Poly(silamine) Derivatives for a New Electron-Beam Lithography

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1. Introduction

The tendency to grow smaller patterns for electronic devices has required the need to explore high performance resists for submicron lithography. The electron beam (EB) resist is one of the promising technologies for nanometer dimensions. To obtain high resolution patterns, a very thin resist film must be used. For this purpose, however, organic polymers do not have enough resistance to O₂ reactive ion etching (O₂ RIE). Organosilicon-containing polymers [1,2] are being considered as one of the candidates for materials with high resistance to O₂ RIE, the mechanism of which is as follows: [3,4] When the etching starts, the surface of the Si-containing polymer reacts immediately with oxygen to form a thin SiO₂ layer on the surface. The thin SiO₂ layer thus formed prevents further etching by O₂ RIE. Such organosilicon-containing polymer resists, however, have several problems. For example, the organosilicon group itself does not show a high sensitivity to EB exposure. To improve this sensitivity, the introduction of EB-sensitive groups into the polymer by certain techniques such as copolymerization must be done. Such a copolymerization, however, sometimes induces lower resolution of the resist [5].

For creation of a new high performance resist, new polymers possessing a new structure must be examined. Poly(silamine) [6], which was synthesized through anionic polyaddition reactions between divinylsilanes and diamines in the presence of a lithium catalyst, has unique repeating units, viz., alternating organosilicon and amine units in the main chain. Recently, we found that poly(silamine) degrades when exposed to EB. In this paper, we report the synthesis of poly(silamine)s and their properties as positive-type polymeric resist.

2. Experiments

All procedures related to the synthesis of poly(silamine) telechelics were carried out under purified argon to eliminate oxygen and moisture.

2.1 Materials: Commercial tetrahydrofuran (THF), 3,6-diazaoctane (DAO) and dimethyldivinylsilane (DVS) were purified by conventional methods [7]. Butyllithium was used as a hexane solution, the concentration of which was determined by Gilman's double titration method [8].

2.2 Synthesis of poly(silamine)s: One of the representative procedures for synthesis of poly(silamine) derivatives is described. In a
100-mL round-bottomed flask equipped with a three-way stopcock, THF (12.23 mL), DAO (12.8 g; 110 mmol), BuLi (1.3 mL; 2 mmol) and DVS (11.2 g; 100 mmol) were placed via syringe. The mixture was allowed to react at 60 °C. After the unreacted double bond was consumed completely which is determined by 1H NMR spectra, a small amount of methanol was added to quench the reaction. After the low boiling materials were removed by evaporation, the remaining viscous liquid was washed by water to remove lithium cation. The polymer thus obtained was analyzed by GPC and 1H NMR.

2.3 Preparation of crosslinked poly(silamine) film: To a THF solution of poly(silamine) (100 mg), a THF solution of triisocyanate compound (Coronate HL®; 36 mg; Japan Polyurethane, Co. Ltd.) was added. The concentration of poly(silamine) was calculated to adjust to 10 wt.% after mixing. Just after the mixing, the solution was placed on spinner and spanned for 30 s at 1,500 rpm. The film was prebaked at 80 °C for 7h then washed with methanol. The thickness of the film was 5,900 Å.

2.4 Resist processing: EB was exposed using a JEOL JSM-5200 scanning electron microscope (SEM) equipped with a Tokyo Technology L & S Pattern Generator LSPG1-1S at probe current of 100 pA and accelerating voltages of 20 kV. A dose that ranged from 1 - 2,000 µC/cm² was employed. The wafer was developed by soaking in water for 1 min and then rinsed by dipping in water for 10 min. The remaining film thickness was measured with an Alphastep (Tencor alphastep 500). Data were handled in the usual manner [9].

2.5 Measurements: 1H NMR spectra were observed on a JEOL EX-400 spectrometer at room temperature, using a 5-mm glass tube containing a solution of the polymer sample in CDCl₃ (1.0g dL⁻¹). Chemical shifts relative to CHCl₃ (1H: δ = 7.26) were employed. Gel permeation chromatography (GPC) measurements were performed on a Shimadzu LC 6A Liquid Chromatograph with an RID-6A IR detector and TSK-Gel G4000HXL + G3000HXL + G2500HXL columns to determine the number-average molecular weight (Mn) and the weight-average molecular weight (Mw).

3. Results and discussion

3.1 Synthesis of Poly(silamine) Derivatives

As we reported previously [6], the reaction between dimethyldivinylsilane (DVS) and 3,6-diazaoctane (DAO) in the presence of a lithium catalyst gives the polyadducts [poly(silamine)], the MW of which is controllable from a few hundred to ten thousands (Scheme 1).

When slightly excess amount of DAO was used as compared with DVS, poly(silamine) having sec-amino group was obtained easily. Figure 1 shows 1H NMR spectrum of the obtained polymer. As can be seen in the figure, no signal derived from vinylsilane protons appears around 5 - 6 ppm. In addition, a signal which is assignable to methylene protons adjacent to sec-amino group appears at 2.7 ppm along with methylene protons adjacent to tert-amino group at 2.5 ppm. On the basis of these results, the obtained poly(silamine) can be regarded as telechelic oligomers which possess sec-amino groups at both ends quantitatively. The molecular weight was determined from the ratio of these two signals.

3.2 Film preparation

Since poly(silamine) possesses organosilicon repeating unit in each repeating unit, the flexibility is very high. For example, the grass transition temperature of the poly(silamine) with the MW of 3,000 was -85 °C. Actually, the obtained telechelic oligomer was viscous liquid. To prepare solid film on a surface, crosslinking of poly(silamine) telechelic was carried out using trifunctional isocyanate compound (Coronate HL®) as a crosslinking agent. According to the experimental part, the crosslinking reaction was examined. After the reaction, the film was insolubilized in good solvents for poly(silamine) such as methanol and THF. The gel fraction was more than 95 % under these conditions.
3.3 Electron-beam patterning of crosslinked poly(silamine) film

MALDI-TOF mass is known as one of the analytical instrument candidates for examining polymer characteristics such as MW, end-groups and repeating units [10]. One of the features of this technique is that no fragmentation takes place during the electron beam dose due to the minimum energy transfer from the matrix used. For example, the molecular weight of each polymer molecule of linear poly(ethylene oxide) having a primary amino group at one end and a hydroxyl group at the other end can be completely determined by this technique [11]. When the poly(silamine) samples were analyzed using the MALDI-TOF mass technique, however, the MW was significantly lower than that expected from the GPC results, indicating the fragmentations of the poly(silamine) molecules even though the minimum energy was obtained from the matrix. These fragmentation can be explained by Scheme 2. If this kind of cleavage reaction proceeds not only under MALDI-TOF mass but also under the normal EB-dose, poly(silamine) can be anticipated to be a highly sensitive positive-type resist with high O₂ RIE resistance.

![Diagram of MALDI-TOF mass spectrum](image)

**Fig.1.** $^1$H NMR spectrum of telechelic poly(silamine)

**Scheme 2**

Due to the extremely high flexibility of organosilicon-linkage, however, poly(silamine) cannot form solid film. Poly(silamine) was prepared by the anionic polyaddition reactions, fortunately, its end groups possess reactive group. Under the appropriate reaction condition, sec-amino group can be introduced to both ends quantitatively (Scheme 1). The obtained sec-amino ended poly(silamine) telechelics was crosslinked easily when it was mixed with trisocyanate compound, Coronate HL®. The obtained crosslinked film was suitable for EB-processing.

Coronate HL®
Using the obtained crosslinked poly(silamine) thin film, the characteristics toward EB-exposure were investigated. After the EB-exposure followed by methanol development, the thickness of the film decreased, indicating positive characteristics. It is rather surprising to us that water was a much better developing solvent than methanol, indicating that the fragmented polymer became charged by the EB-dose making it a water soluble material. Figure 2 shows sensitivity characteristic curve of the crosslinked poly(silamine) film which was developed by water. As can be seen in the figure, the film thickness started to decrease with an EB-dose less than 10 µC cm\(^2\), indicating high sensitivity of the poly(silamine) film against EB. However, the developed thickness attained only 30% even at a 1,000 µC cm\(^2\) EB-dose. In the dose region higher than 1,000 µC cm\(^2\), the remaining film thickness increased again, indicating that the charged polymer due to the EB-dose may prevent further cleavage of the polymer film. Actually, when LiClO\(_4\) was doped into crosslinked poly(silamine) film, the film was developed almost completely at 2,000 µC cm\(^2\), supporting the charged-up mechanism. Namely, lithium cation in the matrix increased the conductivity, which induced the decrease in charge-up in the poly(silamine) film.

Therefore, developed poly(silamine) homologues can be one of the promising candidates for positive type lithographic material which can be drawn by EB.

4. Conclusion
Poly(silamine) telechelic oligomers coupled with triisocyanate compounds form crosslinked gel. The crosslinked poly(silamine) film was degraded by EB-exposure due to the lone pair of nitrogen atoms in the main chain induced cleavage reaction. The developed thickness attained only 30% even at a 1,000 µC cm\(^2\) EB-dose and no thickness change with further high dose. Charge-up of the film by EB-dose prevented further cleavage of the polymer film. LiClO\(_4\) dope into the poly(silamine) gel, the film was developed almost completely at 2,000 µC cm\(^2\). On the bases of these results, poly(silamine) can be one of the candidates for new positive-type polymeric resists.

References