Fluoroaromatic Resists for 157-nm Lithography

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Lithography with 157-nm fluorine lasers is rapidly emerging as the next evolutionary step in optical lithography and is clearly seen as the likely successor to 193-nm lithography. As has been demonstrated with the transition to shorter wavelengths in the past, the resist materials that were developed for the longer wavelength applications are too absorbent for practical use as high-resolution single layer resist with 157-nm radiation. Fluorine containing polymers have been demonstrated to be more transparent in this spectral region than pure hydrocarbon polymers. We have developed and evaluated a number of unique fluoroaromatic-based 157-nm resists including 4-hexafluoroisopropanol styrene copolymers with t-butyl acrylate and acetyl blocked 4-hexafluoroisopropanol styrene. Our recent resist designs are shown to have imaging capability down to 70 nm with a 0.60 NA microstepper.

Keywords: fluoropolymer resist, 157 nm lithography, plasma etching

1. Introduction

The next evolutionary step in optical lithography from 193 nm will be 157 nm using F₂ lasers. The resists that will be used for this technology must be initially capable of 100 nm line resolution and then be projected to less than 70 nm.^{1,2} Unfortunately, as with the transition to shorter wavelengths in the past, the resist materials developed for longer wavelengths appear to be too absorbent for practical use as a traditional high resolution single layer resist imageable with 157 nm radiation.^{3,4} necessitating the need to develop new resist materials.

Polyhydroxystyrene based resists were a necessary development in order to overcome the high 248-nm absorbance of novolac-based resists initially used in i-line lithography. This achievement enabled the introduction of 248 nm lithography into IC manufacturing.^{5,6} In a similar fashion, there was a considerable effort put into the development of a new polymer system to overcome the fatally high absorbance at 193 nm of the phenolic-based polymers used at 248 nm. Two different classes of polymers, polyacrylate^{7,8} and polycyclic^{9,10} copolymer based resists have been developed, and now compete for

predominance in 193 nm lithography. But, once again the high absorbance of these polymers at 157 nm makes these polymers difficult to use in resists at thicknesses greater than 100 nm.¹¹

If thicker resists are needed, then modified polymers will have to be developed that have reduced 157-nm absorbancies while maintaining the level of dissolution switching found with 193 and 248 nm resists. These polymers will have to be tailored so that the carbon π -bonding, such as those found in aromatic and carbonyl groups, are eliminated, reduced or modified to meet absorbance targets for resists at 157 nm. An additional outcome of increased resist absorption at 157 nm is the emergence of new photochemical pathways for decomposition of polymers and photoacid generators (PAGs). The higher energy and increased material absorbance associated with 157 nm has been shown to lead to higher quantum yields of photoproducts and increased material outgassing.^{12,13}

The primary driving force in the development of resists for 157-nm lithography has been to make the polymers more transparent at 157 nm. It has been previously shown that fluorine-functionalized polymers are more transparent in

this spectral region than their pure hydrocarbon polymer counterparts.¹⁴ This finding has prompted a number of researchers to add fluorine substituents to a variety of 193-nm resist polymers and subsequently report on their approaches toward employing fluoroaliphatic polymers in 157-nm resist design.¹⁵⁻¹⁷ Although these approaches may be needed to yield the most transparent resins, we feel that it is worthwhile to consider slightly less transparent resists based on fluoro-functionalized versions of current high-performance 248-nm resists. Due to process design considerations, other properties of the polymers used in resists are desirable and must be kept, such as the etch resistance, dissolution behavior and even the glass transition temperature (T_g). Thus, the design of a resist does not lie solely in the lowering of the absorbance, but also on maintaining similar resist properties that are associated with those polymers developed for 248 nm resists.

Research^{18,19} on ultrathin resists (100-150 nm) used with a hard mask has indicated that the defect levels induced by these resist processes are not fundamentally higher than those using thicker resists. This work has cast optimism on the possibility of using resist thicknesses, which are less than those mandated by the International Technology Roadmap. If hard mask processing with ultrathin resists comes to fruition in manufacturing, the impact on 157-nm resin chemistry may be significant by effectively negating the need for heavily fluorinated resins that maximize transparency at the expense of manufacturing cost and development effort.

It was previously reported²⁰ that 248-nm resists based on poly(4-hydroxystyrene), (HOST), can continue to function after substituting poly(4-hexafluoroisopropanol styrene), (HFIPS), for the base resin. We have previously reported that the HFIPS monomer could be copolymerized with t-butyl acrylate to yield an ESCAP-like polymer capable of 40-nm imaging with 157-nm exposure on an interference lithography system.²¹ Our estimates suggested that such a facile approach to fluorine incorporation could yield over a doubling in the optimal resist thickness when used at 157 nm while retaining many of the properties desired in

a performance resist resin. In this paper we continue to focus our attention on investigating the use of fluoroaromatic polymers for 157-nm lithography by reporting on a series of newly developed acetal functionalized HFIPS copolymers tailored for 157-nm lithography.

2. Method

Projection lithography at 157 nm was performed on HMDS-treated 8-inch silicon wafers with an Exitech 0.60-NA small field stepper located at Sematech using either a binary or phase shift mask. The resist thickness was 100 nm for fluorine containing resists and 60 nm or hydrocarbon resists, the post apply bake (PAB) was at 140°C for 60 seconds on a hot plate and the post exposure bake (PEB) was at 140°C for 90 seconds on a hot plate. Development was by single puddle for 45 seconds with 2.38% TMAH (0.26 N) developer.

Film loss and film retention studies at 157 nm were performed on 4-inch silicon wafers containing an antireflection coating with a laboratory-class projection system. The exposed film thickness loss (FTL) was determined by subtracting the film thickness of an exposed portion of the resist after exposure and prior to any development from the film thickness of the resist prior to exposure. The organic film of interest was spin cast to approximately 55 nm followed by a PAB of 130°C for 60 seconds. The rate of thickness loss (FTL_{Dose}) was determined by dividing the FTL of a resist by the incident exposure dose, typically 100 mJ/cm². Film thickness measurements were made approximately 24 hours after exposure to insure that all material outgassing was complete. Film retention was determined after development for 30 seconds with tetrahydrofuran (THF).

Transmission measurements were made by coating a 75 to 150 nm polymer film on a calcium fluoride substrate followed by baking in a convection oven for 30 minutes at 150°C. Complete details for determining the 157-nm absorbance have been previously reported.²²

Plasma etching was performed on polymer films coated on 6-inch silicon wafers to a thickness of 150 to 200 nm. Thermal oxide etching was performed on a Lam Rainbow etcher

for 60 seconds employing an etch gas mixture of 8 sccm of CF_4 , 12 sccm of CHF_3 , and 200 sccm of Ar, at a pressure of 350 mTorr, with an electrode power of 700 Watts, and a lower electrode temperature of -20°C . Selectivity to oxide is calculated by dividing the material etch rate by the thermal silicon dioxide etch rate of 6.05 nm/second. Polysilicon etching was performed on a Lam 9400 TCP etcher for 60 seconds employing an etch gas mixture of 37.5 sccm of Cl_2 , 13.5 sccm of HBr , 6 sccm of He, and 1.5 sccm of O_2 , at a pressure of 10 mTorr, with a source power of 200 Watts, a plate power of 100 Watts, and a lower electrode temperature of 45°C . Selectivity to polysilicon is calculated by dividing the material etch rate by the amorphous silicon etch rate of 2.85 nm/second.

3. Results

3.1 Polymer photochemistry

The effect of photo-absorption on polymers at 157 nm can be quite different than at longer wavelengths. In particular, the photochemistry of 248-nm resists is driven mainly by the PAG. At 157-nm the base polymer may directly undergo photo-induced transformations such as crosslinking, leading either to an increase in polymer molecular weight or polymer insolubilization, and thus counteracting the dissolution enhancement afforded by the photoacid induced catalytic deprotection of the polymer. The polymer may also undergo a photo-induced chain scission reaction in which either the polymer main chain or side chain is cleaved. Main chain scission leads to a reduction of polymer molecular weight and can result in increased levels of material outgassing. Side chain scission is an established reaction pathway for many acrylate and methacrylate esters, and as such represents a second photochemical pathway for the production of outgassed resist materials and potentially polymer insolubilization via changes in polymer structure.

Polymers representative of those commonly employed in 193 or 248-nm resists along with a fluoroaromatic polymer were selected to study polymer photochemistry as it would affect resist performance. General chemical structures of the polymers used are shown in Figure 1. Poly(hydroxystyrene) (HOST) and poly(t-butyl

acrylate) (TBA) were selected as model polymers due to their use in many 248-nm-based resists. Poly(methyl methacrylate) (MMA), poly(t-butyl methacrylate) (TBMA), and poly(isobornyl methacrylate) (IBMA), were selected as model polymers due to their use in many 193-nm-based resists. The 4-hexafluoroisopropanolstyrene (HFIPS) polymer was employed as a representative of a new class of 157 nm resists.

Figure 1. Chemical structure of homopolymers

The polymers selected for this study can undergo a number of potential photochemical transformations that lead to radical formation through either bond scission or hydrogen abstraction. Acrylate and methacrylate polymers can undergo both Norrish Type 1 and Norrish Type 2 bond cleavage. A Norrish Type 1 cleavage occurs when the ester carbonyl is cleaved adjacent to the polymer main chain. This type of cleavage gives rise to an initial carbon radical on the polymer main chain which can then undergo further reactions that lead to polymer crosslinking. A Norrish Type 2 cleavage occurs when the polymer main chain cleaves leading to two new polymer chains of decreased molecular weight. Methacrylate polymers tend to favor Norrish Type 2 cleavages while acrylate polymers favor Norrish Type 1 cleavage. In addition, both polymer types are known to undergo ester elimination which may

be followed by subsequent loss of carbon dioxide. Styrene-based polymers normally undergo a bond scission reaction which leads again to an initial carbon radical on the polymer main chain which can then undergo further reactions that lead to polymer crosslinking.

Table 1. Summary of exposed FTL at 100 mJ/cm² and the E_N for THF development for homopolymers with 157-nm exposure.

Polymer	FTL ₁₀₀ (nm/mJcm ⁻²)	Negative E _N (mJcm ²)
HOST	0.000	17.2
HFIPS	0.015	7.0
MMA	0.111	> 200
TBA	0.166	15.2
TBMA	0.169	> 200
IBMA	0.099	> 200

A simple method was used to determine the degree of material outgassing by measuring the exposed film thickness loss. A thin film of the polymer was exposed at 157 nm with a series of open frame exposure doses, much like a typical contrast curve experiment, and without further processing the film thickness as a function of exposure dose was determined. Figure 2 shows the film thickness loss of the six polymers at different exposure doses. The film thickness loss (FTL), determined by dividing the film thickness loss by the exposure dose, for homopolymer films are summarized in Table 1. In addition to determining the FTL, contrast curves were determined for the polymer films employing an organic solvent (THF) developer and these are shown in Figure 3. These contrast curves will give mechanistic insights into the non-volatile photo-products formed during 157 nm exposure as retained film after exposure and development will result from either polymer crosslinking or a significant change in polymer structure. The exposure dose that leads to the onset of negative resist behavior was defined as E_N and summarized in Table 1.

The thickness loss observed in Figure 2 can result either by main chain scission, side chain fragmentation, or a combination of both. The six polymers fall into three general classes depending on the rate of film loss. The polymers

with the highest film loss are the two containing t-butyl esters, TBA and TBMA. The FTL for these two polymers are 0.166 and 0.169 nm/mJcm⁻² and at a 200 mJ/cm² exposure dose the polymers have lost nearly half of their mass. The high rates are due to the facial side chain fragmentation of the t-butyl ester. Two other methacrylate based polymers, MMA and IBMA, also show significant film loss with a FTL of 0.111 and 0.099 nm/mJcm⁻² and at a 200 mJ/cm² exposure dose the polymers have lost over a quarter of their mass. The final category is the two aromatic polymers, HOST and HFIPS, where very little film loss occurs with a 200 mJ/cm² exposure dose and a FTL of 0.000 and 0.015 nm/mJcm⁻² respectively.

Figure 2. Change in film thickness due to material loss

Both the HOST and HFIPS polymers are known to have low film loss and materials outgassing. These results are completely consistent with our earlier work where we postulated that the aromatic ring of HOST acted to stabilize the photo-induced free radical and favored a radical termination step versus a fragmentation step. This shows that virtually no side chain fragmentation or main chain scission occurs that leads to volatile products.

Figure 3. Change in film thickness due to insolubilization

The retained film thickness observed in Figure 3 can result either by polymer crosslinking, side chain fragmentation leading to loss of solubility enhancing groups, or a combination of both. The six polymers fall into two general classes depending on whether retained film is observed after exposure and solvent development. The methacrylate-based polymers do not exhibit any retained film after THF treatment implying that no crosslinking has occurred. This is consistent with the known photochemistry of methacrylate polymers where Norrish Type 2 bond cleavage is expected to predominate. The aromatic polymers both exhibit negative resist behavior in that by 50 mJ/cm² exposures, the film is retained to over 90% of its original thickness. The acrylate polymer also exhibits negative behavior in that by 100 mJ/cm² exposure, the film is retained to about 50% of its original thickness. This value does not increase with higher exposure doses as the concurrent film loss drives sufficient material away from the film to limit any further increase in retained film. This behavior of poly(t-butyl acrylate) is not surprising in that crosslinking behavior is expected to occur with acrylate polymers as Norrish Type 1 bond cleavage is expected to predominate unlike the methacrylate polymers where Norrish Type 2 bond cleavage is favored.

3.2. Fluoroaromatic copolymers

Our approach to 157-nm resist development is to employ a polymer that represents an evolutionary step in resist materials development while maintaining the ability to use traditional 2.38% aqueous TMAH developers. The 248 nm resists all achieve base solubility through incorporation of poly(p-hydroxystyrene) as the major component. We employ the incorporation of hexafluoroisopropyl alcohol functionality which has a pKa of 11.2 compared to other typical phenols that have pKa's of 10–12. The acidity of 1,1,1-trifluoro-2-trifluoromethyl-2-propanol is the result of inductive stabilization of the conjugate base. We have synthesized a series of copolymers of 4-hexafluoroisopropanolstyrene (HFIPS), to be analogs to the hydroxystyrene copolymers employed in 248-nm sensitive resists. These copolymers are either copolymers with acrylate esters which are often referred to as high-activation-energy resists or acetal copolymers which are often referred to as low-activation-energy resists. Figure 4 shows the four polymer types that were studied. Copolymers of HFIPS with t-butyl acrylate (TBA) or methyladamantyl methacrylate (MAMA) can be used to prepare high activation resists and copolymers of HFIPS with either the methyl methoxy (MOM) or t-butyl methoxy (BOM) of HFIPS can be used to prepare low activation resists.

Resists that are more transparent and tailored to 157 nm radiation are prepared from fluoroaromatic polymers, in which absorptive C–H bonds are replaced with more transparent C–F bonds. Their lithographic behavior is derived from the same familiar chemical reactions as those tailored for use as 248-nm resists. This includes such properties as chemically amplified deprotection, based on photon-generated acids and post-exposure bake, followed by development in an aqueous base. Thus, the fundamental processing conditions and lithographic performance will be similar to the familiar corresponding issues at longer wavelengths. An added benefit is that the copolymer ratio of HFIPS-based polymers can be readily varied to fine tune resist performance. Examples of different HFIPS-based copolymers

prepared by varying the monomer charge ratio can be seen in Table 2 along with 157-nm absorbance and glass transition temperature of the polymers (T_g).

Figure 4. Chemical structures of HFIPS copolymers with both ester and acetal blocking.

The physical properties of these polymers have been extensively studied and can be tailored to achieve absorbancies below $3 \mu\text{m}^{-1}$ at 157 nm. These values, along with the glass transition temperatures, are presented in Table 2. The ester and acetal platforms offer the ability to tailor lithographic performance from a relatively simple synthetic scheme while building on the knowledge base developed for the 248-nm HOST based resists. Absorbance of the ester platform and that of our acetal blocked polymers enables the ability to coat to up to 150 nm in thickness. Another key advantage of this system lies in the glass transition temperatures associated with the HFIPS backbone. The transport properties of molecules within the resist, such as the diffusion coefficient for the photogenerated acid, are highly dependent upon the polymer T_g . At these temperatures, these polymers can be annealed by baking the resist above its T_g . Annealing at this temperature will provide better environmental stability and lithographic performance through

the reduction of free volume in the resist and the subsequent reduction in permeability of environmental contaminants.

Table 2. Comparison of absorbance and T_g for HFIPS-based polymers with ester and acetal blocking.

Polymer	$\alpha_{157} (\mu\text{m}^{-1})$	$T_g (^\circ\text{C})$
60:40 HOST-co-TBA	6.5	155
60:40 HFIPS-co-TBA	3.7	120
60:40 HFIPS-co-TBMA	4.0	154
70:30 HFIPS-co-MAMA	4.5	135
70:30 HFIPS-co-MOM	3.1	114
60:40 HFIPS-co-BOM	3.2	98
70:30 HFIPS-co-BOM	2.8	106

The acetal functional groups not only yield lower absorbance polymers, but also have the benefit of improved thermal stability. As shown in Figure 5, the acetal functional HFIPS copolymers are thermally stable, without the presence of acid, up to temperatures of over 300°C. This shows that these blocking groups are very stable and should provide excellent shelf life for these resists. However, upon addition of 5% camphor sulfonic acid and heating, the acid labile group is easily removed at temperatures under 100°C, to yield a deprotected polymer. The methoxy acetal shows higher temperature stability than the t-butoxy acetal by about 30°C, and as such the t-butyl acetal would be expected to lead to an increased sensitivity resist with comparable acid generation.

The technique of measuring the exposed film thickness loss to determine the degree of material outgassing was applied the HFIPS based polymers. It was found that HFIPS is known to have low film loss and materials outgassing. These results are completely consistent with our earlier work, where we postulated that the aromatic ring of HOST acted to stabilize the photo-induced free radical and favored a radical termination step versus a fragmentation step. This illustrates that virtually no side chain fragmentation or main chain scission occurs that yields volatile products.

Figure 5. Thermal behavior of partially blocked HFIPS-BOM and HFIPS-MOM showing the thermal stability of blocking group and deprotection in the presence of camphor sulfonic acid.

Figure 6. Comparison of film thickness loss with 157-nm exposure of acrylate and HFIPS based polymers.

The results from 157-nm exposure for the HFIPS homopolymer, the *t*-butyl acrylate homopolymer, the copolymer of HFIPS and TBA and our new fluorinated copolymer of HFIPS with the MOM acetal are shown in Figure 6 and summarized in Table 3. Figure 6 shows that *t*-butyl acrylate has significant film thickness loss resulting from 157-nm exposure. At similar exposure doses HFIPS has virtually no film loss.

The HFIPS copolymer with *t*-butyl acrylate, by nature of the HFIPS moiety stabilizing the photo-induced free radical, again shows very little film loss. The acetal functionalized HFIP polymers also have very little film loss even up to the highest 157-nm exposure dose. Again, the incorporation of the aromatic functionality into the polymer leads to reduced film loss and, more importantly, reduced 157-nm polymer outgassing.

Table 3. Summary of exposed film thickness loss determined at 100 mJ/cm² for copolymers with 157-nm exposure.

Polymer	FTL ₁₀₀ (nm/mJcm ⁻²)
TBA	0.166
HFIPS	0.015
60:40 HFIPS-co-TBA	0.018
70:30 HFIPS-co-MOM	0.026

The similarities in film thickness loss of both the hydroxystyrene and *p*-HFIP-styrene polymers and copolymers in suppressing film loss with 157-nm exposure shows the advantage of employing aromatic rings in polymers used for 157-nm resists. Not only do the homopolymers have very little film loss, but also the incorporation of the aromatic ring in a copolymer provides an added benefit of reducing the high film loss associated with ester cleavage during 157-nm exposure. This is a benefit for fluoroaromatic-based 157-nm resists that may not be available with aliphatic-fluorocarbon based resists.

4. Discussion

4.1. Lithography

A critical assumption in pursuing the fluoroaromatic approach toward the development of 157-nm resists is the ability of these resists to show imaging characteristics appropriate to sub-100 nm lithography at resist thicknesses of 100 nm or greater. We have evaluated experimental resists comprised of the basic ESCAP polymer, poly(HOST-co-TBA), along with resists formulated with the HFIPS-acrylate and HFIP-acetal copolymers. The resist names and the base polymers are reported in Table 4 as is the

exposure dose to size 120-nm lines with a 300-nm pitch (1:1.5) employing a binary mask. It can be seen that all resists have high sensitivity to 157-nm exposure. The hydrocarbon-based resist has about twice the sensitivity of its HFIPS analog, which can be explained by noting that the HOST-based polymer has almost twice the absorbance of the fluoroaromatic polymer. It is also observed that the HFIPS-co-BOM based resist has an higher sensitivity, 14.6 mJ/cm² versus 22.7 mJ/cm². This is consistent with the prediction of higher sensitivity made by observing the thermal decomposition of the two polymers in the presence of camphorsulfonic acid where the BOM polymer showed thermal decomposition at a lower temperature than the MOM polymer.

Table 4. Resists, base polymers, and sizing dose (E_s) with 157-nm exposure.

Resist	Polymer	E_s (mJ/cm ²)
LUVR99071	60:40 HOST-co-TBA	5.0
LUVR99099	60:40 HOST-co-TBA	-
LUVR20045	60:40 HFIPS-co-TBA	10.0
LUVR20046	70:30 HFIPS-co-MAMA	23.7
LUVR20039	70:30 HFIPS-co-MOM	22.7
LUVR20048	70:30 HFIPS-co-BOM	14.6

Table 5. Summary of highest resolution with 157-nm exposure using a phase shift mask.

Resist	Phase Shift Mask		
	1:1	1:1.5	1:3
LUVR99071	100	70	50
LUVR99099	100	70	70
LUVR20045	-	70	60
LUVR20046	-	110	110
LUVR20039	150	100	90
LUVR20048	100	100	70

Projection lithography at 157 nm was performed with the Exitech 0.60-NA microstepper with both a binary and phase shift mask. A summary of highest resolution with 157-nm exposure with phase shift mask is presented in Table 5. The bold numbers in the second row refer to the pitch of the line and space pair with the smallest resolved linewidth given below in nm. All six resists are capable of sub-

100-nm resolution with a 1:3 pitch. The resolution decreases with decreasing pitch, although several resists show 70-nm resolution with a semi-isolated line pitch of 1:1.5.

The resolution capability of the hydrocarbon resists, LUVR99071 and LUVR99099, in 60-nm thick films, is shown in Figure 7. The LUVR99071 exhibits slightly higher resolution, 50 versus 60 nm, than LUVR99099. All subsequent resists were based on the LUVR99071 formulation. The resolution capability of the HFIPS-acrylate based resists are shown in Figure 8 and that of the HFIPS-acetal resists are shown in Figure 9.

Figure 7. Comparison of HOST-co-TBA resists showing 1:3 lines at a 60 nm film thickness

LUVR20045, exhibited 60-nm imaging capability for the phase shift mask (PSM) on the 157-nm projection system with a resist thickness of 100 nm. The resist formulated with MAMA, LUVR20046, exhibited much poorer resolution of only 110 nm. The increased hydrophobicity of the methyladamantyl ester may have contributed to the loss in resolution. The resist LUVR-20039, containing the MOM copolymer, gave 90-nm lines with a 1:3 pitch and LUVR20047, containing the BOM copolymer, gave 70-nm lines with the same 1:3 pitch. All the resists were able to print features over several doses and focus fields implying that potentially excellent overall latitude are possible with these resists.

Figure 8. Comparison of HFIPS-co-acrylate resists showing 1:3 lines at a 100 nm film thickness

Figure 9. Comparison of HFIPS-co-acetal resists showing 1:3 lines at a 100 nm film thickness.

The resist imaging of the fluoroaromatic polymers is very encouraging. It is noted that these resists are not based on optimized formulations and represent only a first generation resist system. It can be expected that further work on HFIPS-based polymers can lead to improved resist performance. The imaging capability observed so far, coupled with the relatively straightforward polymer synthesis, makes insertion of this class of resists into the International Technology Roadmap's 95 nm node in 2004 and the 65 nm node in 2007 very possible if coupled with hard mask resist processing technology.

4.2. Plasma etching

An ongoing concern with using thin resists, even with hard mask technology, is the ability of the thin resist to resist the harsh environments

found during plasma etching. This concern may be magnified when fluoropolymers are employed in the resist, since fluoropolymers are expected to have very high plasma etch rates. It is difficult, if not impossible, to test resists under the variety of different plasma etch conditions found throughout the semiconductor fabrication process. We therefore chose to determine the plasma etch rates under two representative plasma etch processes used in industry today. We employed two standard plasma etch processes that are routinely used in our fabrication facility to test the ability of the fluoropolymers to withstand a plasma etch. These processes are a thermal oxide etch process based on a fluorine plasma that has a thermal oxide etch rate of 6.05 nm/second and a poly etch process based on a chlorine/bromine plasma that has an amorphous silicon etch rate of 2.85 nm/second.

Table 6. Plasma etch rates and selectivities for standard oxide (top) and poly (bottom) etch process.

Polymer	Oxide Etch (nm/sec)	Oxide Selectivity
60:40 HOST-co-TBA	0.86	7.1
60:40 HFIPS-co-TBA	1.34	4.5
70:30 HFIPS-co-MAMA	1.11	5.5
70:30 HFIPS-co-MOM	1.11	5.5
70:30 HFIPS-co-BOM	0.89	6.8
Thermal oxide	6.05	1.0
Amorphous silicon	0.60	10.2
Polymer	Poly Etch (nm/sec)	Poly Selectivity
60:40 HOST-co-TBA	0.71	4.0
60:40 HFIPS-co-TBA	1.01	2.6
70:30 HFIPS-co-MAMA	0.88	3.3
70:30 HFIPS-co-MOM	0.72	4.0
70:30 HFIPS-co-BOM	0.62	4.6
Thermal oxide	0.13	22.6
Amorphous silicon	2.85	1.0

We have evaluated our HFIPS acrylate and acetal functionalized HFIP copolymers against an ESCAP polymer in two standard plasma-etch processes. The choice to look at polymers and not resists was based on removing the effects of other resist components on the plasma etch rate and focusing only on the polymer etch

characteristics. The rates and selectivities of both plasma etches are presented in Table 6. It can be seen that the HFIPS-TBA polymer has a higher etch rate than the HOST-TBA polymer in both the oxide and poly etch. The use of the higher carbon containing MAMA ester improves the etch selectivity but not enough to reduce the etch rate to that of the HOST-TBA polymer. The use of acetal functionalized HFIP gave the most dramatic improvement in plasma etch selectivity toward both oxide and poly. The HFIPS-MOM polymer shows an etch rate similar to that of the hydrocarbon ESCAP polymer in the poly etch, while the HFIPS-BOM polymer not only shows comparable etch selectivity in the oxide etch but superior etch selectivity in the poly etch.

One question that arises in evaluating the plasma etch characteristics of a resist is what is the best figure of merit to employ. The raw plasma etch rate in different plasmas is certainly a useful criterion, but even more useful is the plasma etch selectivity toward the substrate of interest. Although both criteria are useful, there may even be more value in determining the time to strip the resist in a given plasma as a measure of plasma etch resistance for the thin resists envisioned for 157-nm lithography. The 157-nm allowable resist thickness will be dependent on the absorbance of the resist. The time to strip the resist will therefore be a function of both the resist thickness allowed at a defined optical density and the resist etch rate.

Table 7. Calculated time to strip polymer films of 0.4 O.D. in standard oxide and poly etch processes.

Polymer	Thickness (nm)	Oxide (sec)	Poly (sec)
60:40 HOST-co-TBA	62	72	87
60:40 HFIPS-co-TBA	107	80	99
70:30 HFIPS-co-MAMA	89	80	101
70:30 HFIPS-co-MOM	130	117	181
70:30 HFIPS-co-BOM	142	159	227

The plasma etch resistance, given by the time to strip the fluoroaromatic polymers and the ESCAP polymer, was determined based on the polymers' 157 nm absorbance and the plasma etch rate. It is presented in Table 7 and shown graphically in Figures 10 and 11. The y-intercept

of the two graphs represents the thickness of a polymer film with an optical density (O.D.) of 0.4, and the slope of the graphs is the plasma etch rate of the polymer. It can be seen that the higher plasma etch rate of the HFIP-acrylate polymers is more than compensated for by the higher film thickness leading to a net gain in plasma etch resistance as measured by film removal time. The greatest gain in plasma etch resistance is shown by the HFIP-acetal polymers, where the combination of low absorbance coupled with plasma etch rates comparable to those of the ESCAP copolymer shows a more than 2 fold increase in the time to strip, as shown in both Figures 10 and 11. This is compared to the HFIPS-TBA polymer that provides about a 25% increase in plasma etch resistance over the ESCAP polymer when film removal time is used as the figure of merit. Unfortunately, the HFIPS-MAMA polymer, which looks promising as a route to higher etch resistance, has a high absorbance which limits film thickness such that total etch time is only slightly longer than that of the HFIPS-TBA polymer

Figure 10. Performance of 0.4 O.D. fluorocarbon and hydrocarbon polymers during oxide plasma etching.

Figure 11. Performance of 0.4 O.D. fluorocarbon and hydrocarbon polymers during poly plasma etching.

5. Conclusions

An alternative approach to 157-nm resist development was presented, employing fluoroaromatic polymers, that represents an evolutionary step in resist materials development. Acetal blocked hexafluoroisopropanolstyrene-based copolymers have been prepared and compared with both ESCAP based resists as well as hexafluoroisopropanolstyrene analogs to the hydroxystyrene containing ESCAP polymers. Our HFIPS-acetal platform offers the ability to tailor lithographic performance from relatively simple synthetic schemes that allow facile manipulation of the incorporated monomer ratios while building on the knowledge base derived from previous platforms. Absorbance of the HFIP polymer platform can be tailored such that 100-150 nm thicknesses are possible. Thicknesses that, when used with a hard mask, could enable the early introduction of 157-nm lithography into device manufacturing and effectively negate the need for heavily fluorinated resins that maximize transparency at the expense of manufacturing cost and development effort.

The HFIP polymer platforms are known to have very low film loss and materials outgassing. This is completely consistent with our earlier work where we postulated that the aromatic ring acted to stabilize the photo-induced free radical and favored a radical termination step versus a

fragmentation step. The film thickness loss of the copolymers containing HFIPS is much lower at 157 nm than that of fully aliphatic polymers.

The plasma etch rates for the fluorocarbon polymers were determined under two representative plasma etch processes, an oxide etch and a poly etch. The fluoroaromatic acetals are a significant improvement over the fluoroaromatic ester etch rates. The most promising fluoroaromatic acetal is the HFIPS-BOM copolymer in which plasma etch rates are comparable or superior to those of the ESCAP polymer under typical oxide or poly etch conditions. When film removal time is used as the figure of merit in evaluating plasma etch resistance, the HFIPS-BOM polymer provides over a two-fold improvement in plasma etch resistance over the ESCAP polymer.

The preliminary resist imaging of the HFIP based polymers is very encouraging. Examples of the high performance imaging capability of our resist design are shown to have imaging capability of 60 nm for isolated lines with a 0.60 NA microstepper. These resists are not based on optimized formulations and represent only a first generation resist system. It can be expected that further work on HFIPS based polymers can lead to improved resist performance. The imaging capability observed so far, coupled with the relatively straightforward polymer synthesis, makes insertion of this class of resists into the International Technology Roadmap's 95 nm node in 2004 and the 65 nm node in 2007 very possible if coupled with hard mask resist processing technology.

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