Alternatives to Chemical Amplification for 193 nm Lithography

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ABSTRACT

Research has been conducted to develop alternatives to chemically amplified 193 nm photoresist materials that will be able to achieve the requirements associated with sub-32 nm device technology. New as well as older photoresist design concepts for non-chemically amplified 193 nm photoresists that have the potential to enable improvements in line edge roughness while maintaining adequate sensitivity, base solubility, and dry etch resistance for high volume manufacturing are being explored. The particular platforms that have been explored in this work include dissolution inhibitor photoresist systems, chain scissioning polymers, and photoresist systems based on polymers incorporating formyloxyphenyl functional groups. In studies of two-component acidic polymer/dissolution inhibitor systems, it was found that compositions using ortho-nitrobenzyl cholate (NBC) as the dissolution inhibitor and poly norbornene hexafluoro alcohol (PNBHFA) as the base resin are capable of printing 90 nm dense line/space patterns upon exposure to a 193 nm laser. Studies of chain scission enhancement in methylmethacrylate copolymers showed that incorporating small amounts of absorptive a-cleavage monomers significantly enhanced sensitivity with an acceptable increase in absorbance at 193 nm. Specifically, it was found that adding 3 mol% of α-methyl styrene (α-MS) reduced the dose to clear of PMMA-based resist from 1400 mJ/cm^2 to 420 mJ/cm^2. Preliminary data are also presented on a direct photoreactive design concept based on the photo-Fries reaction of formyloxyphenyl functional groups in acrylic copolymers.

Keywords: norbornene hexa fluoro alcohol, *ortho*-nitrobenzyl cholate, α-methyl styrene, formyloxyphenyl, photo-Fries

1. INTRODUCTION

Chemically amplified (CA) resists based on acrylate copolymers possess high sensitivity, high etch resistance, high thermal stability, and base solubility but will suffer from low resolution and poor line edge roughness (LER) when considered for sub-32 nm application. Given the absolute need for both resolution and feature quality in sub-32 nm resist systems, concession can be made only in sensitivity.

Specific resist performance criteria for candidate resist systems include a desired resist thickness less than 80 nm (single layer, linked to 2:1 to 3.5:1 aspect ratio, unexposed actinic absorption less than 6 μm^{-1}, resolution using 193 nm interferometric lithography (IL) for pitch values from 70 to 90 nm (where a pitch of 88 nm corresponds to the double patterning period for a 22 nm half-pitch: 22–32 nm), and desired low frequency line width roughness (LWR) < 8% of the critical dimension (1.3 to 1.8 nm 3σ).

Previous work on each approach that we took, as well as the way their results were interpreted for this research is reviewed below.

1.1 Dissolution Inhibitor Approach

A two-component resist system generated by blending transparent, alkaline soluble base resins with dissolution inhibitors has been one of the main goals of this research. Three transparent resin matrices studied are: 1) copolymer of methyl methacrylate (MMA) and methacrylic acid (MAA), 2) cycloolefin–maleic anhydride polymers with acrylic acid (AA) moieties, and 3) norbornene hexafluoroalcohol (NBHFA) type homopolymers (PNBHFA). The dissolution inhibitors that were blended with base soluble resins were *ortho*-nitrobenzyl cholate (NBC) and DNQ-5.

During the early 1980s, *ortho*-nitrobenzyl cholate and its derivatives studied extensively by Reichmanis et al. at Bell Labs were shown to provide good resolution for deep ultraviolet (DUV) lithography [1]. Its chemical structure and the photochemical change upon radiation are shown in Figure 1.

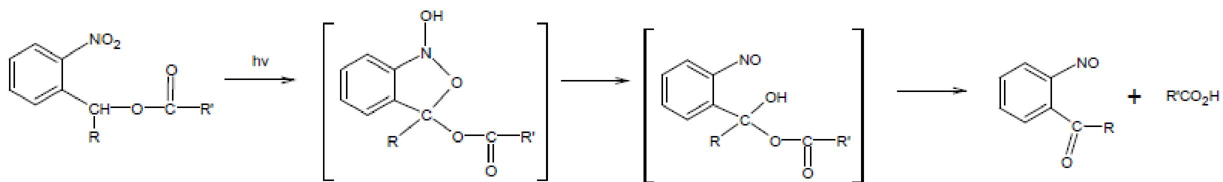


Figure 1.Photochemical reaction of cholate upon radiation [1].

During the late 1990s, Houlihan and coworkers studied the terpolymer of norbornene (NB), maleic anhydride (MA) and acrylic acid (AA), known as poly(NB/MA/AA), for 193 nm and 248 nm lithography systems. Tertiary-butyl cholates (a chemically amplified version of cholate ester) were blended with poly(NB/MA/AA) polymer at different acrylic acid concentrations. Using this terpolymer, Houlihan, et al. were able to leverage chemical amplification kinetics to print a 0.27 µm line/space pattern with good photosensitivity (9 mJ/cm^2) [2].

In the present study, the poly(NB/MA/AA) base polymer described by Houlihan et al. blended with NBC was briefly explored. During 193 nm open frame studies for contrast curve calculations, the composite film exhibited severe cracking, peeling, and non-uniform dissolution characteristics. Another problem with this system was variable dissolution behavior. It was found from dark loss studies (done for 50 nm thick resist films) that sitting on the shelf (under ambient laboratory conditions) for 48 hours causes significant variation in the dissolution behavior of the P(NB/MA/AA) system. One might speculate that this variability is a result of hydration/hydrolysis of the maleic anhydride moiety in the copolymer. Accordingly, studies of the P(NB/MA/AA) system were terminated.

Another dissolution inhibitor that was studied was poly(1-pentene-sulfone) (PPS). In the absence of specific enthalpic driving forces (H-bonding, acid/base interactions, etc.), polymer pairs are rarely miscible. Thus, it was not particularly surprising that PPS blends with acrylate polymers suffer from phase separation. The extent of phase separation was found to increase as the prebake temperature and acid content in acrylate copolymer increased.

Since it was first proposed by Ito, et al. [3] in 1997, the use of the hexafluoroisopropanol (HFA) group as the acidic moiety in an alkaline developable polymer system has received a great deal of attention. Replacing carboxylic acid with HFA offers several advantages such as high optical transparency, reduction of swelling, good lithographic performance [4], etc. The endo/exo ratio in PNBHFA was shown to have a big impact on the dissolution kinetics [5]. From their imaging studies, Ito and coworkers showed that higher resolution was achieved for exo-enriched PNBHFA. They were also able to print dense features with a 120 nm half-pitch by using PNBHFA as a contrast enhancer for a conventional resist material. These studies, as well as studies by Chambers et al. [6], motivated us to use PNBHFA as another candidate for the dissolution inhibitor approach.

1.2 Chain Scissioning Enhancement Approach

Chain scissioning acrylate polymers possess low sensitivity, low etch resistance and some degree of base solubility but have shown excellent resolution and LER for sub-32 nm application. Poly (methyl methacrylate) (PMMA) has been used for decades as a photopolymer for ionizing radiation as well as DUV (190-250nm) exposure. DUV exposure presents an interesting situation as it is the transition between photochemistry and radiation chemistry, where photon energy coincides with both material absorption bands and energy in excess of C-C binding energy. Exposure to ionizing or DUV radiation thus cleaves the C-C bond adjacent to the carbonyl (α-fission) followed by rearrangement and backbone

scissioning in what is known as a "Norrish-type I" process. This process is not efficient in PMMA, with a scission yield (Gs) of ~1.3, resulting sensitivity in the 1–4 J/cm^2 range at DUV wavelengths.

The goal of this part of the project has been to explore whether a chain scission resist system could be created that would meet the requirements of sub-32 nm lithography. Previous work had been done with several co-polymerizations including poly(fluorobutyl methacrylate) [7] and glycidyl methacrylate with methyl methacrylate [8]. We have explored the use of α-MS together with other components, including t-butyl methacrylate (TBMA) and 1-Adamantyl methacrylate (ADMA).

1.3 Photoresists Based on Polymers Containing Formyloxyphenyl Functionality

The utility of poly[*p*-(formyloxy)styrene], prepared by chemical modification of poly(p-hydroxystyrene) and free radical polymerization of the corresponding monomer as a positive 248 nm resist was first reported in the early 1980s by Frechet, et al. [9]. As direct photocleaved, non-chemically amplified resists, polymers bearing formyloxybenzene functional groups are advantageous because of their relative low absorbance and high quantum yield for conversion to phenolic functionality. As a 248 nm resist, poly[*p*-(formyloxy)styrene] was shown to exhibit high contrast and high resolution images.

In the design of 193 nm photoresist compositions based on the photo-Fries reaction of copolymers containing formyloxyphenyl functional groups, acrylic copolymer systems were synthesized. As an extension to the acrylic system, norbornenyl based monomers can be used to achieve high resistance to plasma etch. This polymer can be derived through the polymerization of norbornene, norbornenyl hexafluoroisopropanol, and norbornenyl phenyl formate. The generic structures of the two target polymers are shown in Figure 2.

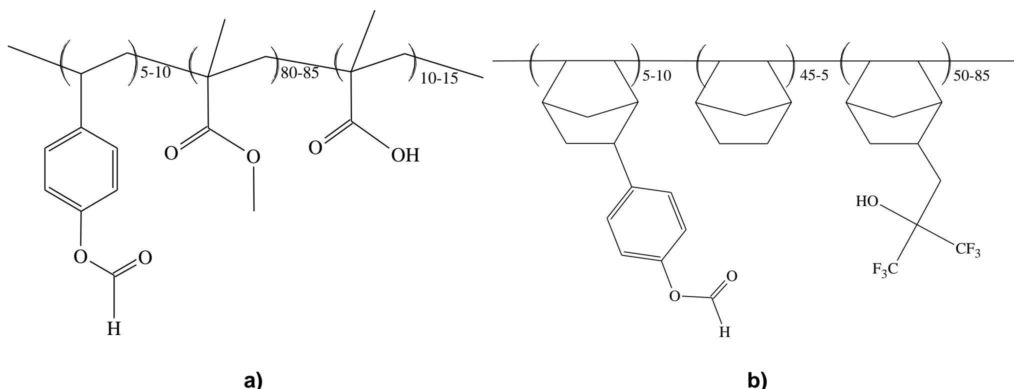


Figure 2. a) Acrylic system polymers and b) Norbornenyl system polymers.

2. EXPERIMENTAL

2.1 Materials for Dissolution Inhibitor Studies

Nitrobenzyl cholate: *ortho*-nitrobenzyl cholate was synthesized from 2-nitrobenzyl bromide and cholic acid in accordance with a procedure reported by Chandross, et al. [10].

Diazonaphthoquinone sulfonate: DNQ-5 was donated by AZ Electronic Materials.

P(MMA-MAA) copolymers: Copolymers of MMA and MAA were prepared by free-radical polymerization of methylmethacrylate and methacrylic acid in isopropanol initiated with AIBN (0.1% by weight, based on monomer) in a process analogous to that reported by Kiatkamjornwong and Tessiri [11]. Monomers were obtained from Sigma Aldrich and were used as received without removing the inhibitor. Polymers were isolated by precipitation twice in hexane and drying *in vacuo* at 100°C.

Poly(norbornenyl hexafluoroalcohol): PNBHFA was donated by Promerus LLC (Brecksville OH).

P(NB/MA/AA): Poly(Norbornene/Maleic Anhydride/Acrylic Acid) (1/0.9/0.1) molar, (M_w = 64k, polydispersity = 3.4) was synthesized using a procedure analogous to that is published by Wallow, et al. [12].

2.2 Materials for Chain Scissioning Studies

Table 1 lists the composition, molecular weight, and polydispersity of various polymers used in the present study to enhance chain scissioning in methylmethacrylate copolymers. All polymers were by prepared by free-radical polymerization in solution (ethyl acetate/isopropyl alcohol) initiating with AIBN (1 wt% or 0.5 wt% with respect to monomer). All the polymers were isolated and purified by precipitation in hexanes and centrifuged to isolate solid polymers, which were subsequently air-dried. Styrene-equivalent molecular weights were obtained by standard gel permeation chromatography, eluting with tetrahydrofuran over an Agilent trimodal S column set with a 0.5–1000K molecular weight range. Copolymer compositions given in Table 1 are the molar composition of the monomers. NMR analysis indicated that polymer compositions were nominally identical to the monomer charge ratio.

Table 1. Composition, M_w and poly dispersity of the polymers synthesized for chain scissioning studies.

Polymer composition	Mw	Polydispersity
PMMA	79k	2.7
P (MMA- αMEST) (97/3) molar	77k	2.7
P (MMA-MAA) (85/15) molar	105k	2.0
P(MMA-MAA- αMEST) (78/15/ 7) molar	30k	2.1
P(MMA-TBMA-MAA- αMEST) (39/39/15/ 7) molar	44k	2.4
P(ADMA-TBMA-MAA- αMEST) (39/39/15/ 7) molar	70k	2.4
P(ADMA-MMA-TBMA-MAA- αMEST) (20/19/39/15/ 7) molar	44k	2.0

2.3 Synthesis of Polymers Containing Formyloxyphenyl Functional Groups

2.3.1 Hydrolysis and formylation of acetoxystyrene (*Base-catalyzed hydrolysis of acetoxystyrene)*

4-Acetoxystyrene (96%) was purchased from the Aldrich Chemical Co. *p*-hydroxystyrene was prepared by hydrolysis of acetoxystyrene, adapting the historic procedure of Corson, et al. [13]. Thus, 26.5 g of *p*-acetoxystyrene doped with 0.025 g of N,N-dimethyl-4-nitrosoaniline was cooled to 0°C and diluted with an aqueous solution of 23 g of KOH in 232.5 ml of water. To suppress free-radical polymerization, N,N-dimethynitrosoanliane was added, and the reaction mixture was purged with air. After 3–4 hours at 0°C, the reaction mixture was neutralized (i.e., "blown down" to pH~8 with CO_2). The neutralized reaction mixture was exhaustively extracted with aliquots of diethyl ether and concentrated *in vacuo* to afford a quantitative yield monomeric p-hydroxystyrene.

2.3.2 Synthesis of formyloxystyrene (FOxS)

Formyloxystyrene was synthesized by esterification of p-hydroxystyrene with formic acid/acetic anhydride (formic acid (99%) and acetic anhydride (>98%), Aldrich Chemical Co). Thus, 83.4 g of acetic anhydride was cooled to 0°C and 37.6 g of formic acid was slowly added and stirred over about 30 minutes. This cold mixture was slowly added to a flask containing a solution of 16 g of p-hydroxystyrene in diethyl ether, stabilized with a trace of N,N-dimethyl-4-nitrosoaniline, 99% (Acros Organics). The system was blanketed with air and the reaction mixture was allowed to warm to room temperature and was stirred for four days at ambient temperature. Hydrolysis with water and exhaustive extraction with aliquots of diethyl ether yielded a solution from which FOxS was isolated by removal of the solvent and distillation (40–60°C) in vacuo (yield ~78%).

2.3.3 Synthesis of formyloxystyrene copolymers

FOxS was free-radically copolymerized with methylmethacrylate (MMA) and methacrylic acid (MAA) in solution (ethyl acetate) initiating with AIBN (1 wt% or 0.5 wt% with respect to monomer) in sealed Carius tubes from which air had been removed by standard freeze-thaw steps. All the polymers were isolated and purified by precipitation in hexanes, and centrifugation to isolate solid polymers which were subsequently air-dried. Copolymers whose nominal molar

composition is (5/85/10), (10/80/10), (5/75/20), (10/70/20) and (15/65/20) (FOxS/MMA/MAA), respectively, were synthesized.

3. RESULTS AND DISCUSSIONS

3.1 Results on Dissolution Inhibitor Study

3.1.1 Optical characterization of resist materials

To make two component photoresist prototypes, polymers were dissolved in conventional solvents (cyclopentanone, cyclohexanone, etc.) at a concentration of 3–5 solid% by weight, and the solutions were blended with dissolution inhibitors (20% by weight with respect to the polymer weight). The solutions were filtered, twice through 0.45 µm syringe filters.

Absorbance spectra of the blended resist materials were measured on a Perkin-Elmer Lambda 11 UV-VIS spectrometer down to 190 nm as shown in Figure 3. At equivalent loadings, nitrobenzyl cholate blends are 50% less absorptive than DNQ-5 composites.

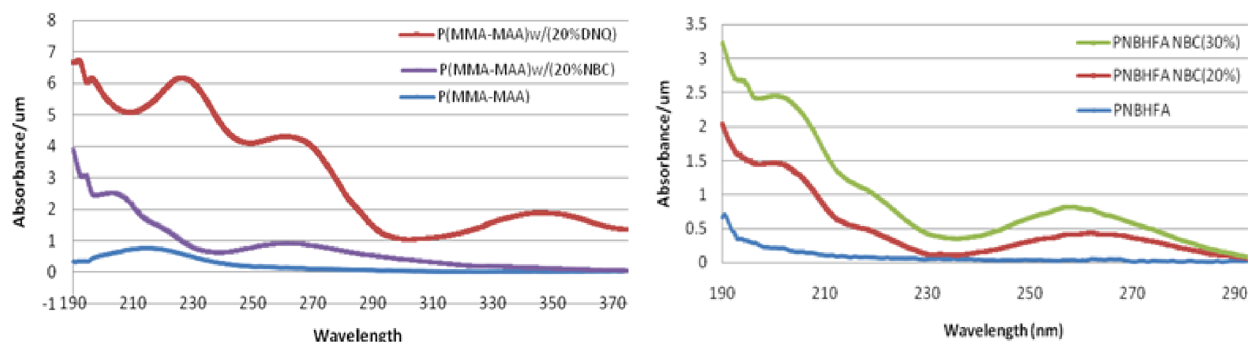


Figure 3. Absorbance spectra of acrylate copolymer and PNBHFA compositions with and without dissolution inhibitor.

3.1.2 Dark Loss Study

In the design of a viable photoresist system, development conditions should not cause a significant loss of resist thickness in the unexposed regions while effectively delineating the image in the exposed regions. P(MMA-co-MAA) (65:35) and (70:30) copolymers, the control formulations without dissolution inhibitor, were found to be extremely soluble in even a very weak alkaline developer (weak developer: pH approximately 8).

The copolymer with 15% acid [(MMA:MAA) of (85:15)] was less soluble in alkaline solutions. Using a developer comprised of 10% aqueous Na_2CO_3, pH ~12, there is no dark loss after thin films of the 15% acid copolymer underwent 15 sec of immersion followed by 30 sec of water rinse. However, a small amount of swelling was seen.

The dissolution behavior in an aqueous base of polymers bearing hexafluoroisopropanol (HFA) functionality was studied by Ito, et al. Poly(norbornene hexafluoroisopropanol) (PNBHFA) was reported to dissolve in aqueous 0.26N tetramethylammonium hydroxide (TMAH) at a rate that was not correlated with its molecular weight. Dissolution behavior in 0.21N TMAH, was found to be complex, involving swelling and a gel layer formation. Figure 4 shows the results of the present dark loss studies on PNBHFA and blends incorporating 20 and 30 wt% NBC, in which different dilutions of TMAH were used as the developer. Development time was kept to 15 sec, followed by a 15-sec water rinse to generate the results in Figure 4a. The homopolymer itself is extremely soluble, even in a diluted developer (0.19N, and 0.13N TMAH); however, blends of PNBHFA with NBC exhibit slower dissolution rates. As reported in the study by Ito et al., dissolution in diluted solutions of TMAH is non-linear.

Figure 4b shows the normalized remaining thickness of unexposed PNBHFA loaded with 20% NBC. Development time was varied from 10 sec to 60 sec for 0.26, 0.19, and 0.13N TMAH solutions. There is almost no dark loss, even after a 60-sec immersion in 0.13N TMAH.

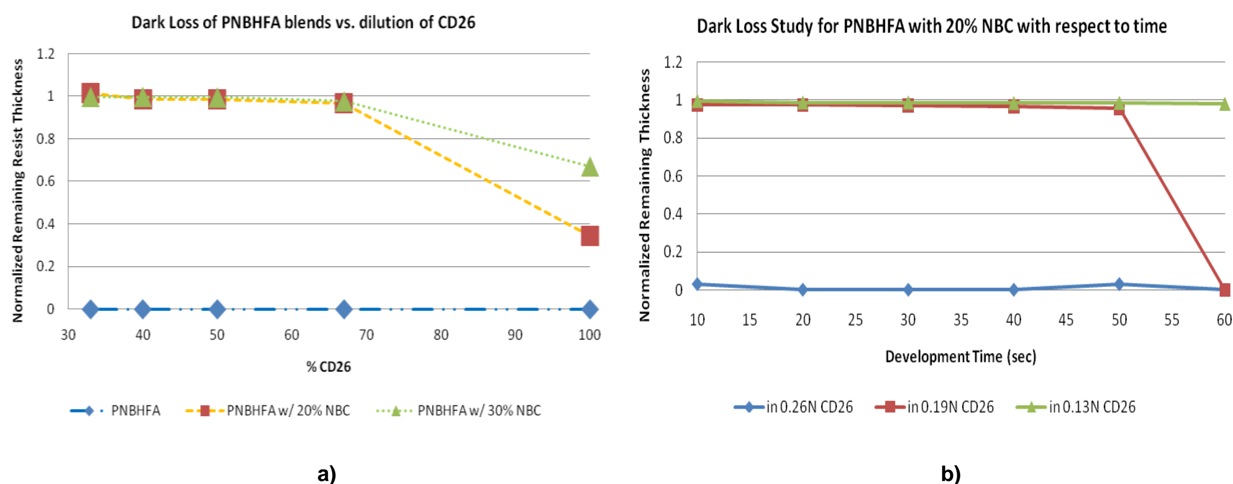


Figure 4. a) Effect of developer strength on unexposed PNBHFA and its DI blends and b) Normalized remaining thickness for PNBHFA with 20% NBC vs. development time in three different developers.

3.1.3 Imaging Results

The ArF imaging results for P(MMA-co-MAA) shown in Figures 5a and 5b correspond to the solution loaded with 20% NBC, whereas Figure 5c is the imaging result for copolymer with no inhibitor. The results are consistent with different mechanisms of imaging. Without dissolution inhibitor, differential solubility results from chain scission. However, while the sensitivity of P(MMA-co-MAA) is comparable to that reported in the literature for PMMA, developed contrast for the copolymer is minimal. When blended with NBC, the photospeed of the P(MMA-co-MAA)/NBC composite is dramatically enhanced (250 mJ/cm^2 vs. 500 mJ/cm^2). The contrast of the image is also greatly improved. However, the developed contrast of the blended acrylic copolymer is insufficient for sub-32 nm lithography.

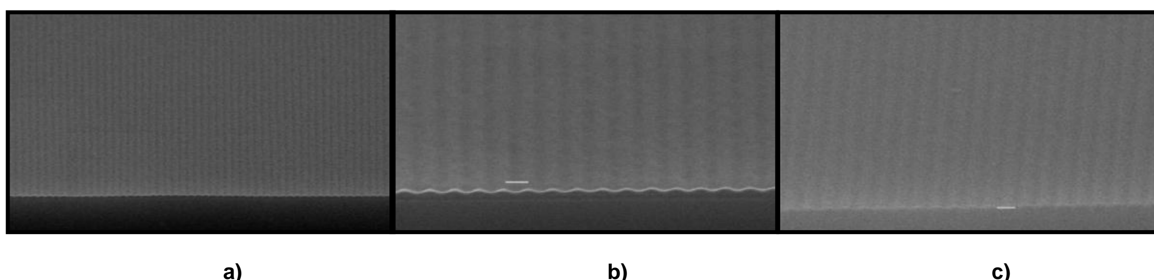
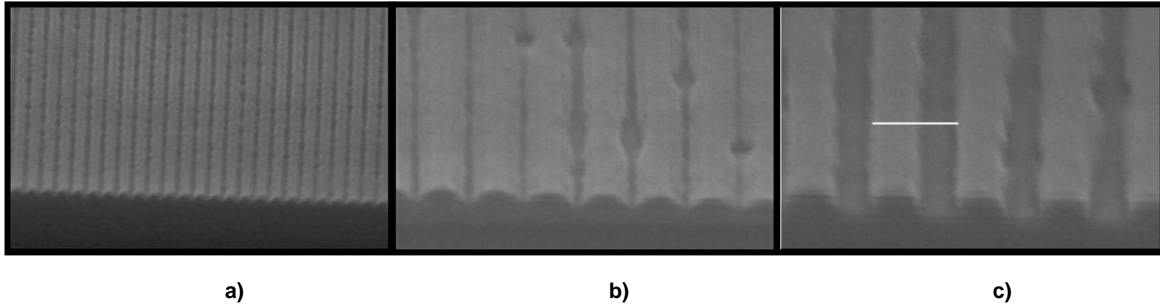


Figure 5. a) and b) show SEM images depicting modulation for 20% NBC loaded acrylate copolymer (exposure around 250 mJ/cm^2), c) SEM image showing modulation for polymer with no inhibitor (exposure around 500 mJ/cm^2).

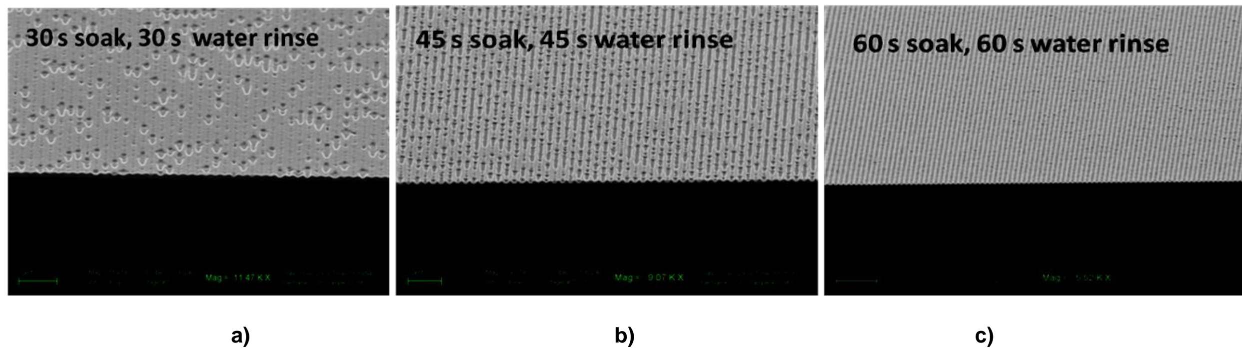
Imaging results on PNBHFA blends were more promising. Several images are shown in Figure 6. They were taken from different parts of the same die of 20% NBC-loaded PNBHFA film exposed at 230 mJ/cm^2. The development time was 45 sec in 0.13N TMAH, followed by a 15-sec water rinse. Further work to optimize the developer composition and development conditions is needed to better assess the resolution limit of this new two-component resist system.



a) b) c)

Figure 6. SEM images of 150 nm half-pitch, 1:1 pattern exposed at 230 mJ/cm^2 using a 193 nm laser.

A development study was done to study the effect of development time on image quality. The developer is again 0.13N TMAH. 20% NBC-loaded PNBHFA film was exposed at 193 nm and developed for 30 sec followed by a 30-sec water rinse, 45 sec followed by a 45-sec rinse and 60 sec followed by a 60-sec rinse. The SEM images corresponding to the three cases are shown in Figure 7. The conclusion from this study is that the development conditions play a significant role in imaging quality of PNBHHFA systems.



a) b) c)

Figure 7. SEM images of 120 nm half pitch, 1:1 pattern, showing effect of development conditions.

The imaging studies at 90 nm half pitch were repeated for the 30% NBC-loaded PNBHFA; the results are shown in Figure 8. The developer was 0.20N TMAH. The development time was kept at 5 sec, followed by a 30-sec water rinse. The resist was 80 nm thick.

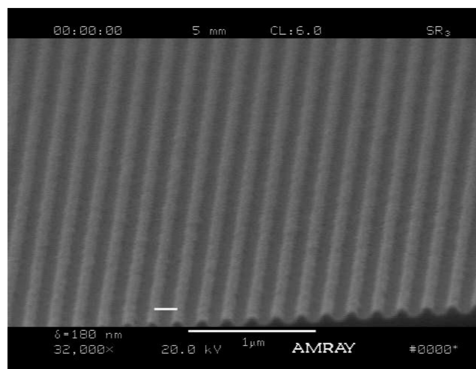


Figure 8. SEM image of 90 nm line/space pattern exposed at 300 mJ/cm^2.

3.2 Results of the Chain Scissioning Enhancement Study

3.2.1 Improvement in Sensitivity of PMMA

PMMA homopolymer and copolymers with 1% and 3% of α-MS were synthesized as described in the experimental section. Optical absorbance spectra of PMMA and α-MS incorporated polymer were calculated for DUV wavelengths. By incorporating 3% α-MS into PMMA, the 193 nm absorption dramatically increased (up to 3.7 /µm). This was an early suggestion of the increase in scission efficiency.

Figure 9 shows the contrast curves calculated for PMMA and PMMA with 3% α-MS for comparable molecular weights. It shows that PMMA with 3% α-MS has a higher sensitivity than PMMA for both ~50 nm and ~100 nm thick resist. Higher contrast is achieved for thinner films of PMMA containing α-MS. The difference in contrast due to resist thickness is not drastic in the PMMA homopolymer resist.

Figure 10 shows the effect of molecular weight and film thicknesses on contrast for PMMA containing 3% α-MS. At comparable resist thicknesses, it was found that copolymers with smaller M_w exhibit slightly higher contrast.

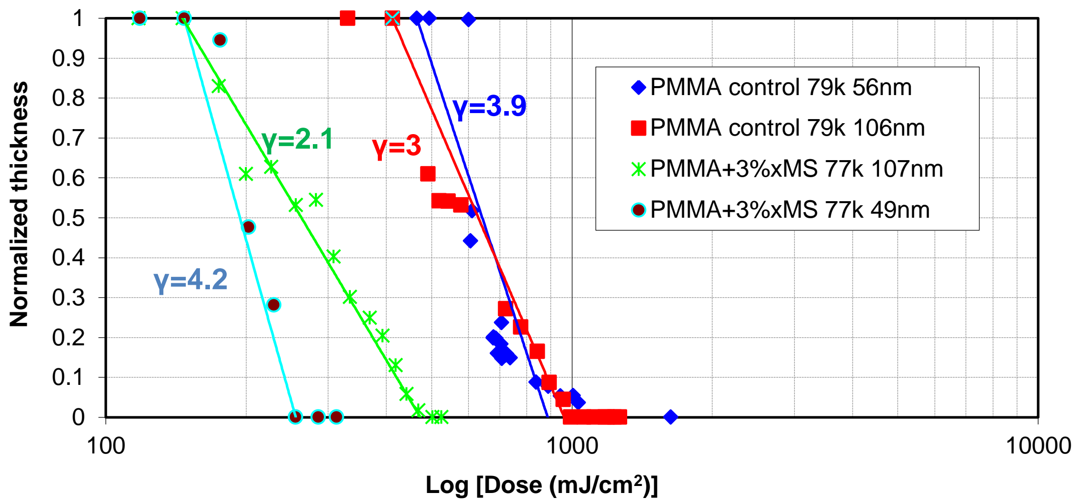


Figure 9. Contrast curves for PMMA and PMMA with 3% α-MS, comparable molecular weight, and different film thickness.

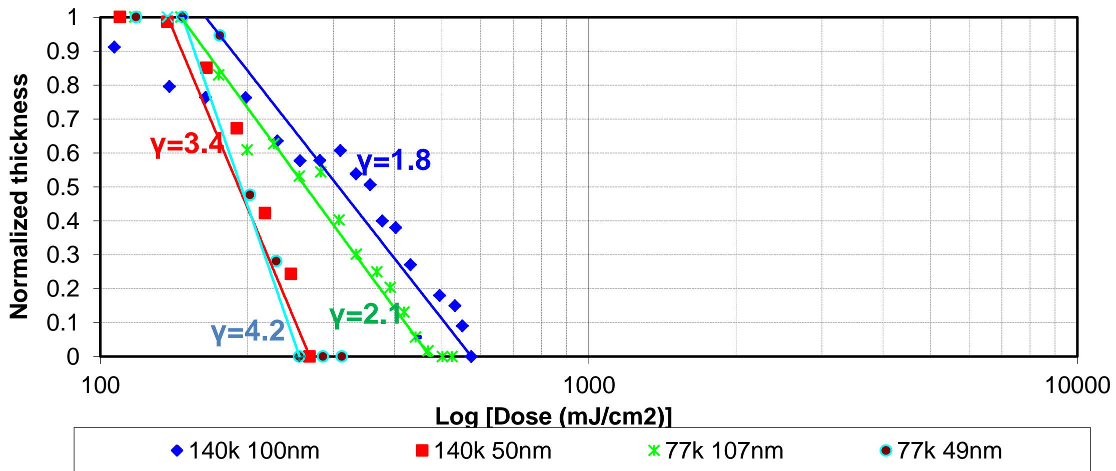


Figure 10. Contrast curve for PMMA with 3% α-MS, showing effect of different molecular weights and film thicknesses.

Contrast curves were also obtained for 45 nm films of the four-component polymer P(MMA-TBMA-MAA-αMS) (39:39:15:7). Aqueous sodium bicarbonate and sodium hydroxide solutions were used as developers. The results showed that the sensitivity of this polymer is 107 mJ/cm^2. In sodium bicarbonate, the contrast of is about 1.9.

P(ADMA-TBMA-MAA-αMS) resist was also spin-coated on HMDS-primed Si wafers to yield ~100 nm thick films. After exposure and development, the film peeled in both exposed and unexposed regions. While this was an indication of an adhesion problem, areas exposed at high doses did not dissolve even in strong base. This can be explained by increased the molecular weight and cross-linking of exposed films of copolymers containing the adamantyl group, as shown in Figure 11.

3.2.2 Improvement on Chain-Scission Efficiency

The polymer films described in Table 1 were irradiated by 193 nm laser. Figure 11 shows the normalized molecular weight change upon irradiation at various doses. From this plot, it is clear that derivatives with 7 mol% α-MS give higher chain-scission efficiency than P(MMA-MAA) copolymer. Incorporating t-butylmethacrylate into the polymer increased chain-scission efficiency slightly. At low doses, chain-scissioning predominates in the copolymer containing ADMA. However, as the exposure dose increases, cross-linking predominates and overcomes the impact of chain-scissioning.

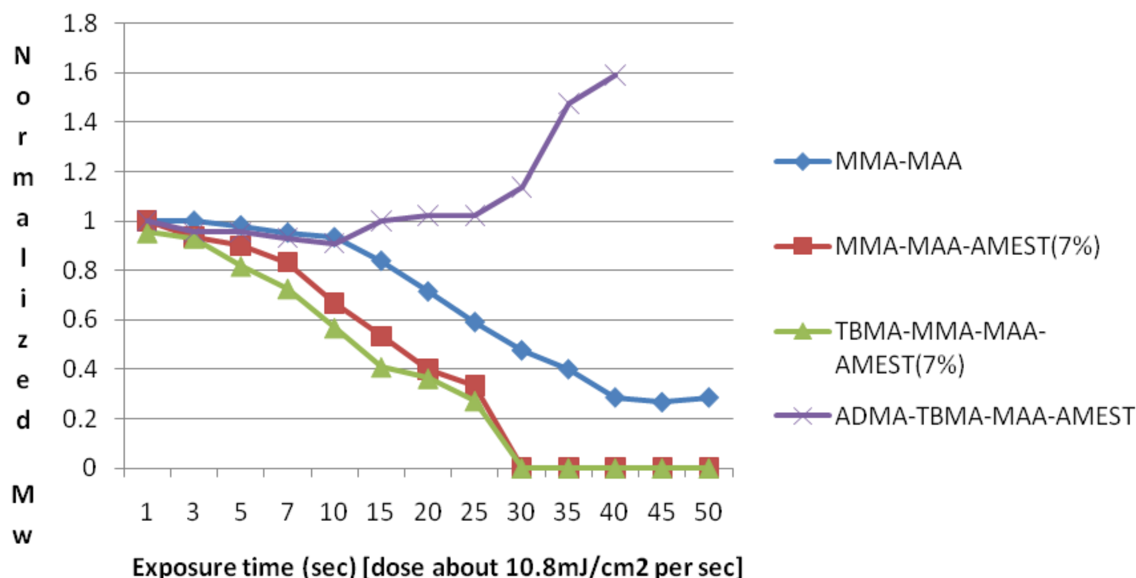


Figure 11. Chain-scission efficiency study on polymers of Table 1.

3.3 Photoresists Based on Polymers with Formyloxyphenyl Functionality

Three potential routes for the synthesis of acrylic copolymers containing the formyloxystyrene functional groups are outlined in Figure 12. The hydrolysis pathway involving the synthesis and copolymerization of formyloxystyrene is the one that has proven to be the most fruitful route. Acid catalyzed trans-esterification is likely to be plagued by cationic homopolymerization. The copolymerization of acetoxystyrene with MMA and MAA has been carried out; however, formylation of the hydrolyzed copolymer containing hydroxystyrene functional groups in the presence of methylmethacrylate and methacrylic acid moieties is likely to be problematic.

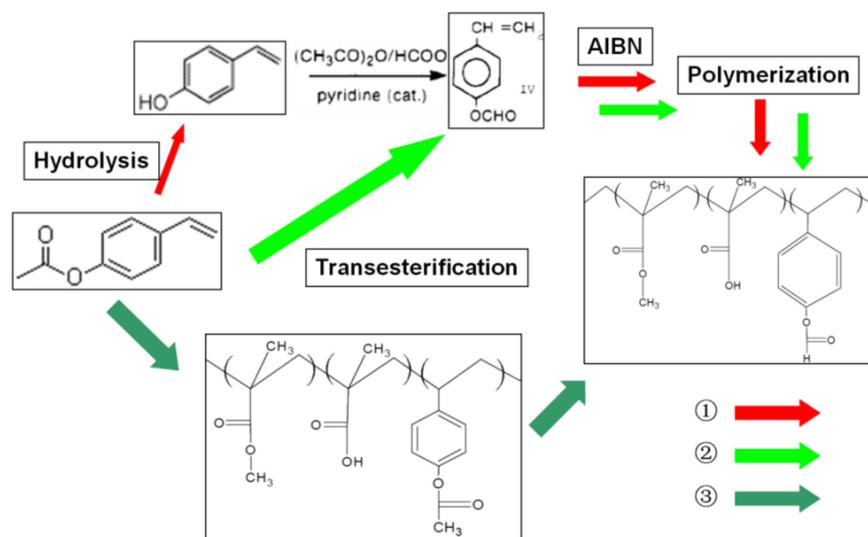


Figure 12. Options for the synthesis of formyloxystyrene copolymers.

Ring-opened polymers, derived through the copolymerization of norbornene, norbornenyl hexafluoroisopropanol, and norbornenyl phenyl formate, are expected to be significantly more etch-resistant and transparent than any acrylic polymer system. While norbornene and norbornenyl hexafluoroalcohol are commercially available, norbornenyl phenyl formate had to be synthesized in our laboratories. This was accomplished by the Diels-Alder reaction of cyclopentadiene and acetoxystyrene, followed by hydrolysis and esterification with formic acid or by the direct Diels-Alder reaction between cyclopentadiene and formyloxystyrene.

3.3.1 Optical Characterization of Resist Materials

Optical absorbance spectra for the polymers with 20% MAA and varying levels of formyloxystyrene (5%, 10%, and 15% FOS) are shown in Figure 13. The absorbance data show that the level of FOS in acrylic copolymers should be kept at or below 7 mol% to avoid scumming. However, for norbornenyl hexafluoroalcohol derivatives, the amount of FOS can be greater than this value due to the transparency induced by hexafluoroalcohol groups.

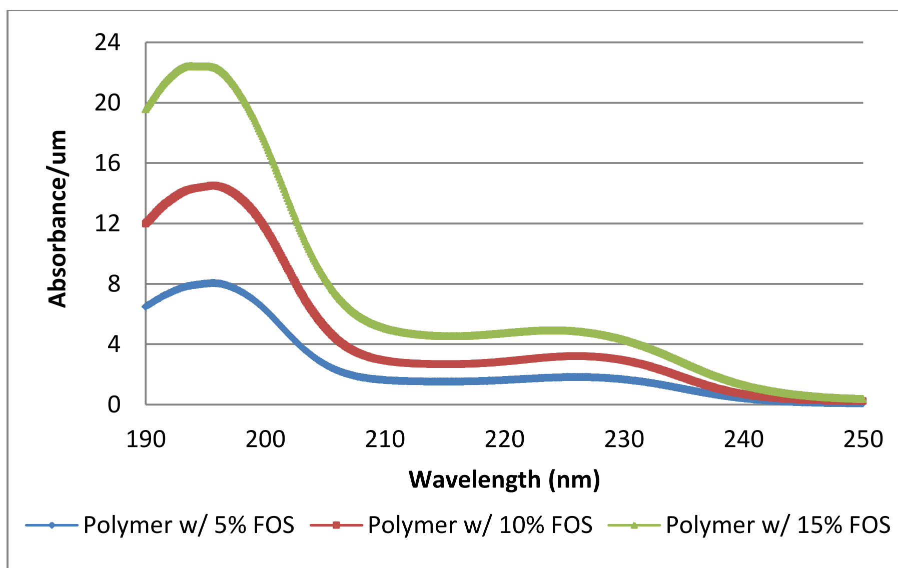


Figure 13. Absorbance results for acrylic copolymers with 5%, 10%, 15% formyloxystyrene.

3.3.2 Discovery of a Developer for the FOS/Acrylic Copolymer System

Frechet, et al. [9] employed an aqueous solution of NH_3/H_2O and IPA to develop high resolution patterns in poly(formyloxystyrene). To prepare a suitable developer for our acrylic copolymers containing FOS, NH_3/H_2O:IPA of different molar ratios (90:10, 80:20, 50:50) were evaluated. No NH_3/H_2O:IPA mixture was able to discriminate between exposed and unexposed areas of our acrylic copolymers. Although NH_3/H_2O is only weakly basic, the nucleophilicity of NH_3 is apparently more than sufficient to rapidly hydrolyze formyloxy residues. The only option was to identify a non-nucleophilic base whose pH was greater than that of aqueous sodium carbonate and less than that of dilute aqueous NaOH. The handbook of physics and chemistry revealed that a dilute solution of an equimolar mixture of NaOH and KCl would provide a solution in the pH rage of 12–13. Surprisingly, a 0.20 M solution (0.1 M NaOH and 0.1 M KCl) was able to dissolve imaged areas of the thin films of our acrylic copolymers containing FOS without disturbing the areas that had not been irradiated. To avoid metal ion content in the developer, dilute aqueous solutions of tetramethylammonium hydroxide (TMAH) and tetramethylammonium chloride (TMAC) were evaluated. Our studies indicate that a 0.12–0.14 M solution (0.06–0.07 M in both TMAH and TMAC) results in low dark loss and good discrimination between exposed and non-exposed areas of the thin films of our acrylic/FOS copolymer. Figure 14 shows the initial 193 nm imaging results obtained for the acrylic polymer with 7% FOS using this new developer.

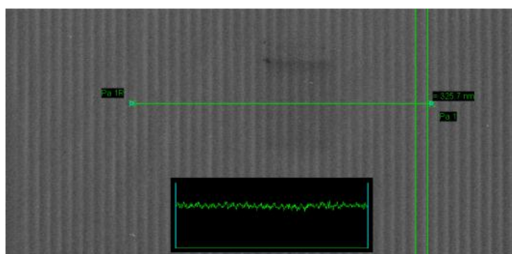


Figure 14. SEM image of acrylic polymer with 7% FOS and 20% MAA. (1:1 dense pattern, 150 nm half-pitch)

3.3.3 Photosensitivity of a FOS/Acrylic Copolymer

The sensitivity and contrast of 68 nm thick film of (5/85/10) (FOS/MMA/MAA) copolymer was briefly evaluated. The pre-exposure bake was 100°C for 2 min. Because of the anomalous dissolution characteristics of the film (swelling and loss of adhesion), a contrast curve mapping the decrease in thickness of exposed areas with increasing exposure dose could not be obtained. An approximate measure of dose to clear was ~250 mJ/cm^2. Given the limited etch resistance of the acrylic copolymer system; future research is being redirected towards FOS-bearing norbornene copolymers.

4. CONCLUSIONS

We have explored several systems as candidate materials, concentrating efforts on three main pathways: dissolution inhibitor photoresist systems, chain-scissioning polymers, and photoresist systems based on formyloxybenzene functional groups. Because the dissolution inhibitor system has shown promise, we are continuing to work on these materials to evaluate their use for 32 nm lithography.

The next steps in the dissolution inhibitor study include optimizing development conditions and BARC thickness, imaging at higher NAs, and studying other dissolution inhibitors including pivaloyl-nitrobenzyl-cholate. It was shown by Ito and coworkers that the imaging capability of exo-rich PNBHFA is superior to endo-rich PNBHFA. Increasing the exo content will not only remedy the imaging results, but also reduce the dark loss of the PNBHFA blends with dissolution inhibitors. This will allow us to use a strong developer like 0.26N TMAH. This is important since the PNBHFA exhibits multi-stage and non-linear dissolution behavior for weak developers, which is not acceptable for higher image fidelity. Another path that will be beneficial is to use partially protected PNBHFA.

The scissioning systems work has shown that the sensitivity of chain-scission resists can be increased by adding absorptive monomers into the backbone. In efforts to increase etch resistance, polymers containing 39 mol% ADMA indicated that a cross-linking mechanism suppresses chain-scission at high doses. The best chain-scission resist system

studied so far has shown a sensitivity of 110 mJ/cm^2 (for 45 nm resist film) with a contrast of 1.9. Other moieties will be explored to improve etch resistance, including the use of tri-methylsilyl functionalities.

Copolymers of formyloxystyrene with norbornene groups are also under investigation and will be studied further.

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