moiety on a phenyl group was considered to enhance σ-π interaction, the stronger electron-donating substitution, e.g., dimethylamino group may increase the refractive index of PMPS [18,19].

Next, we focused our attention on π-conjugation content in polysilane film. Poly(diphenyl-cophenylmethylsilane) (DPPMPS) was employed as a solvent soluble polysilane including diphenylsilane unit. The mixing rate was 1 : 1. The absorption band around 280 nm attributable to π-conjugation was increased by introducing diphenylsilane units. Nevertheless, DPPMPS have only the almost same refractive index as PMPS. This is probably due to the less σ-conjugation on the Si backbone caused by steric hindrance of phenyl substituents. Thus, the photo-modification of refractive index of polysilanes was found to be caused by both the decrease of σ-conjugation due to the incorporation of O atoms and the elimination of π-conjugation moieties of side group.

On the other hand, these photo-chemical reactions also affect on its film thickness. Figure 4 shows the changes in the film thickness of PMPS film upon UV light exposure, which were measured concurrently with the refractive index shown in Fig. 1.

The film thickness first tended to increase with UV exposure dose. The initial increase of the film thickness is due to the insertion of oxygen atom into silicon backbone. Over 600 mJ/cm² doses, then the thickness was decreased to a saturated value of about 5% of initial value. The turning point was just corresponding to the same dose showing inflection in the refractive index reduction shown in Fig. 1. Therefore, this loss of film thickness was apparently caused by evaporation of phenyl substituents from the film.

In order to apply the polysilane films to transmissive optical components, e.g., lens and phase shift mask [9], the performance of the optical modification is determined by the product of its refractive index and optical path length, i.e., optical thickness. Figure 5 shows the average of optical thickness changes (Δ(n x d)) obtained from Figs. 1 and 4.

![Fig. 5. The changes in optical thickness of a PMPS film at λ = 633 nm with UV exposure dose. Optical thickness was calculated from the product of refractive index (Fig. 1) and film thickness (Fig. 4).](image)

Interestingly, the optical thickness was varied linearly with UV exposure dose, because the initial increase of the film thickness was cancelled by the initial abrupt decrease of refractive index. This result strongly suggests that the polysilane films have very useful property of optical modification controllable with UV light exposure.

4. Summary

In this work, we have studied the relationship between the chemical structure and the refractive indices in several polysilanes as well as their changes by UV photo-irradiation. Polysilanes
having phenyl side-group showed higher refractive index ($n = 1.70$) due to $\sigma$-conjugation on the backbone and the $\sigma-\pi$ conjugation between silicon backbone and phenyl substituent. The shorter wavelength UV light exposure causes a large reduction of the refractive index ($\Delta n = -0.14$) in PMPS film due to the elimination of phenyl substituents. With its high transparency in entire visible wavelength and linear optical thickness reduction upon UV light exposure, the polysilane film is strongly expected to be useful materials for the practical applications.

References