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Synthesis and Resist Properties of Hyperbranched Polyacetals

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1. Introduction

Many polymers or molecular glass materials with pendant photo-acid labile groups have been reported as novel chemical amplification photo-resist materials. Very recently, next generation photoresist system using electron beam (EB) and extreme ultraviolet (EUV) have been expected to offer high resolution resist pattern with less than 20 nm [1]. To produce such high resolution, the resist materials must be high sensitive to exposure. However, high sensitivity is associated with increased roughness. There is a trade-off relationship among three factors such as sensitivity upon exposure, resolution and roughness of resist pattern [2]. To overcome this problem, the development of superior photo-resist materials have been required. We also have been investigated to offer higher resolution resist pattern based on ladder cyclic oligomer "noria" (noria = water wheel in Latin) [3]. The synthesis, physical properties, and patterning properties of noria derivatives with pendant *t*-butyl ester groups [4], *t*-butyloxycarbonyl groups [5], adamantyl ester groups [6 - 8], and cyclohexyl acetal moieties [9], and oxetanyl groups [10] using EB and EUV exposure system. In these previous works, acetal moieties showed higher sensitivity. Furthermore, Matsuzawa et al. [11] examined the relationships between the resist properties and physical properties of various resist materials based on polymers and reported that lower-density polymers are more transparent and would also show higher sensitivity in the photoresist system.

In this time, we designed hyperbranched polyacetal, anticipating that branched structures induce lower density and acetal groups can be decomposed lower exposure dose, to offer higher resolution resist pattern. The synthesis and resist properties of hyperbranched polyacetals by the polyaddition of tetrahydroxyphenylethane (THPE) as a A₃ type monomer, calix[4]resorcinarene (CRA[4]) as a A₈, and β -cyclodextrin (β -CD) as a A₂₁ type monomer with 1,4-bis(4-vinylloxy)cyclohexane (BVOC) as a B₂ type monomer.

2. Experimental

2.1. Synthesis of Hyperbranched Polyacetals

Hyperbranched polyacetals poly(THPE-*co*-BVOC), poly(CRA[4]-*co*-BVOC), and poly(β -CD-*co*-BVOC) were synthesized according to our previous report [12].

2.2. Thickness Loss Property on the Silicon Wafer after Soaking in Tetramethylammonium Hydroxide (TMAH) aq.

The solutions of poly(THPE-*co*-BVOC), poly(CRA[4]-*co*-BVOC), and poly(β -CD-*co*-BVOC) in propylene glycol monomethyl ether acetate (PEGMEA) were spin-coated on the silicon wafer to prepare corresponding thin films with about 50 nm thickness. The value of thickness of the thin films was determined by ellipsometry before and after soaking in TMAH aq. for 30 sec.



2.3. Resist Sensitivity

The resist solutions were filtered through a 0.20 μm PTFE syringe filter prior to spin-coating on silicon wafers which were primed with hexamethyldisilazane (HMDS). Spin-coating was performed at 3000 rpm for 30 s to form thin films on the silicon wafers. Then these spin-coated films were prebaked at 110 °C for 90s. The film thickness was adjusted to 100 nm. The resulting films were exposed to EUV lithography (energetic EQ-10M) [13]. The area of exposure was approximately 1 × 1.cm². After the exposure, they were developed by dipping in TMAH solution at 23 °C for 30s and then rinsed in deionized water before drying. The resist film thickness was measured with an ET200 surface profiler to obtain sensitivity curves.

2.4. Etching Durability

The etching rates of the thin films on the silicon wafers were determined using a reactive ion etching (RIE) plasma process. The plasma conditions were a 15 SCCM CF₄ gas flow, a 5 sccm Ar gas flow, and an RF power of 100 W. The pressure in the process chamber was 1.0 Pa.

2.5. EB Patterning Property

The mixture of polymer, perfluoro-1-butananesulfonate (TPS-Nf) as a photo-acid generator (PAG), and trioctylamine as a quencher was dissolved in PEGMEA, which feeds weight-% ratio was as follow.; polymer / TPS-Nf / trioctylamine = 100 / 10 / 1.25. The spin-coating thin films on the silicon wafers were soft baked (SB) at 90 °C under N₂ gas flow. The films were exposed to a 75 kV EB (ELIONIX, ELS-7700). After the exposure, the films were post exposure bake (PEB) at 90 °C for 60s. They were developed by dipping in 2.38 wt% TMAH solution at 23 °C for 30 s and then rinsed in deionized water for 30 s before drying. Resist patterns were recorded with a Hitachi-hitec S-5500 SEM. The values of line width roughness (LWR) of resist patterns are average those taken from ten different lines with a 1 μm inspection length.

3. Results and Discussion

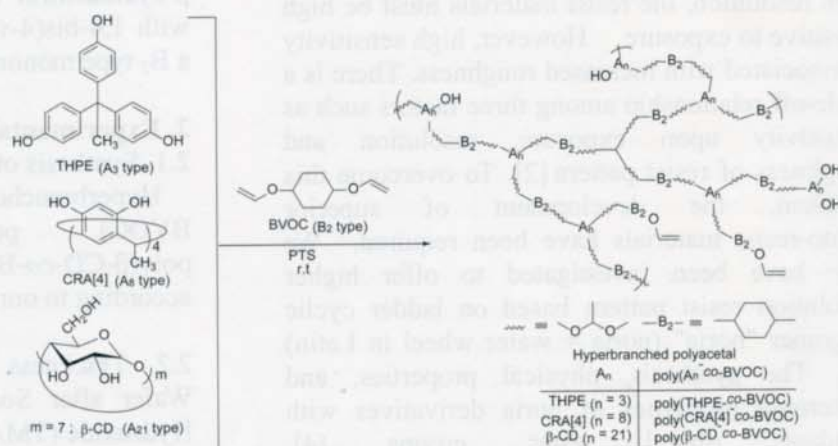
3.1. Synthesis of Hyperbranched Polyacetal

Hyperbranched polyacetals were synthesized by the A_n + B₂ type polyaddition using tetrahydroxyphenylethane (THPE) as a A₃ type monomer, calix[4]resorcinarene (CRA[4]) as a A₈, and β-cyclodextrin (β-CD) as a A₂₁ type monomer with 1,4-bis(4-vinyloxy)cyclohexane (BVOC) as B₂ type monomer (Scheme 1). The synthesized hyperbranched polyacetals had good solubility, good film-forming ability, and high thermal stability. These are summarized in Table 1.

Table 1. Hyperbranched polyacetals.

Polymer	M _n (M _w /M _n) ^{a)}	T _d ^{b)}
Poly(THPE-co-BVC)	7,200 (1.60)	115
Poly(CRA[4]-co-BVC)	3,900 (1.60)	98
Poly(β-CD-co-BVC)	10,000 (2.47)	93

^{a)} Estimated by SEC based on polystyrene standards; LiBr and phosphoric acid solution in DMF (20 mM). ^{b)} T_dⁱ; Initial decomposition temperature determined by TGA.



Scheme 1. Synthesis of hyperbranched polyacetals.

3.2. Thickness Loss Property on the Silicon Wafer after Soaking in TMAH aq.

In the positive type photoresist process, the unexposed part must remain on the silicon wafer after the developing with TMAH aqueous solution. The resist film was prepared on the silicon wafer by the spin-coating from the solution of PEGMEA containing poly(THPE-co-BVOC), poly(CRA[4]-co-BVOC),

and poly(β -CD-co-BVOC). The value of thickness of the thin films was determined by ellipsometry before and after soaking in TMAH aq. for 30 sec. These results are summarized in Table 2. In the case of the thin films of poly(THPE-co-BVOC) and poly(CRA[4]-co-BVOC), 2.5% and 3.8 %-decreases of their thicknesses were observed. However, 27.8%-decrease was observed in the case of poly(β -CD-co-BVOC). These results mean that poly(β -CD-co-BVOC) is inappropriate for resist material.

3.3. Resist Sensitivity

From the mentioned above results on thickness loss properties after soaking in TMAH aq. of synthesized hyperbranched polyacetals, poly(THPE-co-BVOC) and poly(CRA[4]-co-BVOC) are applicable to positive type photo lithography system. Their resist-sensitivity was examined under EUV exposure tool. Solution of these polymers in the presence of 10 wt% of TPS-Nf as a PAG were spin coated on silicon wafer to prepare corresponding thin films in the absence of a quencher with 119 nm thickness. The postexposure baking (PEB) temperatures and time were 90 °C and 60 s, respectively. The value of the thickness of remained thin films was measured by means of ellipsometer after the

means that these polymers have high sensitivity in EUV photoresist system. In the presence of a quencher, their thin films were soluble with about 1.00 ~ 1.25 mJ exposure doses. It is indicated that the sensitivity of these polymers could be controlled using trioctylamine as a quencher and its order was poly(THPE-co-BVOC) > poly(CRA[4]-co-BVOC). In generally, it has been required that the resist material should soluble fully with developer under less than 10 mJ exposure dose in EUV lithography exposure tool. This indicates that poly(THPE-co-BVOC) and poly(CRA[4]-co-BVOC) have adequate resist-sensitivity in the application of EUV photoresist system.

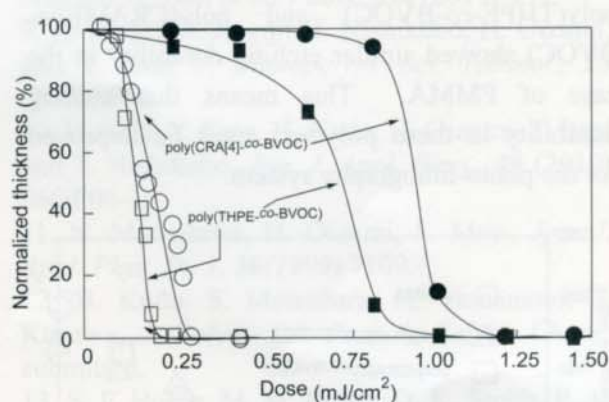


Figure 1. Resist-sensitivity curves of resist materials

Table 2. The ratio of thickness lost after soaking in TMAH aq.

Polymer	poly(THPE-co-BVOC)	poly(CRA[4]-co-BVOC)	poly(β -CD-co-BVOC)
Thickness Lost ^a	2.50%	3.80%	27.80%

^aDetermined by ellipsometry

lithography process. In the same way, their resist-sensitivity was examined by the preparation of thin films containing trioctylamine as a quencher. These results are depicted in Figure 1. In the absence of a quencher, thin films of poly(THPE-co-BVOC) and poly(CRA[4]-co-BVOC) were soluble in alkali aqueous solution fully with about 0.25 mJ exposure dose. This

based on poly(THPE-co-BVOC) and poly(CRA[4]-co-BVOC). ○; poly(THPE-co-BVOC) without PAG, ●; poly(THPE-co-BVOC) containing PAG, □; poly(CRA[4]-co-BVOC) without PAG, ■; poly(CRA[4]-co-BVOC) containing PAG.

3.4. Etching Durability

The etching durability is very important factor to keep the resist pattern during etching process in photo-lithography resist system, and was examined using RIE plasma process. The plasma conditions were a 15 sccm CF₄ gas flow, a 5 sccm Ar gas flow, and RF power of 100 W under 1.0 Pa pressure in the process chamber. Figure 2 depicts the etching rate of the thin films prepared from poly(THPE-*co*-BVOC), poly(CRA[4]-*co*-BVOC), polymethyl methacrylate (PMMA), and polyhydroxy styrene (PHS). PMMA and PHS are typical polymers in the application of resist materials. It was observed that poly(THPE-*co*-BVOC) and poly(CRA[4]-*co*-BVOC) showed similar etching durability in the case of PMMA. This means that etching durability in these polymers must be improved for the photo-lithography system.

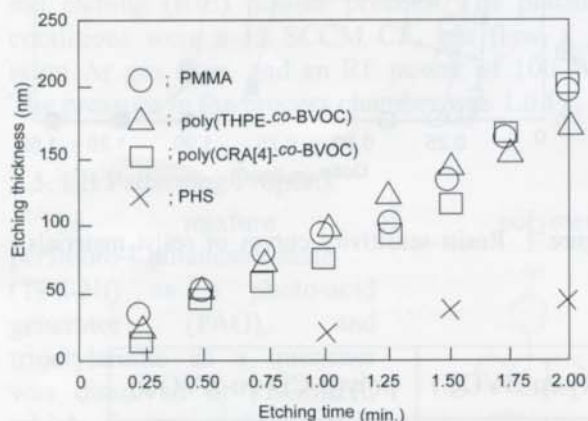


Figure 2. Etching durability of the thin films on the silicon wafer prepared from poly(THPE-*co*-BVOC), poly(CRA[4]-*co*-BVOC), poly(methyl methacrylate)(PMMA), and poly(hydroxystyrene)(PHS).

3.5. EB Patterning Property

Patterning properties were examined using thin-film prepared from poly(THPE-*co*-BVOC) in the EB exposure system, anticipating that poly(THPE-*co*-BVOC) shows higher resolution resist pattern due to its higher sensitivity compared to another hyperbranched polyacetals. Figure 3 depicts SEM images of the patterns with resolution in the range between 30 and 100 nm, which were obtained using trioctylamine as a quencher at 90 °C SB temperature and 90 °C PEB temperature, and 2.38 wt% TMAH aqueous solution as a developer. A clear 60 nm resolution pattern with line width roughness (LWR) = 21.4 nm was obtained using exposure

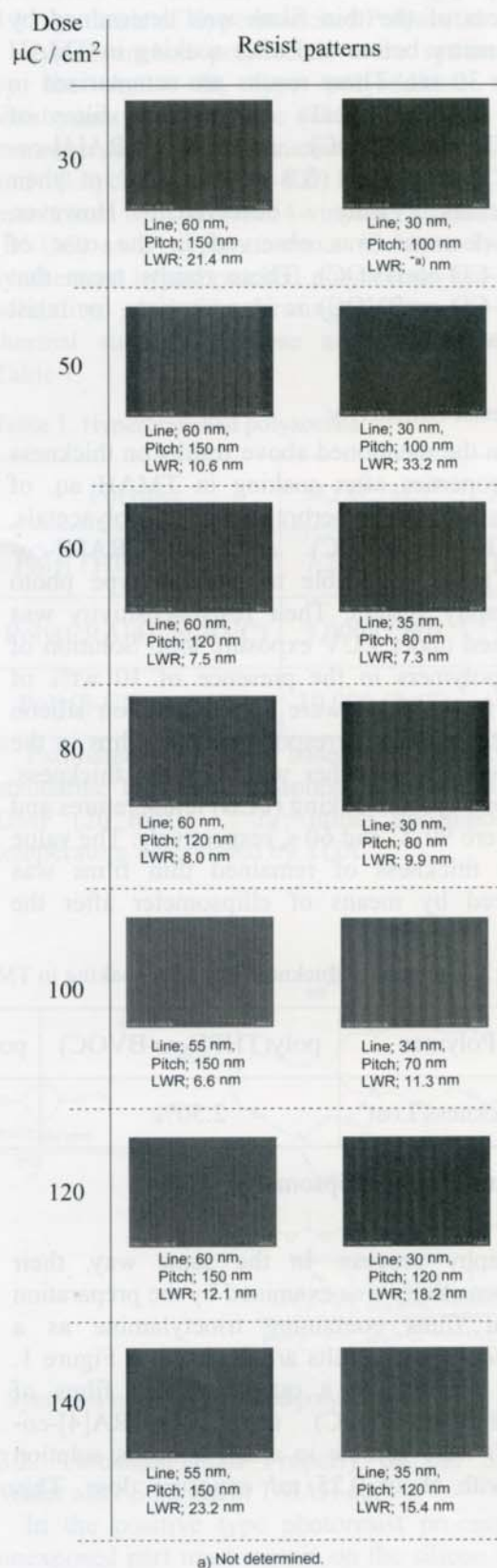


Figure 3. EB-resist patterns obtained with poly(THPE-*co*-BVOC) at various exposure doses at 30 ~ 140 μC/cm².

dose at $30 \mu\text{C}/\text{cm}^2$. Furthermore, LWR of 60 nm resolution patterns slightly decreased with increase of exposure dose until at $100 \mu\text{C}/\text{cm}^2$. At this point, a clear 60 nm resolution pattern was obtained with $\text{LWR} = 6.6 \text{ nm}$. However, at $120 \mu\text{C}/\text{cm}^2$ exposure dose, its LWR increased to be 18.2 nm. Furthermore, the similar tendency was observed and a clear 35 nm resolution pattern was obtained with $\text{LWR} = 7.3 \text{ nm}$ at $60 \mu\text{C}/\text{cm}^2$ exposure dose, which was best resolution resist pattern under these EB exposure conditions. In our previous report, EB and EUV resist patterning property of noria derivative with pendant adamantyl ester groups (noria-AD) were examined. The synthesized noria-AD offered 40 nm resolution resist pattern with $\text{LWR} = 9.5 \text{ nm}$ [14] in the case of EB exposure tool and a clear 26 nm resolution pattern with $\text{LWR} = 8.3 \text{ nm}$ by means of EUV exposure tool [7]. These results indicate that the present poly(THPE-co-BVOC) would have higher potential to offer higher resolution pattern using EUV lithography system.

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