Synthesis and Evaluation of Adamantane-Containing Fluorinated Block Copolymers for Resist Modifiers in Immersion Lithography

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The fluorinated block copolymer containing 2-methyl-2-adamantyl methacrylate (adMM) and perfluoroalkyl methacrylate (Zonyl[®]) was synthesized via atom transfer radical polymerization (ATRP) using a copper catalyst. High reactivity of adMM was observed. AdMM was polymerized even at room temperature and the polymer which with narrow polydispersity was observed. Fluorinated homopolymer (PZonyl[®]) and random copolymer (PadMM-*r*-PZonyl[®]) were also synthesized. The polymers were added to the resist model polymer and the relationship between polymer structure and film characteristics were investigated such as hydrophobicity and development behavior. The fluorinated polymers (0-1 wt%), photoacid generator (PAG) (0.2 wt%) and the resist model polymer (9-10 wt%) were dissolved in α,α,α -trifluorotoluene (TFT) and the blend polymer films prepared on Si wafer. The film containing PadMM-*b*-PZonyl[®] showed good hydrophobicity and resist performance compared with films containing the other polymer because self-segregation was promoted with the block copolymer and the low surface energy of perfluoroalkyl group. It is expected that adMM units in fluorinated additives increase resist performance.

Keywords: fluorinated block copolymer, immersion lithography, hydrophobic surface, self-segregation, phase-separation, room temperature ATRP

1. Introduction

Semiconductor devices are mainly manufactured by photolithography. The resolution in photolithography have been drastically improved to get high integration density device [1,2]. Recently, immersion lithography was beginning to be introduced and the resolution increased up to 40-nm half pitch [3]. In immersion lithography, high refractive index fluid ($n > 1$) such as water was filled between resist and exposure lens to increase resolution. However, the contact of the fluid with a resist caused some problems, for example, water penetration, chemical leaching from resist materials, water droplet, and air bubbles. These problems decrease resist performance and increase defects of resist pattern [4]. One of the most typical solutions for these

problems is that top-coat, a highly hydrophobic film is coated onto the resist surface [5]. However, process cost increases because additional coating and the removal process is required. Other solution is the use of hydrophobic resists such as fluorinated polymers, but fluorine atom decreases resist performance such as sensitivity and etching resistance, and increases material cost [6,7]. According to recent works, perfluoroalkyl group dramatically increased hydrophobicity of resist surfaces even though fluorine content is very low [8]. The fluorinated unit effectively makes self-segregated surface utilizing their low surface energy nature as a driving force [9]. From this point of view, the introduction of perfluoroalkyl group into resist additives is expected to suppress the loading amount required for hydrophobicity.

Particularly, fluorinated block copolymer expected to offer appropriate self-segregation because of the phase separation [10].

Some studies on polymerization of adamantane containing methacrylate were reported [11-13]. However reactivity of monomer has been not investigated in detail. It is very important to precisely control molecular weight, polydispersity, and chemical composition to get high resolution pattern.

In this paper, fluorinated block copolymers containing adamantyl unit were synthesized via atom transfer radical polymerization (ATRP) as hydrophobic additives. Polymerization was carried out in various conditions to determine the reactivity of adMM. Since adamantane units showed good resist performance, it is expected to avoid to decrease resist performance of base polymers such as etching resistance. Fluorinated homopolymer and random copolymer were synthesized for comparison. The fluorinated polymers were added to resist model polymer and hydrophobicity of blend films was evaluated. The effect of polymer structure on hydrophobicity and resist performance were investigated in detail.

2. Experimental

2.1 Materials

2-Methyl-2-adamantyl methacrylate (adMM) was provided from Idemitsu Kosan Co., Ltd. Zonyl[®] TM fluoromonomer (Zonyl[®]), α, α, α -tri-fluorotoluene (TFT) and (4-methoxyphenyl)di-phenylsulfonium trifluoromethanesulfonate were purchased from Sigma-Aldrich Co. Methyl 2-bromopropionate (MBP), 2,2'-azobis(isobutyronitrile) (AIBN) was purchased from Tokyo Chemical Industry Co., Ltd. All other materials were purchased from Wako Pure Chemical Industries, Ltd. and used without any further purification unless otherwise noted.

2.2 Polymer synthesis

2.2.1 Synthesis of resist model polymer

A 50-mL two-necked flask equipped with a stirrer bar, a condenser, and a nitrogen inlet was charged with AIBN (414 mg, 2.5 mmol) under nitrogen. After the evacuation followed by backfilling of nitrogen, dry tetrahydrofuran (THF) (23.0 mL), methyl methacrylate (MMA) (2.65 mL, 25 mmol), and adMM (5.50 mL, 25 mmol) were added into the flask. After four times of freeze-pump-thaw cycles, the flask was heated at 70 °C for 18 h. The reaction mixture was cooled to

room temperature, and poured into methanol to recover the product. The polymer was dried overnight *in vacuo* and resulted in 7.67 g (87 %) of white powder.

2.2.2 Synthesis of PadMM macro initiators

A 20-mL two-necked flask equipped with a stirrer bar and a stop cock was charged with CuCl (29.7 mg, 0.30 mmol) under nitrogen. After the evacuation followed by backfilling of nitrogen, anisole (0.620 mL), *N, N, N', N'', N'''*-pentamethyldiethylenetriamine (PMDETA) (78.0 mg, 45 mmol), adMM (2.11 g, 9.0 mmol) were added with a gas-tight syringe. After four times of freeze-pump-thaw cycles, the mixture was allowed to stir at room temperature for 30 min. Then, MBP (50.1 mg, 0.30 mmol) was added with a gas-tight syringe, and stirred at room temperature for 2 h. The reaction mixture was diluted with THF and filtered with alumina column in order to remove the catalyst. The resulting mixture was poured into methanol to recover the product, and the resulting polymer was dried overnight *in vacuo* and resulted in 1.54 g (73 %) of white powder.

2.2.3 Synthesis of PadMM-*b*-Zonyl[®]

A 20-mL two-necked flask equipped with a stirrer bar, a condenser, and a stop-cock was charged with CuBr (340 mg, 2.38 mmol) and adMM macroinitiator (950 mg, 0.119 mmol) under nitrogen. After the evacuation followed by backfilling of nitrogen, PMDETA (515 mg, 2.97 mmol), toluene (6.0 mL), TFT (6.0 mL), and Zonyl[®] (3.80 g, 7.12 mmol) were added with a gas-tight syringe. After four times of freeze-pump-thaw cycles, the mixture was heated at 100 °C for 22 h. The reaction mixture was diluted with chloroform and poured into methanol to recover the product. The precipitated polymer was washed with acetone, hexane, and methanol. The polymer was dried overnight *in vacuo* and resulted in 1.37 g (29 %) of slightly blue powder.

2.2.4 Synthesis of PadMM-*r*-PZonyl[®] and PZonyl[®]

A 20-mL two-necked flask equipped with a stirrer bar and a stop cock was charged with CuBr (71.7 mg, 0.50 mmol), CuBr₂ (11.2 mg, 0.050 mmol) under nitrogen. After the evacuation followed by backfilling of nitrogen, anisole (0.517 mL), PMDETA (173 mg, 1.0 mmol), adMM (0.469 g, 2.0 mmol), Zonyl[®] (2.67 g, 5.0 mmol) were added with a gas-tight syringe. After four times of freeze-pump-thaw cycles, the mixture was allowed

to stir at room temperature for 30 min. Then, MBP (83.5 mg, 0.50 mmol) was added with a gas-tight syringe, and stirred at 70 °C for 18 h. The reaction mixture was diluted with THF and filtered with alumina column in order to remove the catalyst. The resulting polymer was poured into methanol to recover the product, and was dried overnight *in vacuo* and resulted in 1.04 g (32 %) of white powder.

PZonyl[®] was synthesized by a similar method (M/I/CuBr.PMDETA = 30/1/1/2, solvent:TFT ([Zonyl[®]] = 15 M)). Polymerization was carried out at room temperature or 70 °C. The polymer was obtained by reprecipitation into methanol without the alumina column treatment.

2.3 Resist film Preparation

In TFT, 9 wt% of the resist model polymer, 1 wt% of the fluorinated polymer, and 0.2 wt% of (4-methoxyphenyl)diphenylsulfonium trifluoromethanesulfonate as a photo acid generator (PAG), were dissolved. The solution was filtered through a membrane filter with pore size of 0.45 μm (Advantec Tokyo) and was spin-coated on a silicon wafer (3000 rpm, 15 s). After baking at 95 °C for 60 s, the resist film with about 500 nm thickness was used for following evaluation.

2.4 Measurements

2.4.1 Characterization of polymers

The degree of polymerization and chemical composition of the polymers were determined by ¹H-NMR spectroscopy. ¹H-NMR spectra were recorded at room temperature or 50 °C with a JEOL ECX 400 spectrometer operating at 400 MHz for ¹H. The molecular weight and its distribution of synthesized polymers were estimated by gel permeation chromatography (GPC) using a column packed with styrene-divinylbenzene gel beads. Chloroform was used as an eluent and the molecular weight was calibrated using polystyrene standards (Shodex STANDARD SM-105). Thermal property of polymers was investigated by differential scanning calorimetry (DSC, RIGAKU DSC8230). Scan range was 30-200 °C at a heating rate of 10 K min⁻¹ in nitrogen atmosphere. Glass transition temperature (*T_g*) were obtained from a second heating.

2.4.2 Contact angle measurement

Contact angles of resist films were estimated from snapshots of a water droplet. The droplets

were formed on films by dropping 5 μL of deionized water with a micro syringe.

2.4.3 Exposure test

Photoreactivity of a resist film was confirmed by simple UV exposure and alkaline development as follows. Half area of resist films on Si wafer chips was masked with a glass slide coated by aluminum foil and exposed with UV lamp of 254 nm wavelength (MINERALIGHT[®] LAMP UVGL-15, UVP) for 30 s. After that, the half exposed wafer was baked at 95 °C for 30 s and developed with 2.38 wt% tetramethylammonium hydroxide (TMAH_{aq}). The developed films were rinsed with deionized water and dried quickly by nitrogen gun. Finally, the film was observed by scanning electron microscopy (SEM, JEOL JSM-6510) in order to evaluate the edge roughness and residue.

3. Results and discussion

3.1 Polymer synthesis

3.1.1 Resist model polymer

PMMA-*r*-PadMM random copolymer was synthesized via a conventional free radical polymerization for a resist model polymer (P1). The polymer structure and composition was determined by ¹H-NMR spectrum and the molecular weight was determined by GPC (Table 1, P1, *M_n*=6400 g mol⁻¹, PDI=2.4, adMM/MMA=51/49). The polymer showed good solubility in various organic solvents such as THF, chloroform, propylene glycol monomethylether acetate (PEGMEA), and TFT.

3.1.2 Synthesis of PadMM macroinitiator

PadMM macroinitiators were synthesized by a typical ATRP method using CuBr and ligand. Polymerization conditions and results were summarized in Table 1. When adMM was polymerized at 100 °C, viscosity of the reaction mixture rapidly increased, and the polymerization almost finished in 30 min. The polymer was obtained in a good yield, but the polydispersity was high (Run 1). Generally, when the concentration of Cu(I) is decreased, polymerization rate decreases and well-controlled polymer is obtained. However, when the amount of CuBr catalyst was reduced by half, the yield was drastically decreased (Run 2). The catalyst may be deactivated by inhibitors and or a trace of oxygen which can not be removed completely because the concentration of catalyst was low. The

polymerization was conducted at 70 °C to control the reaction. As a result, the polymer was obtained in high yield with narrow polydispersity (Run 3). Finally, the reaction temperature was decreased to room temperature (Run 4). Polymerization proceeded even at room temperature. The resulting polymer was obtained in high yield with narrow polydispersity only in 45 min. It was suggested that adMM possesses high activity for ATRP, and harsh reaction conditions lead to excessive termination or other side reactions. In order to obtain more defined polymer, CuCl was used as a catalyst instead of CuBr. When the mole ratio of CuCl to MBP was 1, polydispersity was high (Run 5). On the other hand, using half amount of CuCl, PadMM could be synthesized in good yield with narrow polydispersity (Run 6).

3.1.3 Adamantane-containing fluorinated block copolymers

Fluorinated block copolymers containing Zonyl[®] was synthesized using macroinitiator (Table 1, Run 6, Table 2, P2) via ATRP at 100 °C for 22 h (P3). The high reaction temperature and a large amount of catalyst were necessary, because the concentration of the active chain-end was low. The obtained polymer structure was characterized by ¹H-NMR and the spectrum is shown in Figure 1. The broad peaks at 0.80-3.00 ppm were attributed to adamantane unit overlapped with signals from main chain. The signal at 3.66 ppm was attributed to -OCH₃ group at initiating end. The signal of fluoroalkylethoxy group in Zonyl[®] appeared at 4.28 ppm. Chemical composition of the polymer was calculated from integral ratio of these peaks. The block copolymer showed good solubility for fluorinated solvent such as TFT. The solubility was improved compared with fluorinated homopolymer. For example, the block copolymer was partially soluble in common organic solvents such as THF and chloroform.

Figure 1 ¹H-NMR spectrum of PadMM-*b*-Zonyl[®] (P3) in CDCl₃ at 50 °C (400 MHz).

3.1.4 Fluorinated homo- and random polymers

PadMM-*r*-PZonyl[®] (P4) and PZonyl[®] (P5) were synthesized via ATRP. P4 showed good solubility in chloroform, THF, and TFT even with high fluorine content. However, P5 showed poor solubility of common organic solvents. It was soluble only in fluorinated solvent. The polymer structure was characterized by ¹H-NMR and GPC. In the case of Zonyl[®] polymer synthesis, the reaction proceeded at room temperature. It was suggested that the ATRP activity of adMM and fluorinated methacrylate was high, and therefore, the reaction conditions should be selected appropriately.

3.2 Surface properties

Fabrication of the polymer films was carried out by spin-coat method using TFT as a solvent. The fluorinated polymer (P3, P4, and P5) was added to the resist model polymer (PadMM-*r*-PMMA, P1) with weight ratio of 10:90. Figure 2 shows snapshots of the blend polymer films. The blend polymer films containing fluorinated copolymers (P3, P4) showed homogeneous appearance (Figure 2a, 2b). It is suggested that adMM unit involved in these copolymers increased compatibility between the resist model polymer and the fluorinated copolymers. On the other hand, the films

Table 1 Polymerization conditions and characteristics of PadMM macroinitiators

Run	adMM/MBP/CuBr/PMDETA (mole ratio)	[M+I] / mol L ⁻¹	Temperature / °C	Time / min	Yield / %	M_n^a / kg mol ⁻¹	PDI ^a
1	60 / 1 / 1 / 2	40.0	100	30	70	6.4	1.9
2	60 / 1 / 0.5 / 1.5	40.0	100	^b	29	4.1	1.6
3 ^c	30 / 1 / 1 / 2	30.0	70	15	84	4.8	1.6
4	20 / 1 / 1 / 2	20.0	r.t	45	67	6.0	1.5
5 ^d	30 / 1 / 1 / 1.5	15.0	r.t	120	73	4.0	1.7
6 ^d	30 / 1 / 0.5 / 1.5	9.4	r.t	180	54	4.1	1.5

^a Molecular weight and polydispersity were determined by GPC. ^b Reaction time was 48 hours. ^c CuBr₂ bromide (10 mol% to CuBr) was added. ^d CuCl was used instead of CuBr.

Figure 2 Resist film appearance (a)P3 (b)P4 (c)P5.

containing PZonyl[®] homopolymer (P5) showed heterogeneous appearance (Figure 2c). It is suggested that macroscopic phase separation occurs between P5 and the resist model polymer in blend film because of low compatibility of fluorinated unit to the resist model polymer, and high aggregability of fluorinated unit. There is a possibility that this heterogeneous surface may cause resist defect in lithographic process.

Using fluorinated polymer additives, the contact angles of the films dramatically increased. The blend film containing P4 shows slightly low contact angle compared with P3 and P5. The amounts of additives (P3-P5) to resist model polymer (P1) were changed from 1:99 to 10:90 in weight ratio to determine effect of the additives in detail (Figure 3). The blend with P3 shows high contact angles even at low fluoropolymer content. P4 was lower contact angles than P3 and P5. Fluorinated units in random copolymer may be fixed main chain and widely distributed in films, therefore, the surface segregation might be prevented. Therefore, the contact angle was not improved even at high fluorinated monomer content. In contrast, blending the block copolymer and homopolymer additives dramatically increased contact angle. Particularly the block copolymer additive makes resist surface hydrophobic with a good film condition. The formation of microphase separation of block copolymer and having fluorinated unit which shows low surface energy, enhanced to form surface self-segregated film and increased compatibility of the fluorinated additive with the resist model polymer.

3.3 Exposure and alkaline development test

Lithographic performance of the films was preliminarily examined by simple UV exposure

Figure 3 Contact angles of the blend films containing the fluorinated copolymer (1-10 wt%) (Δ :P3, $\circ$:P4, $\square$:P5).

and alkaline development. The snap shot and SEM image of the film using the block copolymer additive (P3) after development was shown in Figure 4. When the block copolymer was added in the resist model polymer, the exposed area can be dissolved in alkaline development without any defects. Generally, fluorinated additives cause pattern defects and decrease etching resistance in lithographic process. These results suggested that this additive might give no significant influence on lithographic performance because PadMM segments increased compatibility between the resist model polymer and the additive. In addition, it is expected that etching resistance of the resist film is maintained by the adamantane structure in the block copolymer. Where PZonyl[®] or random copolymer (P4) was added into the resist model polymer, the resist films also showed high hydrophobicity, but the films have many crazing. Hence, it is considered that the fluorinated block copolymer was the best structure as a hydrophobic additive for resist.

3.4 Thermal properties

Thermal properties of the fluorinated polymers were examined by DSC. T_m and T_c derived from the side chain of Zonyl[®] unit in the P3 and P5 were obtained at 80 and 77 °C, respectively. As perfluoroalkyl chains tend to crystallize, fluorinated units in the block

Table 2 Characteristics of polymers

No.	Polymer	M_n^a / 10^3 g mol ⁻¹	PDI ^a	Contact angle / °		Composition (weight ratio) ^c
				Bulk	Blend film ^b	
P1	PadMM- <i>r</i> -PMMA	6.5	2.4	103	-	67/33
P2	PadMM	12	1.5	90	-	-
P3	PadMM- <i>b</i> -PZonyl [®]	21 ^c	-	121	117	59/41
P4	PadMM- <i>r</i> -PZonyl [®]	5.0	1.5	117	116	26/74
P5	PZonyl [®]	20 ^c	-	119	117	-

^a Molecular weight and polydispersity were determined by GPC. ^b Blend films were contained 10 wt% fluorinated polymer. ^c Molecular weight and chemical composition were determined by ¹H-NMR spectrum.

Figure 4 Snap shot and SEM image of P1 polymer film containing P3 (5 wt%) after development. The upper half area was non-exposed area, and the resist film was remained.

copolymer or the homopolymer segregated at the surface of blend films. These results also suggested that the surface segregation was prevented in the random copolymer because fluorinated units are dispersed in the polymer main chain. In the meantime, T_m and T_c were not observed for P4.

4. Conclusion

Macroinitiator and fluorinated polymers containing adamantyl methacrylate were synthesized via ATRP. 2-Methyl-2-adamantyl methacrylate showed high reactivity in ATRP. When the polymerization was carried out at room temperature using CuCl, the obtained polymer showed preferable characteristics such as the narrow polydispersity and desirable molecular weight. The polymers were blended as an additive with the resist model polymer and the effect on surface properties, hydrophobicity, and resist performance were evaluated. The fluorinated polymers containing perfluoroalkyl unit drastically enhanced hydrophobicity of the resist surface. Particularly, fluorinated block copolymer has appropriate surface characteristics and high hydrophobicity. One reason was that the block copolymer could form microphase separation and promoted self-segregation of fluorinated moieties having low surface energy. Another reason was that adMM unit increased compatibility of the additives for the resist model polymer without

depression of etching resistance. These results indicated the fluorinated block copolymer was the best structure for hydrophobic additives.

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