Novel Low Reflective Index Fluoropolymers based Top Anti-reflective Coatings (TARC) for 193-nm Lithography

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Implant lithography, which has up to now utilized 365-nm (i-line) and 248-nm (KrF) light sources, must now turn to 193-nm (ArF) sources. In implant lithography, an anti-reflective material is often used to coat the resist-film. The top anti-reflective coating (abbreviated to TARC) is most often used to reduce CD swing. TARC materials must have low refractive index and water solubility. The TARC materials for used 193-nm use must have very low reflective index and alternatives to perfluorooctylsulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) must be found. We synthesized some novel fluorinated amorphous polymers as 193-nm TARC candidates. Their fundamental properties were characterized, such as transparency and reflective index at 193-nm (wavelength) along with their solubility in water and a standard alkaline developer. High transparency, i.e., k value less than 0.01, and very low reflective index, i.e., lower than $n=1.4$ at 193-nm wavelength are confirmed. Their dissolution behaviors are studied using the Quartz Crystal Microbalance (QCM) method. In surprise finding, we find that several of the polymers examined, those that have high fluorine content, dissolved in water. Test results show that the proposed polymers can be applied as top anti reflective coatings.

Keywords: 193-nm lithography, implant lithography, resist, fluoropolymers, Quartz Crystal Microbalance (QCM), TARC (Top Anti-Reflective Coating), low reflective index, perfluorooctylsulfonic acid (PFOS), amorphous polymers perfluorooctylcalboxylic acid (PFOA).

1. Introduction

Fluoropolymers shows high transparency from a visible light domain to the domain of vacuum ultraviolet. This is because the absorption based on electronic changes of C-F bonds lies in the domain of vacuum ultraviolet, unlike C-H bonds. Fluoropolymers have long been thought of as one of the best approaches to achieving high transparency at shorter wavelengths, and particular attention has 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].

Our previous study on the dissolution behavior of fluoropolymers [9-12, 15, 16] showed their excellent characteristics. We have synthesized main-chain and side-chain fluorinated polymers using hexafluoropropanol (HFA) containing monomers and characterize their dissolution behavior. 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 the phenol group. Consequently, HFA containing polymer had small swelling and moderate dissolution speed.

Furthermore, a low refractive index appears to be characteristic of fluoropolymers. By the Lorentz-Lorenz formula (1), if the sum of atomic refraction is small and polymer density is low, the refractive index of polymer will be low.

$$n_D = (1 + 2[R]/V) / (1 - [R]/V)^{1/2} \quad (1)$$

n_D : Refractive index of polymer, $[R]$: The sum of atomic refraction, V : molecular volume ($=M/\rho$ M : monomer molecular weight and ρ : polymer density)

Unlike hydrogen or carbon, fluoride has a low atomic reflective index. By increasing the number of C-F bonds, while retraining the same main chain structure and polymer density, we can create a resin that has a low refractive index. The optical absorption bands of a fluoropolymers lie in the short wavelength side of the vacuum ultraviolet domain; their low refractive index is relative constant against wavelength from visible light up to the vacuum ultraviolet domain. We started development of new materials for TARC use based on these excellent characteristics. Conventionally, TARC material was the mixture of PFOS or PFOA and a water-soluble polymer. This approach, unfortunately, yields an inadequate refractive index and raises the problem of environmental damage. The need for a satisfactory alternative is urgent.

This paper introduces novel low reflective index fluoropolymers that are suitable as TARC materials. We synthesized novel fluorinated amorphous polymers, called trifluoroallyloxyether polymers, and characterize their fundamental properties, such as transparency and reflective index at 193-nm (wavelength), along with their dissolution behavior in water and 0.262N TMAH.

2. Experimental

2.1. Materials

All materials were obtained from commercial suppliers and used without further purification, unless otherwise noted.

2.1.1. Synthesis of monomer

Trifluoroallyloxyether monomers were prepared by the oligomerization of 2,2,3,3-tetrafluorooxetane and hexafluoropropyleneoxide as described in the literature [13] (Scheme 1). These monomers have a

unique; a combination of a functional group and a perfluoro ether moiety. A functional group is

Functional group	n	monomer name
COOH	0	AEC-0
	1	AEC-1
	2	AEC-2
CH ₂ OH	1	AEH-1
C(CF ₃) ₂ OH	0	AEHFIP-0

Scheme 1. Synthetic method of new trifluoroallyloxyether monomer.

convertible for carboxylic acid, alcohol, ester, etc. Moreover, fluoride content can be optimized by setting alkylchain length. In this paper, we chose three functional groups, carboxylic acid, alcohol, and hexafluoroalcohol (HFA). The carboxylic acid (called AEC) was easily prepared by hydrolyzed of corresponding ester. The alcohol (AEH) was prepared from the reduction and elimination fluoride and Iodine of 1. The HFA (AEHFIP) was directly 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.

[2,3,3,3-tetrafluoro-2-(1,1,2,3,3,3-hexafluoro-2-(1,1,2,3,3,3-hexafluoro-2-(1,1,2-trifluoroallyloxy)propoxy)propoxy)propanoic acid (AEC-2)]

Methyl

2,3,3,3-tetrafluoro-2-(1,1,2,3,3,3-hexafluoro-2-(1,1,2,3,3,3-hexafluoro-2-(1,1,2-trifluoroallyloxy)propoxy)propanoate was slowly dropped into 12N-NaOH aq at 0°C and stirred at room temperature for overnight. 50% H₂SO₄H aq was slowly dropped into the reaction mixture which was kept below 20°C. The reaction mixture was separated and collected under layer. The under layer was washed with water three times and n-hexane twice, evaporated to yield (92%) of AEC-2 as a colorless oil.

[1,1,1,3,4,4,4-heptafluoro-3-(1,1,2-trifluoroallyloxy)-2-(trifluoromethyl)butan-2-ol (AEHFIP-0)]

Methyl

2,3,3,3-tetrafluoro-2-(1,1,2,2-tetrafluoro-3-iodopropoxy)propanoate 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 50°C for 3 hours. Next, water and t-butylammoniumfluoride were added to the mixture and stirred at 50°C for 3 hours. 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 then brine. The ether solution was dried over MgSO₄, evaporated and distilled at 50°C at 5 mmHg to yield (50%) of AEHFIP-0 as a colorless oil.

2.1.2. Polymerization

The radical polymerization procedure was carried out at 10-30°C in N₂ with

[Polymerization conditions]

In bulk under nitrogen, Room temperature for 24 hr, Initiator; 1 mol % of (RfCOO)₂

Scheme 2. Polymerization of trifluoroaryloxyether

perfluoroalkylperoxide as the initiator in R-141b or in bulk [13]. The polymers were purified by precipitation in hexane and dried in a vacuum. The copolymers, i.e. poly(AEC/AEH), were synthesized using the same procedure. Standard copolymerization conditions are shown in (Scheme 2). The resulting copolymer was shown to exhibit alternate copolymerization based on F¹⁹-NMR.

2.2. Characterization

The polymer structures and compositions were determined from the NMR spectra. Namely, ¹H and ¹⁹F NMR spectra were obtained at room temperature in acetone-d₆ or CDCl₃ 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 wavelength were performed using a VUV-VASE spectroscopic ellipsometer (M-2000D, J. A. Woollam Co., Inc.). Sample films were cast on a CaF₂ 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 base 10.

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

3. Results and Discussion

3.1. Synthesis of monomer and polymer, and polymer characterization

Our approach to designing novel fluorinated amorphous polymers is to employ trifluoroalkoxyether monomer. These polymers are generally transparent, solvent-soluble, and have high alkaline-solubility. Their alkaline-solubility depends on the acidities set by the fluoroalcohol and carboxylic acid group. They demonstrate improve adhesion to the substrate during the spin-coating process and wettability and solubility during the development process. Their fluorine atom content, higher than that of side-chain fluorinated polymers, avoids intermixing with the resist film and yields the low reflective index. We prepared several homo- and co-polymers from the monomer with three kinds of functional groups. The data of the prepared polymers were shown in Table 1. All polymers were prepared with high yield (over 80%), and purification is simple to achieve by re-precipitation. Since all polymers have high enough molecular weights, they are well suited to forming thin films.

Polymer No.	monomer		comonomer		Ratio of monomer		F content (wt%)	Mn	Mw
	X	n	X	n	x	y			
1	COOH	0			100		52.0	57k	110k
2			CH ₂ OH	1	30	70	58.9	17k	26k
3					50	50	56.3	17k	26k
4					55	45	56.8	17k	28k
5					60	40	55.4	22k	40k
6			COOH	2	50	50	56.7	52k	92k
7					60	40	55.8	ND	ND
8					70	30	54.8	ND	ND
9			C(CF ₃) ₂ OH	0	50	50	58.7	12k	17k
10					40	60	60.0	12k	17k
11	COOH	1			100		58.5	29k	42k
12	C(CF ₃) ₂ OH	0			100		65.3	65k	76k

Table 1. Composition of prepared polymers

3.2. Dissolution behavior

The dissolution rates of the polymers in water and 0.262N TMAH were investigated using the QCM method as shown in Table 2.

Polymer No.	Dissolution rates (nm/s)		pH
	water	0.264N TMAH	
1	>1000	>1000	1.4
2	insoluble	70	
3	swelling	79	
4	slitry soluble	>1000	
5	56	>1000	2.0
6	insoluble		
7	swelling	140	
8	320	>1000	1.7
9	insoluble	>1000	
10	120	>1000	
11	soluble		2.1
12	insoluble	360	

Table 2. Dissolution behaviors of fluoropolymers

All polymers very rapidly dissolved in standard developer. In a surprise finding, we found that several polymers that had high fluorine content dissolved in water. The polymer containing AEC showed a low pH value when in aqueous solution. It is known that the pH of a TARC material influence the performance of the resist form, and low pH values are better. These excellent dissolution characteristics suggest that fluoropolymers are usable as TARC materials. Furthermore, these polymers also dissolved very well in alcohols, esters, ketones, and ethers. The vinylidene structure of the main chain and the perfluoropolyether structure of a side chain contribute to this characteristic [13]. We found that our prepared polymers could be dissolved in a solvent that does not affect the resist, coating on the resist, and then removed by the water rinse or the standard developing solution.

3.3. Optical propaties

TARC materials must have low refractive indices. All trifluoroaryloxyether polymers showed low reflective index and absorbance at 248-nm and 193-nm wavelength (Table 3). The homopolymer of AEC-0 and some copolymers of AEC-0 and AEC-2, AEH-1 or AEHFIP-0 were showed less than n=1.5 at 193-nm even though they were water soluble. A key finding is that the homopolymer of AEHFIP-0 demonstrated a very low reflective

index, $n=1.39$, at 193-nm. We are now pushing the development of these polymers as TARC materials.

Polymer No.	reflective index		k	
	@248nm	@193nm	@248nm	@193nm
1	1.43	1.46	>0.001	>0.001
3	1.41	1.44	>0.001	>0.001
5	1.41	1.44	>0.001	>0.001
8	1.40	1.44	>0.001	0.003
9	1.41	1.44	>0.001	>0.001
10	1.41	1.44	>0.001	>0.001
11		1.42		>0.001
12	1.37	1.39	>0.001	>0.001

Table 3. Optical properties of fluoropolymers

4. Conclusion

We prepared novel fluorinated amorphous polymers, trifluoroaryloxyether polymers, and investigated their chemical and optical properties. We demonstrated that these fluoropolymers could be used as TARC materials for 193-nm lithography due to their excellent dissolution behavior and optical properties. We showed that these fluoropolymers have the advantages of excellent optical transmittance, k value <0.01 at 193 nm (wavelength), and a water-soluble and low refractive index, i.e. less than $n=1.4$. They offer excellent potential as TARC materials.

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