

Synthesis and Solubility Study of the Polyamides Containing 4,4'-(9-fluorenylidene)dianiline in the Backbone as an Antireflecting Spin-on Hardmask Materials

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Abstract

Due to the continuous demand for smaller microelectronic devices, there exists a need to reduce the size of structural shapes in microelectronics and other related industries. Toward this end, effective lithographic techniques are essential to achieve a reduction in the size of microelectronic structures. Typical lithographic processes involve etch resistant photoresist underlying materials having antireflecting properties at a certain wavelength exposure.

In this work, such materials were synthesized by the step-polymerization of diamines 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FP) and 4,4'-(9-fluorenylidene)dianiline (BAFL) with a variety of diacid chlorides [terephthaloyl, isophthaloyl, glutaryl, and succinyl chlorides] and characterized by ¹H NMR in tetrahydrofuran (THF-d₈), and gel permeation chromatography (GPC) using polystyrene standards. The effect of the structure of the components on the copolymer solubility in mixture of propylene glycol monoethylether acetate (PGMEA) and cyclohexanone used in microelectronics processing was studied by UV-visible spectroscopy. The solubility of the copolymers was found to be in trade-off relationship with BAFL content needed for its antireflective properties and high plasma etch resistance. The polymers that were prepared by using the equimolar mixture of isophthaloyl dichloride and glutaryl dichloride equimolar mixture showed the best solubility, processability and functionality and are applicable as spin-on antireflecting hardmask materials for deep ultra violet (DUV) lithography technology. They showed good coatibility, chemical resistance, plasma etch resistance, and plasma etch selectivity.

Introduction

Microlithography at 193 nm using an ArF excimer laser as the deep UV exposure tool is essential for most semiconductor devices with feature sizes lower than 65 nm. Current technology utilizes a series of multi-layered steps of photoresist layers, back antireflective coatings (BARC), and plasma etch-resistant hardmasks. To reduce the cost of this process, several research groups in 2001 proposed the development of a single polymer-based spin-on hard mask which would combine the features of the BARC and the etch-resistant hard mask [1,2]. This material would need to have excellent deep UV absorbing ability (at 193 nm), high etch selectivity, the ability

to withstand plasma etch processes and transfer the exact pattern to the substrate.

Many of high-performance materials employ high aromatic-content polymers with ester, amide or imide linkages. While they have high melting points and glass transition temperatures, they have limited solubility, especially in non-polar solvents. This limits their utility. To improve the polymer's solubility, a variety of techniques have been used such as: (1) a two-step polycondensation using a soluble precursor which is commonly used technique in polyimide processing [3,4]; (2) co-polymerization with fluorine-containing monomers [3,5,6,8]; and (3) incorporation of flexible linkages, bulky pendant groups, and asymmetric structures into the polymer structure [3,5,7,9].

In this work, we combined two different amines, 4,4'-(9-fluorenylidene)dianiline (BAFL) and 2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FP), with four different diacid chlorides, two of

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which are aromatic-based and the other two are aliphatic based. BAFL was selected to give the final polymer its desired functionality. BAFL is known for its absorption properties at 193 nm as well as its high etch resistance. Unfortunately, because of its rigid structure, polymers based on BAFL typically exhibit low solubility in propylene glycol monoethyl-ether acetate (PGMEA), a common solvent used in semiconductor processing. To solve this problem, 6FP was selected as a co-monomer to increase the final polymer's processibility. The bulky trifluoromethyl groups usually favor formation of irregularly structured polymers with high free volume. 6FP has been reported to provide good solubility for some poly(hydroxyl)amides even after cyclodehydration [8].

Typically, use of dianhydrides is unfavorable due to the high content of acidic groups in the resulting polymer. These acidic protons can migrate into the photoresist layer and cause undercut defects after development in tetramethyl ammonium hydroxide (TMAH). In addition, carboxyl groups are known to contribute to poor polymer stability under dry etch conditions. Therefore, diacid chlorides were employed for polycondensation with the amines. The solubility of the synthesized polymers was examined as a function of the solutions transparency vs. solvent composition.

Experimental

Reagents and Solvents

2,2'-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FP), >98% was obtained from TCI. 4,4'-(9-fluorenylidene)dianiline (BAFL), 99% was supplied by Osaka Gas Co., Japan. Terephthaloyl chloride, 99%; isophthaloyl dichloride, 99%; glutaryl dichloride, 97%; succinyl chloride, 95% were purchased from Aldrich. All the monomers were stored in desiccators over anhydrous calcium chloride to prevent moisture absorption and used without further purification.

N,N-Dimethylacetamide (DMAc) (Mallinckrodt ChromAR, 99.9%), propylene glycol monoethyl ether acetate (PGMEA), and cyclohexanone (Anon) (Kanto Chemical CO., Inc., 99%) were used as received.

Polymer Synthesis

Novel polyamides were synthesized by the condensation polymerization of 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (6FP) and 4,4'-(9-

fluorenylidene)dianiline (BAFL) taken in various molar ratios, with four different diacid dichlorides: terephthalic, isophthalic, glutaryl and succinyl, alone or in a combination. Molecular structures of the initial monomers are given in Fig. 1.

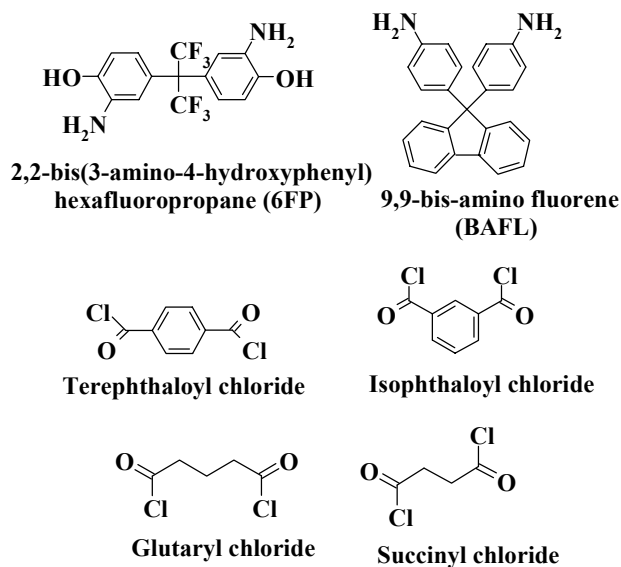


Fig. 1. Molecular structure of the monomers.

Molar ratio between the amines and the diacid dichlorides in feed was 0.9:1.0 or 0.8:1, respectively. Aniline was used as an end-capping agent, and Pyridine was added in order to scavenge the by-product of the polycondensation, HCl. Total solid content of the solution was 15 wt.%. Reaction was carried out in N,N-Dimethylacetamide (DMAc) at 4°C in a jacket reactor. The cool temperature was maintained by a water circulator. The typical recipe was as follow:

- To a 250 ml round bottom jacket reactor charged with a mechanical stirrer, nitrogen inlet and a thermometer, 6FP (2.64 g, 7.2 mmol) and BAFL (3.76 g, 10.8 mmol) were loaded and dissolved in 86.09 g of DMAc.
- Pyridine was added in amount of 6.33 g, 80.0 mmol.
- The mixture was stirred for 30 min. As the solution in the reactor reached 4°C, Isophthaloyl chloride (2.84 g, 14.00 mmol) and Glutaryl chloride (1.01 g, 6.0 mmol) were dissolved in 10.00 g of DMAc prior adding into the reaction mixture.
- The polymerization was allowed to proceed for 4 hours.
- The products were purified by precipitation in water, methanol or diethyl ether depending on polymer composition. The procedure was repeated twice.

- The resulted precipitates were dried at room temperature under vacuum for 24 hours and kept in a desiccator over dry CaCl₂ for further experiments.

Characterization

Yield was measured as polymer weight after purification to sum of all monomers taken for polymerization, expressed in weight percentage. Molecular weight of the polymers was characterized by GPC Waters 510 system, integrated with a Waters 515 high-pressure liquid chromatography pump, a Waters 717 autosampler, column Shodex LF804, and a Waters 2414 R₁ detector. H¹ NMR study was performed on Bruker AC 200/50 (Germany) in THF-d₈.

Solubility was observed on Perkin-Elmer Lambda-950 UV/visible spectrometer. For that 4 ml of 5 wt.% solution of each polymers in cyclohexanone were prepared. PGMEA was gradually added, and the solution was well stirred for 1 minute. Transparency of the solutions was measured at 600 nm using a quartz cell.

The solutions of the polymers for coating were formulated with the common commercial melamine-type cross-linker Powder Link 1174 and p-toluene sulfate monohydrate in PGMEA-cyclohexanone = 70:30 vol.% mixed solvent, with the resulting solid content 10 wt.%, as we described previously in Ref. [10].

Spin-coating was performed on Mikasa, IH-DX2 machine (Japan) in a three-step mode. The coated wafers were baked at 215°C for 60 seconds to yield a well-cross-linked polymer layer. The measurements of optical properties like refractive index *n*, extinction coefficient *k*, and film thickness have been carried out by using a VB-400 J.A.Woollam Ellipsometer. The topography of the interface was examined by atomic force microscopy (AFM) XE-300P (Park Science Co., Korea).

Results and Discussion

Polymer Synthesis and Characterization

Different combinations of two diamines – 6FP and BAFL, and four dicarboxylic acid dichlorides – terephthaloyl, isophthaloyl, glutaryl and succinyl, were employed as monomers at low-temperature solution polycondensation reaction. The synthesis was designed in three series (see Table 1 *a-c*) with one variable parameter in each. In the first series, the two diamines were premixed in different molar ratio giving in sum 0.9 mol, and copolycondensation with one mol of isophthaloyl dichloride was performed (Table 1 *a*). In the second series, the two diamines (0.8 mol in sum) were taken at constant mol ratio as [6FP]:[BAFL] = 40:60, and diacid dichlorides (1 mol) were varied (Table 1 *b*). Aniline was complimentary added as end-capping agent. Third series described in Table 1 *c*, was designed to study the influence of a flexible linkage between aromatic rings represented by glutaryl (Table 1 *c-1*) and succinyl (Table 1 *c-2*) chlorides on the copolymer solubility. The monomer ratio, yield, and some molecular characteristics of the resulted polymers are given in Table 1.

As it is seen from Table 1*a*, the yield, molecular weight and polydispersity of the final polymers increases with the BAFL content in feed. The value of Mw of the copolymers varied in the 11300-18300 range, and polydispersity exceeded 2.5 approaching 3.0. These characteristics are not favorable for solubility and good film forming properties such as smooth uniform surface coating and further performance. Therefore an end-capping agent, aniline, was used in subsequent syntheses to control molecular weight and narrow polydispersity [8]. With the addition of aniline, molecular weight and polydispersity decreased without a loss in polymer yield (Table 1 *b-c*).

Table 1
Synthesis conditions of 6FP/BAFL – Diacid chloride copolymers

a) Copolymers varied by [6FL]:[BAFL] ratio in feed. [Amines]:[Isophthaloyl dichloride] = 0.9:1 mol/mol						
Polymer code	Amino monomers, mol		Yield, wt. %	Mn	Mw	Polydispersity
	6FP	BAFL				
1	0.3	0.7	97.94	6195	18300	2.95
2	0.4	0.6	93.84	5895	17100	2.90
3	0.5	0.5	80.11	5640	15700	2.78
4	0.6	0.4	77.41	4425	11300	2.56

Table 1
Continued

<i>b)</i> Copolymerization of [6FP]:[BAFL] = 0.4:0.6 mol/mol with different diacid dichlorides. [Amines]:[Diacid dichloride] = 0.9:1 mol/mol; [Aniline] = 0.2 mol					
Polymer code	Diacid dichloride	Yield, wt. %	Mn	Mw	Polydispersity
5	Terephthaloyl	92.22	3500	5500	1.57
6	Isophthaloyl	89.10	2760	4950	1.79
7	Glutaryl	72.19	1594	3000	1.89
8	Succinyl	79.29	5200	9700	1.86
<i>c)</i> The copolymers of [6FP]:[BAFL] = 0.4:0.6 mol/mol with two acid chlorides mixed in different ratio. [Amines]:[Diacid dichloride] = 0.9:1 mol/mol; [Aniline] = 0.2 mol					
<i>c-1)</i> Isophthaloyl chloride:glutaryl chloride series					
Polymer code	Acid chlorides ratio in feed		Mn	Mw	Polydispersity
	Isophthaloyl chloride, mol	Glutaryl chloride, mol			
6*	1.0	0.0	2760	4950	1.79
9	0.9	0.1	2800	5150	1.84
10	0.8	0.2	2860	5350	1.87
11	0.6	0.4	3120	5900	1.89
12	0.5	0.5	4140	7800	1.88
13	0.2	0.8	2040	3800	1.87
14	0.1	0.9	1876	3700	1.97
7*	0.0	1.0	1594	3000	1.89
<i>c-2)</i> Isophthaloyl chloride:succinyl chloride series					
Polymer code	Acid chlorides ratio in feed		Mn	Mw	Polydispersity
	Isophthaloyl chloride, mol	Succinyl chloride, mol			
6*	1.0	0.0	2800	5150	1.84
15	0.8	0.2	3040	6300	2.09
16	0.5	0.5	4200	8450	2.01
17	0.2	0.8	6280	11800	1.88
8*	0.0	1.0	5200	9700	1.86

* see Table 1-b).

As seen from Table 1 *b*, in the second series, yield and molecular weight of the terephthaloyl chloride-composed polymer was higher than that of the isophthaloyl dichloride-based polymer; the succinyl moiety containing polymer yielded in a greater amount than the glutaryl-based ones, and molecular weight of the glutaryl-based polymers was the highest among whole series.

In the systems of mixed aromatic-aliphatic diacid dichlorides, maximum molecular weight of the resulted copolymer comes at 40:60 mol.% ratio of isophthaloyl-glutaryl chlorides, and when the molar ratio of isophthaloyl-succinyl chlorides mixture is 20:80 (Table 1 *c-1,2*). This result may be due to a difference in reactivity of the diacid dichlorides, and their different affinity to the solvents.

¹H NMR Characterization

The ¹H NMR spectra of the copolymers were taken in THF-d₈. Common for all the copolymers, the intense multi-peak signal between 7.8 and 8.4 ppm was assigned to the aromatic protons. The signals in vicinity of 9.6 ppm were attributed to –NH group of amide bond, and –OH group of 6FP monomer overlapped. The copolymers comprising glutaryl and succinyl moieties revealed intensive peaks at 2.6–2.9 ppm region assigned to the aliphatic protons.

At ¹H NMR spectrum of the copolymer composed of isophthaloyl and glutaryl/succinyl chlorides, both aromatic and aliphatic peaks were found in the corresponding ppm regions. However, the intensity of all the peaks was lower than that of single diacid dichloride polymer.

UV-vis Spectrophotometric Study of the Copolymer Solubility

5 wt.% polymers solutions were prepared in cyclohexanone. PGMEA was added gradually, and transparency of the resulted solution was measured on UV-vis spectrophotometer at 600 nm. Above a critical PGMEA volume percent, the transparency of the solution dramatically decreases. This is due to conformational transition of the macromolecules which transforms the polymer into an insoluble state. Graphs "Transparency as a function of Anon:PGMEA mixed solvent composition" were plotted (Figs. 2, 3). Solubility of the copolymers was judged by PGMEA content at the inflection point of the curve.

Surprisingly, the solubility of copolymers of the same composition is independent on their molecular weight when varied in the range 3700–17100. The inflection point only oscillates within a 1–2 wt.% of PGMEA content in the mixture with Anon (data not shown). Therefore, this parameter was disregarded in further discussion.

As it was expected, solubility of the polyamides synthesized in the first series, significantly worsened as BAFL content in feed increased (Fig. 2). Indeed, PGMEA content at the inflection point dropped from ~75 to 38 vol.% as the concentration of BAFL increased from 40 to 70 mol.% in the feed.

Therefore, in order to keep a higher BAFL content, we attempted to balance the polymer solubility by varying the structure of the other component – diacid dichlorides. Thus, the polymerization was performed with isophthaloyl, glutaryl, and succinyl

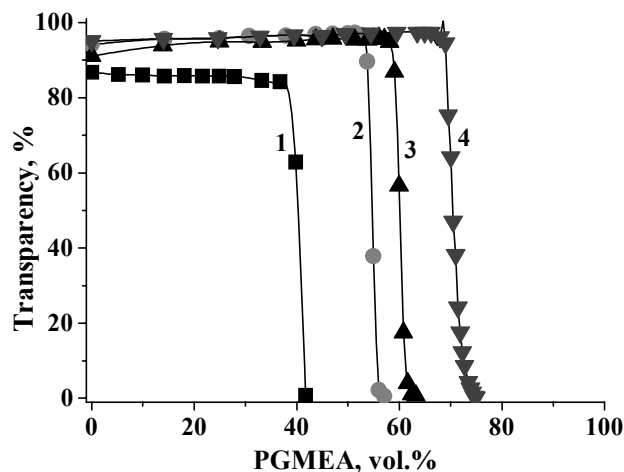


Fig. 2. Effect of [6FP]:[BAFL] ratio on the solubility of the afforded polymers in PGMEA–Anon mixture. The curve number corresponds to the polymer code in Table 1 *a*.

chlorides, in addition to terephthaloyl chloride used in the first series. The polymer synthesis was summarized above in Table 1 *b*. There, amino-monomers ratio in feed was kept constant as [6FP]:[BAFL] = 40:60 mol.%. The transparency curves were plotted against PGMEA content in the mixed solvent (Fig. 3). It should be noticed, that the copolymers of terephthaloyl and isophthaloyl chlorides give colorless solutions while glutaryl chloride-based samples were of yellowish brown color, and succinyl-containing samples were of more intensive rose-color. Although that affected initial transparency, giving a value significantly lower than 100%, estimation of the critical composition of PGMEA:Anon mixed solvent was still possible.

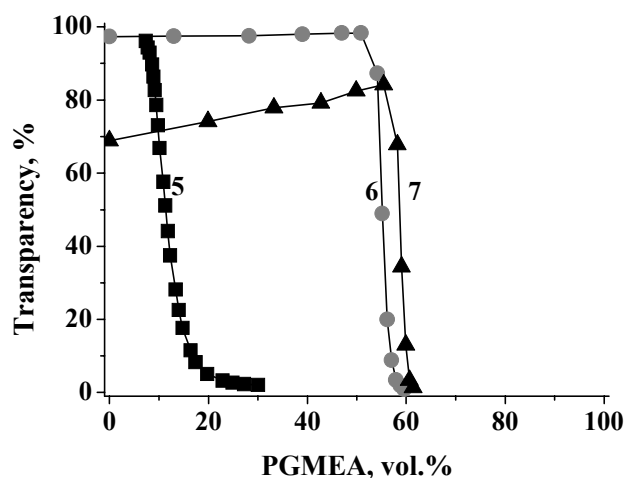


Fig. 3. Effect of diacid dichloride type on solubility of the afforded polymers in PGMEA–Anon mixture. The curve number corresponds to the polymer code in Table 1 *b*.

The terephthaloyl chloride based copolymers revealed poor solubility, while the copolymers of isophthaloyl chloride exhibited much better affinity to the mixed solvent. As seen from Figure 3, the terephthaloyl chloride based polymers precipitate with just 10 vol.% PGMEA (curve 5), while the isophthaloyl chloride ones precipitated at 55 vol.% PGMEA (curve 6). The meta-isomeric orientation seems to provide more flexibility to the resulting macromolecules. These results are in agreement with previously reported data, where para-type poly(ester-imide)s were semicrystalline and showed poor solubility [3].

As reported in Ref. [7], aliphatic segments with $>CH_2$ number 5-12, when incorporated into a polymer chain, increase polymer crystallinity. Therefore, we have chosen alkyl spacers of shorter lengths in order to make polymer chains more flexible but with a low potential to crystallize. Shorter spacers are also believed to have less effect on etch resistance of the polymers. Our data also seem to be consistent with their findings. Copolymerization with glutaryl chloride resulted in the best soluble copolymers remaining soluble up to 60 wt.% PGMEA, while use of succinyl chloride afforded a polymer totally insoluble even in 100% cyclohexanone, however did find this polymer well-soluble in THF and DMAc.

Although use of the single glutaryl chloride showed the best result, we require the final polymer to have solubility greater than 70 vol.% PGMEA. Therefore, 6FP and BAFL were copolymerized with isophthaloyl chloride/glutaryl chloride or isophthaloyl chloride/succinyl chloride mixture taken in different ratios, as described in Table 1 *c*. As in the previous experiments, solubility of the copolymers was characterized by maximum PGMEA at which the copolymer solutions remain transparent. The dependence of this parameter on the amount of the aliphatic acid chloride in feed was plotted (Fig. 4). Between 0.0-0.2 mol of the aliphatic component does not cause a significant influence on the copolymer solubility. However, in vicinity of equimolecular amount (0.4-0.6 mol) of the acid dichlorides in feed, succinyl moiety containing polymers exhibited lower solubility, while glutaryl dichloride based ones showed maximum solubility.

The observed phenomenon is not fully understood and requires further investigations. We hypothesize that there is a dual effect of the alkyl bridges incorporated along the aromatic chain. On the one hand, it may decrease rigidity and thus, promote solubility. On the other hand, it may provoke chain folding

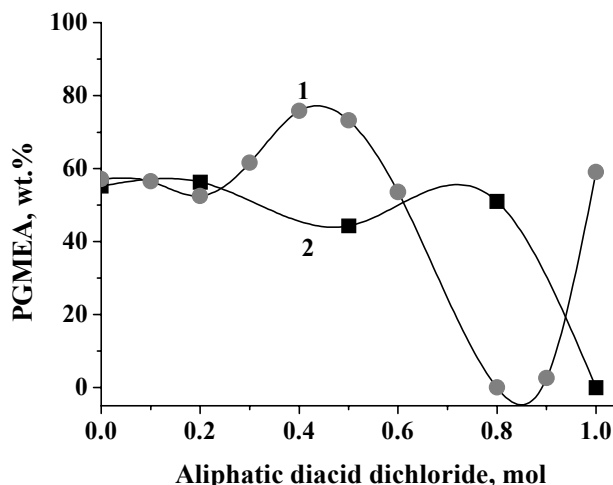


Fig. 4. Dependence of solubility of the poly(hydroxy amides) on the aliphatic acid content. 1 – the glutaryl chloride based copolymers (Table 1 *c-1*); 2 – the succinyl chloride based copolymers (Table 1 *c-2*).

and increase crystallinity of the copolymers that worsens solubility. Depending on interaction of these two factors, the solubility improves or deteriorates. Another reason may lay in odd and even number of methylene groups in alkyl bridges along the highly aromatic polyamides, and consequently, peculiarity rotation around the aliphatic bonds.

Nevertheless, the copolyamides containing alkyl units along the aromatic chain, coded as 11 and 12 in Table 1 *c-1* are soluble in PGMEA up to 75 vol.%. Their performance as spin-on hardmask was tested and is described in the following section.

Application Tests

The polymers 11 and 12 exhibiting best solubility in PGMEA:Anon = 70:30 vol.% solution were mixed with a cross-linker and a catalyst in accordance with the coating recipe developed in our lab for spin-on hardmask application [10]. The formulation was then spin-coated on a silicon nitride wafer, and baked at 215°C for 60 seconds. The resulted thickness measured on the elipsometer was 3650 Å for the polymer 11, and 4030 Å for the polymer 12. The polymer coatings were found to be resistant to tetramethyl ammonium chloride (TMAH) solution, a commonly used developer in memory chip production, giving difference in thickness before and after the treatment less than 10 Å. The coating surface roughness was characterized by AFM method showing well-acceptable *Rq* parameter 310 and 316 pm for the polymers 11 and 12 correspondently, as for example shown in Fig. 5.

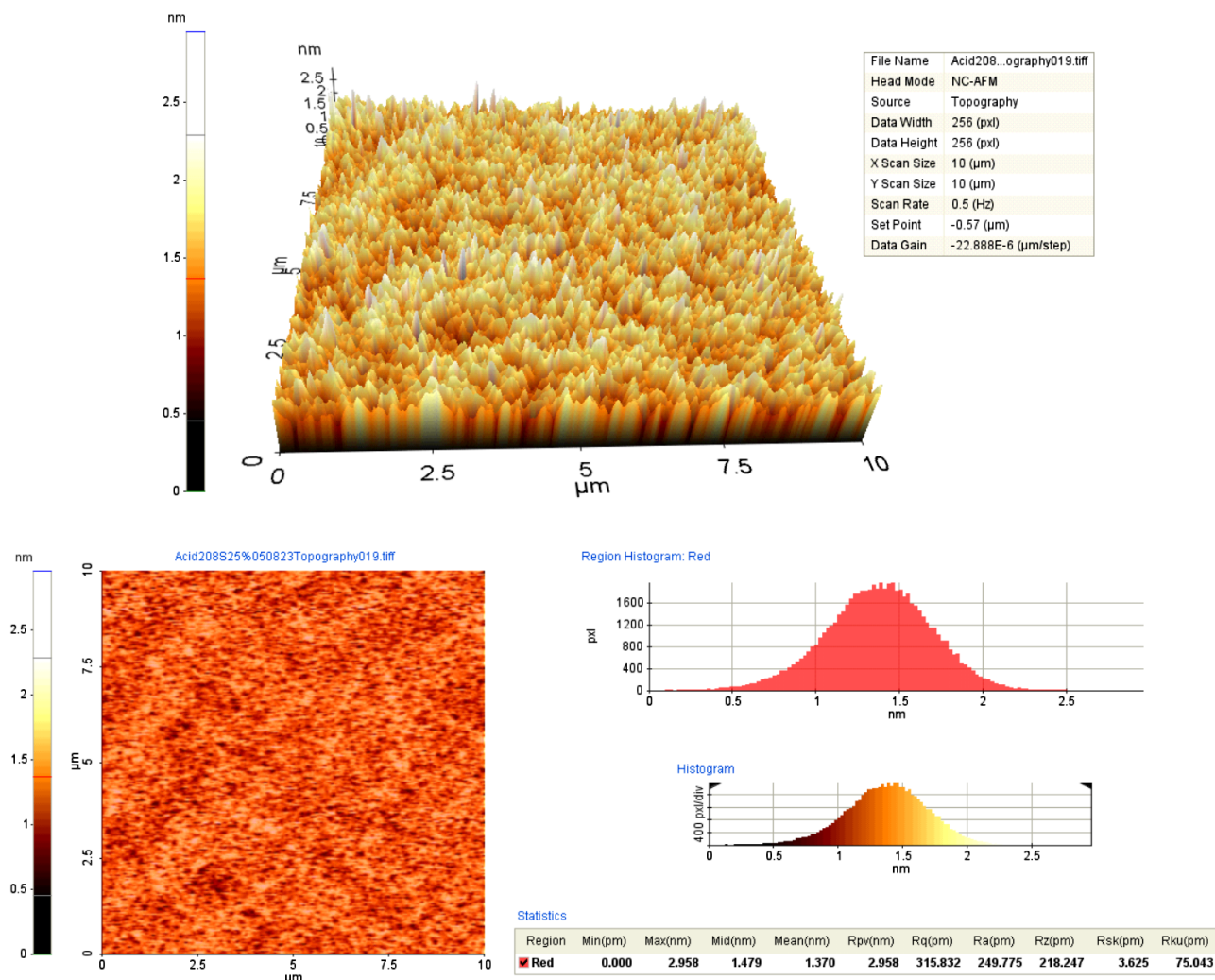


Figure 5. AFM image and characteristics of the coating surface for the polymer 11.

For the purposes of our research we were most interested in determining extinction coefficient, k that is directly related to the absorption of a material and can be obtained from the ellipsometry data. Figure 6 presents the dependence of the extinction coefficient k on wavelength starting from 190 nm for the copoly(hydroxy amides) differed by composition. As one can see, curves 6 and 11, which stand for the polymers with BAFL content 0.6 mol are almost coincided in the short wavelength region, but differ from curve 4, which stands for the polymer with the lower BAFL content, disregarding presence of the alkyl bridges. In particular, k value of the samples at 193 nm was 0.56, 0.54, and 0.47 correspondently.

The preliminary dry etching tests were conducted using the same coated samples. A photoresist for ArF was coated on the film, baked at 110°C for 60 seconds, light-exposed using an exposure system manufactured by ASML (XT:1400, NA 0.93), and devel-

oped with tetramethylammonium hydroxide (TMAH) (2.38 wt.% aqueous solution). A vertical profile pat-

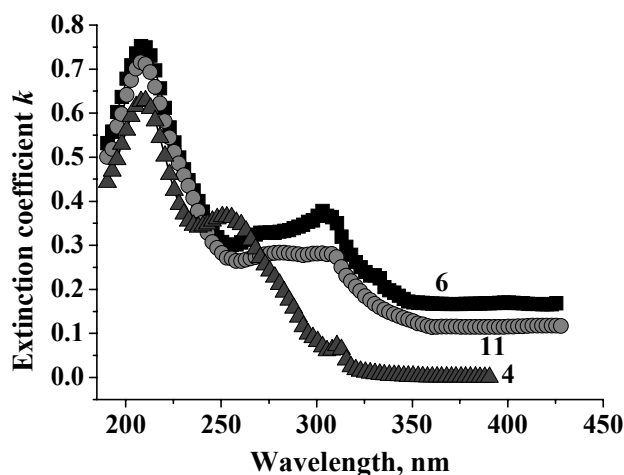


Fig. 6. Ellipsometry data. The curve number corresponds to the polymer code in Table 1 *a-c*.

terned images were observed using scanning electronic microscopy.

The patterned specimens were dry-etched using a mixed gas of CHF_3/CF_4 , and further dry-etched using a mixed gas of BCl_3/Cl_2 . Finally, all remaining organic materials were removed using O_2 , and a cross section of the specimens was observed using an FE SEM. A difference in thickness of the coated layer before and after the etching test was determined, from which an etching rate was computed per minute, and it was 98 nm/min. According to these results, the copolymers are very promising antireflecting spin-on hardmask materials for use in semiconductor processing, and are now under further investigation.

Conclusions

In the present study, the copolymerization of BAFL and 6FP with four diacid dichlorides was performed. The solubility of the polymers in Anon: PGMEA mixed solvent was dependent on the ratio between the diamines: the higher BAFL content, the worse solubility. Comparing effect of terephthaloyl and isophthaloyl chlorides, it was found that the isomeric structure is more favorable for better solubility, than the para-substitution. As to the aliphatic diacid dichlorides, the sequence of three methylene groups also provided good solubility, while " $-\text{CH}_2-\text{CH}_2-$ " bridges affected opposite. Combination of isophthaloyl and glutaryl chlorides in equimolar ratio afforded the best soluble polymers. Those could endure PGMEA up to 75 vol.% what is appropriate for use as a spin-

on hardmask in semiconductor processing. The polymers demonstrated high-performance in terms of coatability, strip-resistance, surface roughness, and optical parameters at 193 nm.

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Received 12 September 2006.