Lithography using siloxane polymers is reasonable for process reduction compared to mask etching process. Generally, crosslinkable groups, such as acrylates and epoxides, and protecting groups are added to siloxane polymers for lithography. We synthesized polydiphenylsilane without those functional groups, and the thermal behavior of that was observed with TG-DSC-MS. The thermal elimination of phenyl group from polydiphenylsilane was observed and the thermal weight loss until 500 °C was under 3%. The polysilane film was directly imaged with EB nano melting apparatus (ENF-3500) and line width of pattern was 12.9 µm. The film thicknesses before and after development were same. The partial heating by EB irradiation caused oxidation of polydiphenylsilane after elimination reaction of phenyl group and cleavage of Si-Si bond by XPS analysis.

Keywords: Polysilane, Electron beam, Lithography

1. Introduction

Patterns of siloxane polymers are used as insulation materials for semiconductor and optical materials for light guide from the view point of the thermal resistance and insulation properties [1,2]. Lithography using siloxane polymers is reasonable for process reduction compared to mask etching process. Generally, crosslinkable groups, such as acrylates and epoxides, and protecting groups are added to siloxane polymers for lithographic property [3,4]. However, these functional groups decrease thermal resistance because of their thermal decomposition.

Polysilane has been studied from 1950s as a highly thermal resistance material. Method of preparation was limited to “Kipping method”, which was the condensation of dichlorosilanes with alkali metal [5]. It was difficult to control the molecular distribution of polysilane by the method. Recently, a highly practical method for the synthesis of polysilanes was found with Mg metal in the presence of LiCl and Lewis acid such as ZnCl₂ [6]. It was carried out under the mild reaction conditions.

Polysilane is decomposed by Ultraviolet (UV) irradiation, which generates the silyl radical after Si-Si bond cleavage, leading to formation of siloxane [7-10]. However, there are few reports of pattern forming of polysilane by UV irradiation.

Pattern forming by EB direct imaging to polysilane film with photosensitive functional group was reported [11], however, there were few reports without reaction groups. Recently, ELIONIX has developed Electron Beam (EB) nano melting apparatus (ENF-3500) with high beam current to increase the lithography performance. The melting apparatus was developed on the basis of EB direct imaging apparatus. ENF-3500 contains optical systems which can generate higher beam current over 1.0×10⁻³ A than general Scanning Electron Microscope (SEM) or direct imaging EB apparatus.
Therefore, it could heat a film partially by EB irradiation to local region. It was actually reported that Au nano particle formed by EB irradiation to Au thin film [12].

In this paper, we observed the thermal behavior of polysilane. On the basis of the results, EB lithography of polysilane films was performed with ENF-3500. We confirmed oxidation of EB irradiated parts in a polysilane film by observation of the element ratio with XPS.

2. Experimental

2.1. Synthesis of polysilane

2.1.1. Polymethylphenylsilane

Polymerization reaction was carried out as described in the literature [6]; Into a 30 mL round bottomed flask were added THF (30 mL, dried over Na), Mg powder (40 mmol), LiCl (20 mmol), and ZnCl₂ (4 mmol) as a Lewis acid under N₂ atmosphere and stirred to solve LiCl and ZnCl₂ to THF for an hour. Methylphenyldichlorosilane (30 mmol) was added into the flask, and the mixture was stirred for 24 h at room temperature. After 3 mL of water and toluene (50 mL) were added into the reaction mixture, it was filtered to remove Mg salts. The filtrate was poured into an ice cold solution of HCl (1N, 100 mL) and the aqueous solution was extracted with toluene (50 mL × 3). The combined organic layers were washed twice with 50 mL of brine, dried over MgSO₄, and concentrated. The products were purified by reprecipitation from IPA (100 mL). The polymethylphenylsilane was measured by Gel permeation chromatography (GPC). GPC was done with a TOHSO HLC-8320GPC. THF was used as an eluent. Molecular weights were calibrated using polystyrene standards.

2.1.2. Polydiphenylsilane

The polymerization of dichlorodiphenylsilane was carried out by the same procedure of methylphenyldichlorosilane.

2.2. Observation of kinetic behavior of polysilane

The thermal analyses of polydiphenylsilane and polymethylphenylsilane were performed with system composed of the thermogravimetry and differential scanning calorimetry coupled gas chromatography mass spectrome-

try (TG-DSC-MS) equipment with a 10 K min⁻¹ constant heating rate from 40 to 500 °C flowing clean dry air. TG-DSC model was STA 449 F1 Jupiter made by NETZSCH, GC model was GC 7890B made by Agilent Technologies, and MS model was JMS-Q1500GC made by JEOL.

2.3. Lithography by EB

The solutions were prepared by dissolving these polysilanes in cyclohexyl acetate by 10 weight percent and then were filtered through a 0.10 µm filter. The thin films of polysilanes were formed on Si wafer by spin-coating of the solution at 400 rpm and then baked at 100 °C for 2 minutes in air. The thickness of thin films was measured using a contact-type thickness meter (ULVAC Deaktak³). EB irradiation was carried out using an ELIONIX ENF-3500. The thin films were irradiated with EB of which irradiation current was 1.0 µA, and were developed by toluene for 60 sec. The pattern shape was observed with FE-SEM (HITACHI S-4300).

2.4. Analysis of polysilane films after EB irradiation

Bonding state of each element in polydiphenylsilane films before/after EB irradiation was observed by XPS. XPS model was K-Alpha made by thermofisher SCIENTIFIC. X-ray spot size was 400 µm and flood gun was turned on. The other conditions were below; Pass energy was 50 eV, energy step size was 0.1 eV, dwell time was 50 msec, number of scans was 5.

3. Results and discussion

3.1. Characterization of polysilanes

GPC charts of the synthesized polymethylphenylsilane and polydiphenylsilane were shown in Fig. 1. Molecular weight of polysilane was determined by GPC with THF as an eluent in Table 1.

Both polymethylphenylsilane and polydiphenylsilane had sharp peak around R.T. = 13 ~ 13.5 min and broad peak around R.T. = 9 ~ 13 min. The sharp peak was cyclic structure and the broad peak was linear structure in previous report [6]. It was confirmed that the obtained polymethylphenylsilane and polydiphenylsilane were mixture of linear and cyclic structures.
3.2. Thermal properties of polysilanes

TG-DSC-MS chart of polymethylphenylsilane was shown in Fig. 2.

As shown in TG chart, the thermal weight loss of polymethylphenylsilane was observed over 330 °C. Chromatograms of $m/z$: 120 (methylphenylsilane) and $m/z$: 78 (benzene) were observed over 330 °C by MS. It was suggested that Si-Si cleavage of polymethylphenylsilane occurred at the temperature.

TG-DSC-MS chart of polydiphenylsilane was shown in Fig. 3. Chromatograms of $m/z$: 78 (benzene) was observed over 160 °C and chromatograms of $m/z$: 182 (diphenylsilane) was not observed. It was suggested that phenyl group of polydiphenylsilane was eliminated at heat process. However, the thermal weight loss until 500 °C was under 3%. To investigate the reason for these results, we observed XPS spectra of polydiphenylsilane after curing at 500 °C under air. The obtained Si 2p spectrum data was shown in Fig. 4.

Si-binding peak shift from 99.3 eV (Si-Si binding), 100.3 eV (Si-C binding) to 102.3 eV (Si-O binding) was observed after 500 °C curing in air. It was suggested that oxidation of polydiphenylsilane occurred and siloxane was formed from the results of phenyl group elimination reaction and Si-binding peak shift.
Therefore, we examined the reactivity of the phenyl group in polydiphenylsilane was higher than that in polymethylphenylsilane.

3.3. Lithographic properties of polydiphenylsilane
The thin film of polydiphenylsilane was irradiated with EB and then was developed with toluene. The shape of pattern was observed with FE-SEM (Fig. 5).

![Fig. 5. SEM images of line pattern profile of polydiphenylsilane film after development (a) top view, (b) cross-section view.](image)

Irradiated parts of polydiphenylsilane film were remained after development. Line width of pattern was 12.9 µm as shown in SEM image. The film thickness was estimated as 1.3 µm by Dektak. The film thicknesses before and after development were same. From the result, it was suggested that crosslinking reaction was performed from top to bottom of the polydiphenylsilane film by EB irradiation (1.0 µA). Figure 6 shows XPS spectra of polydiphenylsilane film before and after EB irradiation.

It was confirmed that Si-Si bond peak (99.3 eV) disappeared after EB irradiation. It showed all Si-Si bond was cleaved by EB energy. Element ratio estimated by XPS was shown in Table 2. It was seen that O ratio increased and Si and C ratio decreased after EB irradiation. Therefore, it was presumed that the partial heating by EB irradiation caused oxidation of polydiphenylsilane with dissolved oxygen in cyclohexyl acetate solvent after elimination reaction of phenyl group and cleavage of Si-Si as shown in Scheme 1.

![Scheme 1. Oxidation of polydiphenylsilane (a) after cleavage of Si-Si, (b) after phenyl group elimination reaction.](image)

![Fig. 6. Si 2p spectrum of polydiphenylsilane film before / after EB irradiation (solid line: before EB irradiation, broken line: after EB irradiation).](image)
Table 2. Element ratio of polydiphenylsilane before/after EB irradiation estimated by XPS peaks.

<table>
<thead>
<tr>
<th></th>
<th>Si peak</th>
<th>O peak</th>
<th>C peak</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Si-Si</td>
<td>Si-C</td>
<td>Si-O</td>
</tr>
<tr>
<td>Before EB irradiation</td>
<td>8.6%</td>
<td>3.5%</td>
<td>0.2%</td>
</tr>
<tr>
<td>After EB irradiation</td>
<td>0%</td>
<td>0.4%</td>
<td>13.1%</td>
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</table>

4. Conclusion

In conclusion, we synthesized polydiphenylsilane by dichlorodiphenylsilane, and the thermal behavior of that was observed with TG-DSC-MS. It was observed the phenyl group of polydiphenylsilane was eliminated at heating process, however, the thermal weight loss was under 3% until 500 °C. It was suggested that oxidation of polydiphenylsilane occurred. The polysilane film was directly imaged with ENF-3500 and line width of pattern was 12.9 µm. Crosslinking reaction was performed from the top to bottom of polydiphenylsilane film by EB irradiation. It was presumed that the partial heating by EB irradiation caused oxidation of polydiphenylsilane after the elimination reaction of phenyl group and cleavage of Si-Si.

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