Synthesis of Fluorinated Materials for 193 nm Immersion Lithography and 157 nm Lithography

¹T. Yamashita, ¹T. Ishikawa, ¹T. Yoshida, ¹T. Hayamai, ¹T. Araki,
¹H. Aoyama, ²T. Hagiwara, ²T. Itani and ²K. Fujii

¹Daikin Industries, Ltd., 1-1 Nishi-Hitotsuya, Settsu, Osaka, 566-8585 Japan
tsuneo1.yamashita@daikin.co.jp

²Selete, 16-1 Onogawa, Tsukuba, Ibaraki, 305-8569 Japan

Various fluorinated polymers were synthesized for application in 193 nm immersion lithography with the goal of improving 157-nm photoresist performance. Their fundamental properties were characterized, such as transparency at 193-nm and 157 nm (wavelength) and solubility in water and a standard alkaline developer. High transparency, i.e., absorbance better than $0.2 \mu\text{m}^{-1}$ at 193-nm wavelength, was achieved. The dissolution behaviors of them were studied by using the Quartz Crystal Microbalance (QCM) method. We find that the dissolution rate of poly(norbornene-2-fluoro-2-hexafluoroalcohol) (PNB1FVIP) in 0.065N tetramethylammonium hydroxide (TMAH) was >100 times (nm/s) faster than that of the copolymer of tetrafluoroethylene (TFE) and norbornene-2-fluoro-2-hexafluoroalcohol (TFE/NB1FVIP). A resist based on TFE/NB1FVIP was able to delineate 75 nm dense lines by exposure at 193 nm (wavelength) with an alternating phase shift mask using a 0.75 NA ArF scanner. The dissolution rates of the fluoropolymers in water and a 0.262N and 0.065 TMAH can be controlled by optimizing counter monomers containing hexafluoroisopropanol (HFA) unit, carboxylic acid unit and so on. In addition, we have collected water contact angle data. This data shows that fluoropolymers can be used as top-coats for 193-nm immersion lithography resists.

Keywords: 157 nm lithography, 193 nm lithography, 193-nm immersion lithography, resist, fluoropolymer, Quartz Crystal Microbalance (QCM), top-coat.

1. Introduction

Fluoropolymers have long been thought of as one of the best approaches to achieving high transparency at shorter wavelengths, and particular attention has been paid to fluoropolymers for 157 nm lithography. Many fluoropolymers for use as 157 nm resist base resins have been intensively studied over the past six years [1–8]. Two main types of fluoropolymers have been studied for photoresist use, side-chain-fluorinated polymers and main-chain-fluorinated polymers. The former are mainly based on fluorinated polyhydroxystyrene, fluorinated polynorbornene and fluorinated acrylic resins. These polymers have the advantages of aqueous-base solubility and high etch resistance. The latter have a structure in which fluorine atoms are introduced to the main chain. Fluoro-manufacturing companies have been quite active in developing fluoropolymers for use in 157 nm lithography [6–8]. These resists have the

advantage of the high transparency at a wavelength of 157 nm, i.e. their absorption coefficient is less than $1 \mu\text{m}^{-1}$ and as low as $0.4 \mu\text{m}^{-1}$, so they are a practical choice for the single-layer resist process [5].

The field of 157-nm lithography has, however, overtaken by 193 nm immersion lithography as the most viable next generation technology (NGL). Our previous study on the dissolution behavior of TFE based fluoropolymers [9–12] strongly suggested the practicality of 193 nm resists. 193 nm resists mainly make use of carboxylic acid as the polymer's acid group, which result in swelling during aqueous development. The HFA group has acidity similar to that of phenol group. Various new fluoropolymers using HFA as the acid group have been reported [2–8]. We have studied TFE/norbornene copolymers and reported the relationship between their dissolution behavior and the pKa of the HFA group of the

norbornene monomer [10]. We reported that it changing the end group of TFE/NB1FVIP to fluoroalkyl group is an effective way of enhancing solution, transparency, and development characteristic [11]. Furthermore, a copolymer protected only in the exo position has been shown to offer improved transparency, swelling, and improved dissolution rates [12]. Nevertheless, fluoropolymers have been required to improve the dissolution rate and Dry-etching resistance for using 193 nm lithography.

In this paper, we synthesize main-chain and side-chain fluorinated polymers using the various acidic functional group containing monomers, as shown in Figure 1.

Fig. 1. Monomer employed in polymer synthesis

We then characterize their fundamental properties, such as transparency at 193 nm and 157 nm (wavelength), dissolution behavior in water, 0.262N and 0.065N TMAH, and surface properties. Moreover we have made sure of Dry-etching resistance and lithographic performance. In addition, the possibility of top-coats for 193 nm immersion lithography resists is described.

2. Experimental

2.1. Materials

All materials were obtained from commercial suppliers and used without further purification, unless otherwise noted. Functional norbornene was prepared by the cyclo-addition of cyclopentadiene and α -Fluoro-acryl fluoride as described in the literature [13].

2.1.1. Synthesis of monomer

[1,1,1,3,3,3-Hexafluoro-2-(2-fluoro-bicyclo[2.2.1]hept-5-en-2-yl)-propan-2-ol: NB1FVIP]

2-Fluoro-bicyclo[2.2.1]hept-5-ene-2-carbonyl fluoride was added to a suspension of dry KF and dry CsF in anhydrous THF under nitrogen. Trifluoromethyltrimethylsilane was slowly dropped into the mixture under nitrogen at 10°C. The reaction mixture was stirred at room temperature overnight. After reaction, 1.0 N HCl aq was added to the mixture and extracted with diethyl ether. The combined ether extracts were washed with 1.0 N HCl aq, water and brine. The ether solution was dried over $MgSO_4$, evaporated and distilled at 60°C at 5 mmHg to yield (90%) of functional norbornene as colorless oil.

[6-(2,2,2-Trifluoro-1-hydroxy-1-trifluoromethylethyl)-6-fluoro-bicyclo[2.2.1]hept-2-yl methacrylate: MANB1FVIP]

$NaBH_4$ was dissolved in anhydrous THF under N_2 and cooled to 0°C while being stirred. NB1FVIP and Boron trifluoride diethyl etherate were slowly added drop-wise into the solution under N_2 at 0°C. The solution was allowed warm at room temperature and stirred for 1 hour. The resulting solution was diluted with water, and 3N NaOH aq and 30wt% H_2O_2 aq were carefully added. The mixture was stirred at room temperature for 2 hours. The reaction mixture was acidified with 1.0N HCl aq, and was extracted with diethyl ether. The combined ether extracts were washed with water and brine. The ether solution was dried over $MgSO_4$, and evaporated to yield a quantity of diol. It was dissolved in R-141b under N_2 and cooled using an ice-water bath. Triethylamine and methacryloyl chloride were added drop-wise to the solution and stirred at room temperature for 1 hour. The reaction mixture was acidified via HCl aq and added NaCl. The organic phase was separated from the aqueous phase and washed with saturated NaCl aqueous solution. It was dried over $MgSO_4$ and concentrated. The

residue was purified by silica gel column chromatography and recrystallized to obtain MANB1FVIP as a white solid.

2.1.2. Polymerization

The typical radical copolymerization procedure involving TFE and ethenic monomer is as follows. A 100-ml stainless-steel pressure vessel was charged with a solution of monomers, solvents, and initiator. The vessel was closed, purged with nitrogen, cooled, evacuated, and charged with TFE monomer. Radical copolymerization was carried out at 40°C over a period of 18-24 hrs. The polymer solution was poured into hexane, and was precipitated and washed by using a large excess of hexane. The resulting polymer powder was dried in vacuum. TFE/NB1FVIP and copolymer of TFE and 5,5,5-trifluoromethyl-4-hydroxy-4-(trifluoromethyl)pentene (TFE/BTB) were synthesized using the above procedure.

PNB1FVIP was prepared from NB1FVIP with *endo/exo* ratio of 10/90 and using a Pd catalyst in bulk or in solvent [15]. NB1FVIP was added to $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ under N_2 and dissolved in CH_3CN at room temperature. The heterogeneous mixture was stirred at room temperature for 6 hours. The resulting mixture was filtered and concentrated. The residue was dissolved in Ethyl acetate and poured into hexane. The resulting precipitate was filtered and dried in a vacuum to obtain a white powder.

Polymethacrylation of MANB1FVIP (PMANB1FVIP) was carried out at 60-70°C in N_2 with 20mol% 2,2'-azobis(isobutyronitrile) (AIBN) as the initiator in THF. The polymers were purified by precipitation in hexane and dried in a vacuum. The copolymers (AEC/AEH) of 2,4,4,5-tetrafluoro-2-trifluoromethyl-3-oxahex-5-enoic acid (AEC) and 2,3,3,5,6,6,8-heptafluoro-5,8-di(trifluoromethyl)-4-oxanon-9-ol (AEH) were synthesized using the same procedure.

2.2. Characterization

The polymer structures and compositions were determined from the NMR spectra. Namely, ^1H and ^{19}F NMR spectra were obtained at room temperature in acetone- d_6 or CDCl_3 on a Bruker AC-300P FT-NMR spectrometer. The polymer

structures were also confirmed by FT-IR spectra, which were captured by a PERKIN ELEMER 1760X FT-IR spectrometer.

The weight-average molecular weight (M_w) and number-average molecular weight (M_n) were determined by gel permeation chromatography (GPC, GPC-104 SHOWA DENKO K. K.) using refractive-index (RI) data.

UV measurements at 193 nm and 157 nm wavelength were performed using a VUV-VASE spectroscopic ellipsometer (J. A. Woollam Co., Inc.). Sample films were cast on a CaF_2 plate from solutions and baked at 110 °C for 90 seconds prior to measurements. Film thickness was measured by using an interferometer. All absorbance data reported are in the base 10.

Polymers and resists were etched in a Tokyo Electron, Ltd. UNITY II reactive ion etcher. The plasma etching gases were CF_4/O_2 as SiN hard mask condition. The etching rate was obtained from measured changes in thickness before and after the etching. A KrF resist (XP2332C, ROHM AND HAAS ELECTRONIC MATERIALS, LLC) was used as a standard material.

The dissolution behavior (i.e. the dissolution kinetics of the polymer film) during the development of the film was studied by a quartz crystal microbalance (QCM, Maxtek Model TM-400) in a fashion similar to a reported procedure [14]. The QCM instrumentation in a combination with a compensated phase-locked oscillator circuit can measure the changes in film mass and motional resistance simultaneously during the development. The developer used was a 0.262 N tetramethylammonium hydroxide (TMAH) aqueous solution (PD-523) supplied by Japan Synthetic Rubber Co., Ltd.

2.3. Lithography

Polymers were dissolved in casting solvent, and photo acid generator (PAG) was added. Triphenylsulfonium triflate (TPSTf), obtained from Midori Kagaku Co. Ltd., was used in this study as a standard onium PAG. The resist solution was filtered through a 0.2 μm membrane filter. Resist-formulation solvents used included 2-heptanone, propylene glycol methyl ether acetate (PGMEA), fluoroalcohol, and cyclohexanone. The resist solution was spin-coated onto silicon wafers treated with organic antireflective coatings.

Pre-application baking and post-exposure baking were carried out at 90-130°C, and the resist was developed. Contrast measurements were obtained from open-frame exposures. From these measurements the clearing dose for the resist was determined. Cross-sectional scanning electron micrographs were made using a Hitachi S-5000 scanning electron microscope.

3. Results and Discussion

3.1. Synthesis of monomer and polymer, and polymer characterization

Our approach toward the design of fluoropolymers for resist resin has been to employ an alicyclic HFA monomer, i.e. NB1FVIP. These polymers are generally transparent, solvent-soluble, and have a high glass-transition temperature (T_g). The alkaline-solubility depends on the acidities determined by the Fluoroalcohol group. Their properties improve adhesion to the substrate during the spin-coating process and wettability and solubility during the development

process. Copolymers with non-cyclic components, i.e. AEC/AEH and TFE/BTB, have comparatively low T_g . However, their higher fluorine atom content than alicyclic polymers yields the advantage of avoiding intermixing with the resist film and gained high contact angle.

Functional norbornene was prepared in 2 steps with 90% yield, as shown in Scheme 1. The cyclo-addition (Diels-Alder reaction) of cyclopentadiene with 2-fluoro-acryloyl fluoride was carried out in bulk at room temperature. The reaction proceeded smoothly. NB1FVIP was easily obtained by the reaction of **1** with 2 equivalents of trifluoromethyltrimethylsilane $\text{CF}_3\text{Si}(\text{CH}_3)_3$ in THF at room temperature. The ratio of endo/exo of isomer was 30/70 after distillation. While it is known that the Diels-Alder reaction of cyclopentadiene with α -fluoro-acrylate derivatives usually gives an exo-rich addition product, the Diels-Alder reaction of acrylate derivatives yields an endo-rich adduct [13].

Scheme 1

The TFE/NB1FVIP copolymers were easily synthesized in the solution of TFE and NB1FVIP with radical initiators in R-141b (Scheme 2). Standard copolymerization

conditions are shown in Table 1. The resulting copolymer was shown to exhibit alternate copolymerization based on F^{19} -NMR and a T_g of 130 °C.

Scheme 2

Table 1. Standard polymerization conditions

Polymerization temp.	40°C
Polymerization time	30hrs
Solvent	R-141b

PNB1FVIP was obtained by the metal-catalyze procedure using a Pd catalyst. This procedure was carried out at room temperature in bulk or in the presence of solvents; molecular weight and polydispersity were carefully controlled.

MANB1FVIP was obtained by the hydroboration of NB1FVIP and then esterification with methacryloyl chloride. The total yield was 20%, see Scheme 3.

Schem 3

This monomer was polymerized with AIBN and high yield of polymers were obtained. These polymers were found to have high Tg. All characteristic data of the polymers are displayed in

Table 2. The transparency of all polymers is excellent, noticeably those of PNB1FVIP and PMANB1FVIP at 193-nm wavelength which offers better than that of TFE/NB1FVIP.

Table 2. Characteristics of fluoropolymers

		Mw	Mn	Tg [°C]	abs. [μm ⁻¹]	
					193nm	157nm
	TFE/NB1FVIP	4000	3400	130	0.17	0.39
	PNB1FVIP	3900	3400	>150	<0.1	1.06
	PMANB1FVIP	3202	2528	>150	0.15	3.10
	TFE/BTB	2200	1700	106	<0.1	0.19
	AEC/AEH	75000	15000	79	<0.1	1.33

Furthermore, we found that the dry-etching resistance of PNB1FVIP and PMANB1FVIP was improved in previous developing polymers (Table 3). This result shows that both polymers can be used as resist base polymer for 193 nm lithography.

Table 3. Etching rate of fluoropolymers

	Ratio of monomer	etching rate [vs KrF resist]
TFE/NB1FVIP	50/50	2.0
PNB1FVIP	100	1.4
PMANB1FVIP	100	1.4
AEC/AEH	70/30	5.6

3.2. Dissolution behavior

The dissolution rates of the polymers in water, 0.262N and 0.065N TMAH were investigated using the QCM method as shown in Table 4.

Table 4. Dissolution rate and contact angle of fluoropolymers

	Ratio of monomer	Dissolution rate [nm/s]			Contact angle
		Water	0.065N TMAH	0.262N TMAH	
TFE/NB1FVIP	50/50	insoluble	4	890	77°
PNB1FVIP	100	↑	566	—	69°
PMANB1FVIP	100	↑	15	1588	75°
TFE/BTB	50/50	↑	—	892	70°
AEC/AEH	90/10	1252	—	1478	—
	70/30	insoluble	—	1400	76°
	60/40	↑	—	0.78	78°

PNB1FVIP and PMANB1FVIP have been shown to offer dissolution rates as high as those of TFE/NB1FVIP, though the molecular weights of the polymer (M_w) are almost the same. The reason for this is that the acidic group ratios (amount of acidic group/ M_w) in PNB1FVIP and PMANB1FVIP are higher than that of TFE/NB1FVIP. Figure 2 shows the dissolution rates of these polymers as a function of the

reciprocal of the molecular weight of the monomer (M_w^{-1} =amount of acidic group/ M_w).

Fig. 2. Dissolution rate of fluoropolymers in 0.065N TMAH vs M_w^{-1} of monomers

Moreover, we investigated the correlation between the dissolution rate and the M_w of PNB1FVIP. Figure 3 plots the dissolution rate of PNB1FVIP as measured by QCM in 0.065 N TMAH as a function of M_w . It is clear that M_w does not impact the dissolution rate of PNB1FVIP. This result agrees with those of previous works [16]. It also shows that the dissolution rate of fluoropolymers is determined by the content of the acidic function group rather than M_w .

Fig. 3. Dissolution rate of PNB1FVIP in 0.062N TMAH vs M_w

We found that TFE/BTB and AEC/AEH were water insoluble, that they dissolved in standard alkaline developer, and no exhibited swelling

(Table 4). Nevertheless, they had high contact angle ($\geq 70^\circ$). We suggested that TFE/BTB and AEC/AEH could be used as top-coats for 193-nm immersion lithography resists due to these results.

3.3. Lithograph performance

A preliminary formulation was made by dissolving a platform polymer (TFE/NB1FVIP) and TPS-PFOS in 2-heptanone (MAK). Figure 4 shows a scanning electron micrograph of 75 nm 1:1 line and space patterns printed in a resist using an ArF full-field scanner (Canon, FPA-5000AS3, NA 0.75) by using an alternating phase-shift mask. It is clear that dense 75-nm features could be precisely delineated with a 160 nm-thick film.

Fig. 4. Top and cross view of 75 nm 1:1 L/S, 193-nm exposure of a resist based on TFE/NB1FVIP. Conditions; FPA-5000AS3, NA 0.75, σ 0.3, substrate DUV30J(98nm)/300mm Si, 160nm film thickness, Alternating phase-shift mask, PB 110°C, 60 s, PEB 110°C, 90s, DEV 60s.

4. Conclusion

We demonstrated that the fluoropolymers made from HFA containing alicyclic monomers, i.e. TFE/NB1FVIP, could be used as resist resin in 193 nm lithography. We showed that these

fluoropolymers have the advantages of optical transmittance of $<0.2 \mu\text{m}^{-1}$ at 193 nm (wavelength), and high dissolution rates. We found that the dissolution rate of PNB1FVIP is independent of M_w . Preliminary trials showed that resists based on TFE/NB1FVIP can provide excellent lithographic performance in dense 75-nm patterns. Furthermore, we suggested that AEC/AEH and TFE/BTB could be used as top-coats for 193-nm immersion lithography resists due to their excellent dissolution behavior and high contact angle.

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