Ablation of Si-containing Polymers: Application to X-ray Lithography

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X-ray-induced ablation of Si-containing polymers is investigated for application to the surface-imaging process in X-ray lithography. Polysilanes, polystyrene, and polymethacrylates are chosen for this study. Ultraviolet (UV) and Fourier-transfer infrared (FTIR) spectra are observed and all of the polymers are found to have positive tone characteristics against soft X-ray exposure. Based on measurements of remaining film thickness after exposure, polymethacrylates are found to have a high self-development sensitivity. However, copolymerization gives no improvement in sensitivity. Oxygen reactive ion etching (O₂-RIE) rates of these polymers are also measured and found to depend on the Si content of the polymer. A bilayer resist using the polymer as a surface imaging resist is patterned by X-ray exposure and subsequent dry etching. Applicability of Si-containing X-ray resist to self-development is presented.

1. Introduction

Si-containing polymers have been investigated for use as resists for surface imaging processing schemes using O₂-RIE. It is well known that they are sensitive to UV radiation, and recently, their dry-developed characteristics have attracted more attention. Studies on both the fundamentals and applications of these polymers have been reported. For example, laser ablation dynamics of Si-containing copolymers of styrene and sulfone have been reported [1]. Si-containing derivatives of polyphthalaldehyde and polymethacrylate have been discussed in terms of their application to thermally developed resists [2,3]. It is also well known that polysilanes have been used as self-developing UV resists [4,5]. For the case of high energy radiation exposure, however, few characteristics of Si-containing polymers have been investigated, except electron beam (EB) exposure on polysilane [4]. It is necessary to study the behavior of Si-containing polymers against high energy radiation because soft X-ray exposure is needed for sub-0.1-µm resolution. For example, X-ray projection lithography systems have succeeded in patterning with sub-0.1-µm resolution over an image field with a diameter of 60 µm [6].

For these reasons, we focused on the self-development characteristics of Si-containing polymers against soft X-ray exposure. We have previously reported the results of photon-stimulated ion desorption (PSD) measurements on poly(cyclohexylmethylsilane) (PCHMS) [7].

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this paper, one-dimensional polymers containing Si atoms in either the backbone or the substituents are studied in detail. Their reaction to soft X-ray exposure, self-developing characteristics, and O2-RIE selectivity against novolac resin are investigated, and application to X-ray lithography is discussed.

2. Experimental

The polymers used for the measurements are listed in Table 1 and their structures are shown in Fig. 1. These polymers were chosen because of (1) their simple substituents and (2) their solubility in organic solvent, allowing us to make films by spin-coating.

Table 1 Polymers used in the experiments.

<table>
<thead>
<tr>
<th>Backbone</th>
<th>Polymer</th>
<th>Abbr.</th>
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<tbody>
<tr>
<td>Si</td>
<td>polysilane</td>
<td>PCHMS</td>
</tr>
<tr>
<td></td>
<td>poly(cyclohexylmethysilane)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>poly(buthylmethylsilane)</td>
<td>PBMS</td>
</tr>
<tr>
<td>C</td>
<td>polystyrene</td>
<td>PSiMSt</td>
</tr>
<tr>
<td></td>
<td>poly(trimethylsilylmethylstyrene)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>polymethacrylate</td>
<td>PSiMA</td>
</tr>
<tr>
<td></td>
<td>poly(trimethylsilylmethacrylate)</td>
<td>PSiMMA</td>
</tr>
</tbody>
</table>

For Si-backbone polymers, PCHMS and poly(buthylmethylsilane) (PBMS) were chosen. They were synthesized by Wurtz-type coupling. The synthesized PBMS was a highly viscous liquid material resembling paste at room temperature, while the PCHMS was a powder. The weight-average molecular weight (Mw) of PCHMS and PBMS were $4.2 \times 10^4$ and $4.9 \times 10^4$, respectively.

For C-backbone Si-containing polymers, polystyrene and polymethacrylate derivatives were synthesized. Polymethacrylates had rather complex substituents, however, the CO-O bonds in their substituents were expected to be easily broken by soft X-ray exposure [8]. Poly(trimethylsilylmethylstyrene) (PSiMSt), poly(trimethylsilylmethacrylate) (PSiMA), and poly(trimethylsilylmethylmethacrylate) (PSiMMA) were synthesized by radical polymerization using 2,2'-azobis(isobutyronitrile) (AIBN) as an initiator. In addition to these polymers,
poly(trimethylsilylmethylmethacrylate-co-methylmethacrylate) (PSiMMA-MMA) was synthesized to study the sensitivity dependence on the number of CO-O bonds in the polymers. Poly(trimethylsilylmethylmethacrylate-co-styrene) (PSiMMA-St) and poly(trimethylsilylmethylstyrene-co-styrene) (PSiMSSt-St) were also synthesized to investigate the dependence of O₂-RIE resistance on the Si content of the polymers. All of the polymers and copolymers were spin-coated onto substrates using a toluene or tetrahydrofuran (THF) solution and baked at 80 °C for 20 minutes in a convection oven.

Soft X-ray exposure was carried out by the synchrotron radiation with the BL-A1 beam line at SORTEC Corp. [9]. The peak wavelength is 0.7-1 nm. Samples were exposed to soft X-rays in a vacuum (< 1 x 10⁻² Pa) or in a He-gas atmosphere of 1 atm.

The unexposed and exposed films were characterized by UV and IR spectroscopy using UV (U-3410, Hitachi) and FTIR (1720X, Perkin Elmer) spectrometers to investigate the reaction to soft X-ray exposure. Film thicknesses were measured with a surface profile measuring system (DEKTAK3030, Sloan) before and after exposure to study self-development sensitivity. To study their applicability as surface imaging layers, O₂-RIE etch rates were measured. Proximity X-ray exposure was carried out on a bilayer resist to study the feasibility of preliminary pattern replication. The actual fabrication of the X-ray mask has been reported elsewhere [10]. The Si-containing polymer was used as the surface imaging resist and novolac resin OFPR800 baked at 200 °C was used as the bottom layer.

3. Results & Discussion

A. UV and FTIR Spectroscopy

Figure 2 shows observed UV spectra of PBMS before and after exposure in the He-gas atmosphere. The exposure dose was 22 J/cm². The absorption band around 300 nm, which is assigned to the transition of a σ electron delocalized on the one-dimensional Si backbone, is not present after exposure. The same result has been observed for PCHMS [7]. This means that the Si-Si bond is broken by the exposure [5]. Figures 3 (a) and (b) show FTIR spectra of PCHMS and PBMS. The spectral intensity is normalized according to film thickness. The polymers were also exposed in the He-gas atmosphere. The peaks at 700 to 800 cm⁻¹, due to vibration of the Si-C bonds, are also reduced [11,12]. This suggests that Si-C side-chain scission has occurred. With reductions in absorbance by Si-C, the intensity of the broad bands from 1000 to 1100 cm⁻¹ increases. These absorption bands are assigned to the Si-O-Si bonds [11]. This increase in their intensity is explained as follows. Soft X-ray exposure causes Si dangling bonds due to chain scission, and the Si atoms with dangling bonds...
are easily oxidized in the air when samples are unloaded from the vacuum chamber. These results indicate that both PCHMS and PBMS show positive tone characteristics in response to soft X-ray exposure.

In the case of C-backbone polymers, UV absorption is too small to characterize. Therefore, only FTIR spectroscopy was carried out. The FTIR spectra of PSiMSt, PSiMMA, and PSiMA are presented in Figs. 4 (a), (b), and (c). The spectral intensity was normalized according to film thickness. The samples were exposed to soft X-rays in a He-gas atmosphere. The peaks observed from 1150 to 1280 cm\(^{-1}\) in the spectra of PSiMA and PSiMMA are assigned to the CO-O bonds [13]. The peak at around 850 cm\(^{-1}\) was observed in all the C-backbone polymers. This absorption band may originate from the trimethylsilyl group, because such strong absorption is not observed in the spectra of either polymethylmethacrylate or polystyrene. All these peaks were reduced after exposure. The broad bands from 1000 to 1100 cm\(^{-1}\) grew as the peak at 850 cm\(^{-1}\) was reduced, suggesting that the Si atoms in the broken trimethylsilyl groups were oxidized in the same way as described above for polysilanes. These C-backbone polymers with Si in the substituents are found to be positive tone resists against X-ray exposure.

B. Self-development characteristics

The decrease in the film thicknesses of PCHMS was measured after exposure. The ratio of exposed-film thickness to unexposed-film thickness is plotted in Fig. 5. A decrease in film
thickness of less than 5% was observed when the film was exposed in a He-gas atmosphere. On the other hand, a larger decrease in film thickness was observed after exposure in a vacuum, though it leveled off at around 17%. The results of UV and FTIR spectroscopy suggest that the polymer decomposition was caused by core electron excitation. The results of film thickness measurements are described below.

The self-development process consists of two steps. First, decomposition of the polymer by chain scission, followed by desorption of the decomposed products. This second mechanism is expected to be enhanced in the case of PCHMS. To increase the sensitivity of this desorption process, the substrates were heated to 200 °C during exposure. The film thickness after exposure at 200 °C was much smaller than that after exposure at room temperature. Clearly, heating the polymer during exposure enhanced self-development.

The PBMS film used in this study is too soft to measure the surface profile before soft X-ray exposure, however, it is found to be hardened by X-ray exposure, even though chain scission (i.e., decrease in molecular weight) occurs. After soft X-ray exposure at 3 J/cm², spin-coated PBMS becomes solid and has a flat surface and uniform film thickness. This interesting result can be explained if we make the following assumption. The PBMS synthesized for these experiments has a glass transition temperature (Tg) below room temperature. However, after soft X-ray exposure, the Si atoms in PBMS are oxidized, causing it to change into material consisting of Si₅Oy, which has a Tg above room temperature.

In the case of the polysilanes, it was clarified that the decomposed products generated by X-ray exposure have a low volatility. Additional excitation, such as thermal energy, is needed to remove the exposed part.

For the C-backbone polymers with Si in the substituents, remaining film thicknesses were measured after soft X-ray exposure in a He-gas atmosphere of 11 J/cm². Table 2 lists the results. It should be noted that (1) all of these polymers have higher self-development sensitivity than polysilanes, and (2) polymethacrylate (PSiMA and PSiMMA) showed higher sensitivity than PSiMSt. Two possible reasons for the first result are the easily broken C-backbones and high volatility of...
trimethylsilyl groups. The second result indicates that high self-development sensitivity cannot be expected simply because there are C-backbones or trimethylsilyl groups. The CO-O bond is thought to be the origin of higher sensitivity because breaking the CO-O bonds generates CO and CO$_2$, which both have a high volatility. The 50% decrease in film thickness cannot be explained by CO$_2$ desorption alone. Therefore, the combination of a CO-O bond and a trimethylsilyl group at the end of a substituent is considered to be effective in increasing self-development sensitivity.

For these reasons, PSiMMA and PSiMA were chosen for detailed film thickness measurement. PSiMMA-MMA, which is expected to have higher sensitivity because of its greater number of CO-O bonds, was also used in this measurement. The self-development sensitivity curves are plotted in Fig. 6, for polymers exposed at room temperature (23 °C). All of them exhibit a much higher sensitivity than that of PCHMS. No difference is seen between the sensitivity after exposure in a vacuum and in a He-gas atmosphere in the case of PSiMMA. In comparing PSiMMA with PSiMMA-MMA, however, no improvement in sensitivity resulting from copolymerization with MMA is observed. This result shows that the volatility of the trimethylsilylmethyl group in the substituents of SiMMA is equal to the volatility of the methyl group in the substituents of MMA when CO-O bonds are broken by soft X-ray exposure. It is supposed that copolymerization with MMA gives a higher limit of self-development sensitivity, 50% in any polymers' case. Therefore, no further improvement in sensitivity is expected by copolymerization with MMA in the case of polymethylmethacrylate. PSiMA shows a higher sensitivity than that of PSiMMA, though its film thickness also levels off at around 50%. The remaining film thickness is found to decrease drastically at around 2 J/cm$^2$, causing a higher resolution to be expected.

C. O$_2$-RIE resistance

O$_2$-RIE etch rates of Si-containing polymers and novolac resin (OFPR800) were measured. The O$_2$-RIE etch rate of OFPR800 is 60 nm/min. and all of the polymers and copolymers have more than eight times the durability of OFPR800. It is found that O$_2$-RIE resistance depends only on the Si content (weight %) of these polymers and copolymers. For example, in the case that
OFPR800 is used for the bottom layer, O₂-RIE selectivity 10:1 needs a Si content of 10 wt% for a surface imaging resist. PSiMMA, which has high solubility to organic solvent and self-development sensitivity, is found to have enough O₂-RIE resistance (20 times that of OFPR800) for successful pattern transfer.

D. Pattern Replication

The feasibility of pattern replication was investigated by X-ray proximity lithography. From the point of view of sensitivity and solubility to organic solvent, PSiMMA is most suitable among the above polymers for use as a surface imaging resist.

A PSiMMA/OFPR800 bilayer resist was prepared by spin-coating. The thicknesses of PSiMMA and OFPR800 were 0.3 µm and 0.9 µm, respectively.

The 0.2-µm pattern images shown in Fig. 7 were replicated by X-ray proximity printing at room temperature and transferred onto a photoresist (OFPR800) by O₂-RIE. The exposure dose was 12 J/cm², and the proximity gap was 20 µm. Resist residue after self-development was removed by SF₆-RIE at a 100-W power and a 0.27-Pa gas pressure. O₂-RIE was applied for pattern transfer onto the photoresist at 100 W and 1.3 Pa. This new resist is found to be applicable for patterning by dry development.

4. Summary

X-ray-induced ablation of Si-containing polymers has been investigated and its application to the surface-imaging process in lithography has been presented. Polymers containing Si atoms in their backbones or substituents have been studied in detail.

UV and FTIR spectra have shown that all these polymers are positive tone resists against soft X-ray exposure. PBMS is found to be converted into a solid material by soft X-ray exposure due to the oxidation of Si atoms. In the measurement of remaining film thickness after soft X-ray exposure, polymethacrylates are found to have high self-development sensitivity, while PCHMS and PSiMSt are found to have low sensitivity. The high sensitivity is thought to be due to CO-O bonds. Copolymerization with MMA gives no improvement in the sensitivity of PSiMMA. The O₂-RIE etch rates of these polymers are found to depend solely on the Si content of the polymer. A Si content higher than 10 wt% is necessary to achieve O₂-RIE selectivity of 10:1 against novolac resin (OFPR800). PSiMMA is found to have sufficient self-development sensitivity and O₂-RIE resistance. A bilayer resist using the polymer as a surface imaging resist is patterned by X-ray exposure and subsequent dry etching.
In this work, the fundamental characteristics of Si-containing polymers in relation to soft X-ray exposure have been presented. For practical use, increasing the sensitivity and studying the capability of sub-0.1-µm patterning by X-ray projection lithography will be the subjects of future work.

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References