Exploring Acidic Functionalities in the Design and Development of High Performance 193nm Photoresist Polymers

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The combination of immersion lithography and reticle enhancement techniques (RETs) has extended 193nm lithography into the 45nm node and possibly beyond. In order to fulfill the tight pitch and small critical dimension requirements of these future technology nodes, the performance of 193nm resist materials needs to further improve. In this paper, we have systematically studied a variety of acidic functionalities in an effort to improve the dissolution properties of 193nm resists. The hexafluoroalcohol (HFA) and fluorosulfonamide (FSM) are found to be most effective in eliminating the swelling behavior associated with typical 193nm methacrylate resists. The HFA and FSM groups are highly transparent at 193nm. High performance 193nm resists are developed with the HFA and FSM acidic groups. Compared to the HFA group, the trifluoromethyl sulfonamide (TFSM) functionality has a lower pKa value and contains less fluorine atoms. Polymers containing the TFSM functionality have exhibited improved dissolution properties and better etch resistance than their HFA counterparts. Resists based on the FSM-containing polymers have shown superior lithographic performance for line, trench and contact hole levels under the 45nm node exposure conditions. In addition, FSM resists have also demonstrated excellent bright field and dark field compatibility and thereby make it possible to use one resist for both bright field and dark field level applications. Finally, to alleviate the adverse impact of the fluorine content in the etch resistance of the 193nm resists, we have also evaluated a non-fluorinated acidic functional alternative—naphthol.

Keywords: 193nm photoresist, acidic functionality, hexafluoroalcohol, fluorosulfonamide, naphthol, dissolution property, 193nm lithography, immersion lithography

1. Introduction

The semiconductor industry has fully embraced 193 nm immersion lithography as the technology of choice for the 45 nm node. It is likely that the 193nm immersion lithography will further carry the industry through the 32 nm half-pitch node on ITRS. One of the major benefits of the immersion lithography is its capability of constructing projection optics with numerical aperture (NA) greater than 1. In theory, the large increase in NA could dramatically improve the resolution of 193 nm resists. The move from dry to immersion lithography could also increase the depth of focus (DOF) of resists. The realization of these advantages of 193nm immersion lithography, however, requires not only advances in lithography tools and processes, but also great improvement in 193nm resist materials. It is desired that a successful resist for 193 nm immersion lithography would have excellent dissolution properties, good etch resistance, high transparency and immersion compatibility.

As discussed in our previous publication, typical 193nm methacrylate resists do not have an ideal dissolution behavior in 0.26 N tetramethylammonium hydroxide (TMAH) developer. In Fig. 1, the dissolution rate vs. exposure dose curve obtained with a typical 193nm methacrylate resist based on the methyladamantyl methacrylate (MADMA) /methacryloyloxynorbornanecarbolactone (NLM) copolymer reveals significant swelling prior to full dissolution.
To reduce/eliminate the swelling behavior associated with the 193nm methacrylate resists, we have incorporated an acid functionality into the resist polymer. Fig. 2 shows the general design of our 193nm resist polymers. In this design, the acid-labile group is a typical protecting group such as methyladamantyl (MAD) or methylcyclopentyl (MCP). The polarity-etch balancing group is generally a lactone group. We have explored a variety of acidic groups in this design and studied their impact on the material properties and lithographic performance of the resist polymers.

Figure 2: The general design of IBM 193nm resist polymers.

2. EXPERIMENTAL

2.1 Materials

2-Trifluoromethanesulfonylaminoethyl sulfoneamide (TFSM) was synthesized from 2-aminoethylmethacrylate hydrochloride and trifluoromethane sulfonylchloride according to Fig. 3. Polymers were synthesized via free radical polymerization using 2,2'-azobisisobutyronitrile (AIBN) as the initiator and 2-butanone as the polymerization solvent. Polymers generally have a weight-average molecular weight (Mw) of 8,000-12,000, as determined by gel permeation chromatography (GPC).

Figure 3. Synthesis of 2-Trifluoromethanesulfonyl-aminoethyl methacrylate (TFSM).

2.2 Measurements

Thermogravimetric analysis (TGA) was performed at a heating rate of 10 °C/min in N2 on a TA Instrument Hi-Res TGA 2950 Thermogravimetric Analyzer. Differential scanning calorimetry (DSC) was carried out at a heating rate of 10 °C/min on a TA Instrument DSC 2920. A quartz crystal microbalance (QCM) was used to study the dissolution properties of the FSM polymer films in an aqueous TMAH solution by measuring frequency and resistance using 5MHz crystals.

2.3 Formulations and lithographic evaluation

Resist formulations generally comprised of 6-8% of the polymer in propylene glycol methyl ether acetate (PGMEA), photoacid generator(s) and organic base(s). The resist solutions were filtered through a 0.2 μm filter. Resist films were formed by spin-coating the resist solutions onto an AR40 antireflective coating (Rohm and Haas Electronic Materials). The postapply bake (PAB) temperature was 110 °C for 60 sec. Exposure was carried out on ASML 193 nm dry and immersion scanners with NA of 0.75, 0.85, 0.93, 1.1, and 1.2. After exposure, the film was baked at 120 °C for 60
Development was performed in AD-10 (0.26 N, Rohm and Haas Electronic Materials) for 60 sec.

3. RESULTS AND DISCUSSION

3.1 Structures of acidic monomers

The acidic monomers studied in this work are shown in Figure 4. The carboxylic acid functionality has a Pka of 4-5. The hexafluoroalcohol (HFA) functionality has a Pka of 10-11. The Pka of the fluorosulfonamide (FSM) group is 6-7. Thus, the order in acidity for these acidic functionalities is: HFA < FSM < MA.

Figure 4: Acidic monomers employed in polymer design and synthesis

3.2 Dissolution behavior of 193nm resists containing different acidic groups

To study the dissolution behavior of the 193nm resists with different acidic groups, we measured the dissolution rates of resist films at different exposure doses. Dissolution rate vs. exposure dose curves were obtained by flood exposing (254nm wavelength, obtained from Hg-Xe lamp) cast the resist films at various exposures doses, processing at 120 °C PEB and then obtaining dissolution rate information using the QCM method. The resist polymers are terpolymers containing a monomer with the acidic group, MADMA, and NLM. For comparison purposes, all 3 polymers have the same concentrations of the MADMA and NLM monomer units in the polymer structures. The concentration

Figure 5. Dissolution rate vs. exposure dose for resists with different acidic groups.
of the monomer unit with the acidic group is 15 mol%. As shown in Fig. 5, the resist containing the carboxylic acid group exhibits a swelling at low doses, a behavior similar to what had been observed with the typical 193nm methacrylate resists based on MADMA/NLM copolymers. In contrast, both HFA and FSM based resists do not show any swelling behavior at various doses, revealing clean dissolution in the partially exposed areas. Thus, out of the three acidic groups studied, only the HFA and FSM groups are able to eliminate the swelling behavior in the 193nm methacrylate resists. Accordingly, our study on material properties and lithographic performance is focused on HFA and FSM resists.

3.3 Material properties and lithographic performance of HFA and FSM resists.

3.3.1 HFA resists.

In our previous publication, we had demonstrated that the introduction of HFA functionality could eliminate the swelling behavior generally associated with methacrylate-based 193nm resists. Resists based on the HFA structure exhibited reduced PEB sensitivity and improved resolutions and process windows for trench levels applications over the methacrylate-based 193nm resists. As the feature sizes continue to shrink, the dissolution properties of the resists need to be further improved. For example, in order to have good resolution and process windows for trench and contact hole levels, a resist preferably should have a high dissolution rate in the developer in the fully exposed area \( R_{\text{max}} \). Although the HFA functionality is acidic, polymers containing the HFA structure generally have slow dissolution rates in 0.263 tetramethylammonium hydroxide (TMAH) developer. To achieve the desired high \( R_{\text{max}} \), more acidic structures are needed to replace the HFA functionality.

In addition, moving to hyper-NA imaging and smaller feature sizes also entails a thinner resist. In order for the imaged pattern to be successfully transferred to the underlying substrate, it is critical that the 193nm resist materials have adequate etch resistance. Fluorine atoms are commonly known to reduce the dry etch resistance of resist polymers. Since the HFA functionality has six fluorine atoms in its structure, polymers with the HFA structure generally have poor etch resistance. To enable adequate etch transfer for 45nm node and beyond, structures with less fluorine atoms are thus preferred.

3.3.2 FSM resists.

3.3.2.1 Thermal and optical properties of FSM polymers

Fig. 6 is the DSC plot of a 2-Trifluoromethanesulfonylaminoethyl methacrylate homopolymer (PTFSM) with a Mw of 16,000 and a polydispersity (Pd) of 2.2. The TFSM homopolymer has a glass transition temperature of ~80 °C. PTFSM is thermally stable and does not show any decomposition until after 270 °C, as evidenced by the TGA measurement (Fig. 7).

![Figure 6. DSC plot of 2-Trifluoromethane-sulfonylaminoethyl methacrylate homopolymer (PTFSM).](image-url)
The optical property of PTFSM was measured on a VB-250 VASE ellipsometer. PTFSM has a refractive index (n) of 1.6 at 193nm, which is higher than most HFA homopolymers (<1.55). The increased n value is attributable to the lower fluorine content and the existence of the sulfur atom in the TFSM structure. PTFSM is very transparent at 193nm. The absorption parameter (k) of PTFSM is calculated to be 0.0021, which corresponds to an optical density of 0.06 $\mu$m$^{-1}$ at 193nm. The high transparency of the FSM group makes it suitable for 193nm application.

3.3.2.2 Dissolution properties of FSM polymers

The FSM structure has a pKa value of 6–7, which is considerably lower than that of the HFA functionality (10–11). Due to the increased acidity, the FSM homopolymers exhibit much faster dissolution rate in aqueous base developers than the HFA homopolymers. Figure 8 presents the QCM dissolution curve of PTFSM in 0.263 N TMAH aqueous solution. The dissolution rate of the polymer is calculated to be 24,000 A/sec. As a comparison, we also measured several HFA homopolymers under the same condition. As shown in Table 1, the dissolution rates of the HFA homopolymers are several orders of magnitude lower than that of PTFSM.

![Figure 7. TGA plot of PTFSM.](image)

![Figure 8. QCM dissolution curve of PTFSM in 0.263 N TMAH aqueous solution.](image)

### Table 1. Dissolution rate comparison of FSM and HFA polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular Weight Mw (Pd)</th>
<th>Dissolution Rate (A/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTFSM</td>
<td>16,000 (2.2)</td>
<td>24,000</td>
</tr>
<tr>
<td>PNBHFAMA</td>
<td>11,000 (1.42)</td>
<td>4</td>
</tr>
<tr>
<td>PIPHFAMA</td>
<td>10,400 (1.81)</td>
<td>230</td>
</tr>
</tbody>
</table>

To utilize the high dissolution rate of the FSM group in aqueous base developer, and in the mean time to minimize the adverse effect of fluorine atoms on etch resistance, we have designed our resist polymers to contain 15-30 mol% of TFSM. We measured the dissolution rates of these resist polymers before and after deprotection ($R_{\text{min}}$ and $R_{\text{max}}$). To measure the $R_{\text{max}}$ of the resist polymers, the polymers were mixed with 5 wt% of perfluorooctanesulfonic acid in solutions. Films
cast from the solution were then baked at 130 °C for 70 sec. Fig. 9 demonstrates the QCM curves of a TFSM/MADMA/NLM terpolymer before and after deprotection. The terpolymer contains ~15 mol% of TFSM. The polymer has a slow dissolution rate of 3.3 Å/sec in the base developer before deprotection. The slow dissolution of the resist polymer is useful because it would allow a slight thickness loss in the unexposed area of the resist film, which might help reduce the defect level of the formed patterns. Once deprotected, the terpolymer exhibits a fast dissolution rate of 9,300 Å/sec in the developer. This dissolution rate represents the dissolution rate of the resist polymer in fully exposed areas (Rmax). The high Rmax of the TFSM terpolymers would enable the resists to have good resolution and process windows, especially for trench and contact hole levels.

3.3.2.3 Etch resistance of FSM resists

Besides the improved dissolution properties, another motivation for us to utilize the TFSM functionality replacing the HFA group is its lower fluorine content. In general, lower fluorine content would lead to an enhanced etch resistance. To confirm the improved etch resistance of the FSM resists over the HFA resists, we measured the blanket etch rate of a resist based on the TFSM/MADMA/NLM terpolymer in comparison to a resist based on the NBHFAMA/MADMA/NLM terpolymer using the nominal Ar/CF4 etch process. The two polymers have the same protecting group and lactone moiety with the same concentrations in their structures. The only difference is that the former contains 15 mol% of TFSM while the latter has 15 mol% of NBHFAMA. As shown in Table 2, due to the fluorine content in the polymers, both resists have faster etch rate than an industry standard 193nm resist which contains no fluorine in the resist polymer structure. Although the resist based on the TFSM/MADMA/NLM terpolymer only has a marginal improvement in etch resistance over the one based on the NBHFAMA/MADMA/NLM terpolymer, the effect of fluorine content on etch resistance is more evident when the monomer structures are taken into consideration: the NBHFAMA monomer unit has an alicyclic norbornyl group between the polymer backbone and the HFA group which acts to compensate the reduction of the etch resistance caused by the HFA group; while the TFSM monomer unit does not have
such a compensation effect. It is expected that FSM monomer units containing alicyclic structures would have further improved etch resistance over the HFA monomers.

Table 2. Etch rate comparison of FSM and HFA polymers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Etch Rate (A/min)</th>
<th>Relative Etch Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Industry Standard 193nm Resist</td>
<td>550</td>
<td>1.00</td>
</tr>
<tr>
<td>Resist Based on TFSM/MADMA/NLM</td>
<td>590</td>
<td>1.07</td>
</tr>
<tr>
<td>Resist Based on NBHFAMA/MADMA/NLM</td>
<td>595</td>
<td>1.08</td>
</tr>
</tbody>
</table>

3.3.2.4 Lithographic performance of FSM resists

Generally, under the bright field illumination conditions, a resist tends to be over-exposed. In order to keep the integrity of the line features under the bright field illumination conditions, a 193nm resist polymer with high activation energy protecting groups (such as methyladamantyl) is often needed. However, polymers with high activation energy protecting groups normally do not have good lithographic performance for dark-field application under which the resist polymer is under-exposed. For this reason, at 193nm lithography, it is generally difficult to have one resist fit both bright field and dark field applications. The situation is changed with the FSM resist polymers. The FSM group has a relatively high acidity which not only dramatically improves the dissolution properties of the resist polymer, but also profoundly affects the deprotection chemistry of the protecting group. As a result, FSM polymers containing high activation energy protecting groups have superior lithographic performance for both bright field and dark field applications. To demonstrate the excellent compatibility of the FSM resists for both bright field and dark field applications, we studied the lithographic performance of a FSM resist based on the TFSM/MADMA/NLM terpolymer under both bright field and dark field illumination conditions.

For the bright field evaluation, we exposed the FSM resist under the PC illumination condition (0.93 NA, att. PSM, 0.8-0.5 Sigma, Resist thickness: 1700 nm). The FSM resist demonstrated superior resolution, decent profiles and good process windows under the PC condition. Shown in Fig. 10 are x-section pictures of 65 nm semi-isolated and isolated lines.

![Figure 10. X-section pictures of the FSM resist under the PC illumination condition.](image-url)
prevent potential contamination of the immersion tool. Identical illumination conditions were applied to both dry and immersion lithography. As shown in Table 3, the FSM resist has decent process windows for the 65nm semi-isolated lines even with a very stringent spec (+/- 3nm). When put under the immersion condition, the resist demonstrated further improved DOF for the semi-isolated features. The profiles of the resist under the dry and immersion conditions are identical.

Table 3. Process windows of the FSM resist under both dry and immersion conditions (target CD: 65nm; spec: +/-3nm).

<table>
<thead>
<tr>
<th>Feature</th>
<th>Max EL/DOF</th>
<th>Dry condition</th>
<th>Immersion condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>65nmL/160nmP</td>
<td>5.80/0.24</td>
<td>4.88/0.45</td>
<td></td>
</tr>
<tr>
<td>65nmL/190nmP</td>
<td>8.84/0.44</td>
<td>7.00/0.50</td>
<td></td>
</tr>
<tr>
<td>65nmL/380nmP</td>
<td>9.94/0.32</td>
<td>8.56/0.48</td>
<td></td>
</tr>
</tbody>
</table>

For the dark field evaluation, we exposed the same FSM resist under the metal level illumination condition with immersion lithography (1.1 NA, att. PSM, 0.8-0.6 Sigma, Resist thickness: 1700 ̃). The FSM resist again exhibited superb lithographic performance for metal levels applications. Fig. 11 shows top-down pictures for 60nm dense trenches and 84nm semi-dense trenches. The process window of this resist for these two features is listed in Table 4.

Table 4. Process window of the FSM resist for 60nm dense trench and 84nm semi-dense trench under the metal level illumination condition.

<table>
<thead>
<tr>
<th>Feature</th>
<th>DOF@ 5% EL</th>
</tr>
</thead>
<tbody>
<tr>
<td>60nmS/120nmP</td>
<td>0.4</td>
</tr>
<tr>
<td>84nmS/240nmP</td>
<td>0.19</td>
</tr>
</tbody>
</table>

Figure 11. Top-down SEM pictures of the FSM resist under the metal level illumination condition.

Owing to their high Rmax, the FSM resists also showed excellent lithographic performance for contact hole levels applications. The evaluation for contact level was conducted under the immersion condition (1.2 NA, att. PSM, Resist thickness: 2000 ̃). As shown in Figure 12 and Table 5, the FSM resist has good resolution and process windows for 75nm dense and isolated contacts. The x-section of a semi-dense feature further confirms that the contacts have straight profiles and are clean down to the bottom (Fig. 13).
3.4 Material properties and lithographic performance of 193nm resists based on naphthol.

As discussed above, the fluorine-containing HFA and FSM acidic functionalities could greatly improve the dissolution properties of the resulting resist polymers. However, the fluorine content of these groups also tends to decrease the etch resistance of the resists. To eliminate the adverse effect of fluorine content on etch, we have also evaluated non-fluorinated acidic groups and studied their impact on lithographic performance of the resulting resist polymers. One of such non-fluorinated acidic groups is naphthol.

The naphthol-containing monomer, 5-hydroxy-1-naphthalenyl methacrylate (NAMA), was obtained from St-Jean Photocchemicals through a collaborative project. A homopolymer of NAMA (PNAMA) with Mw of 14,800 and Pd of 1.8 was synthesized through traditional free-radical polymerization. The dissolution rate of PNAMA in 0.26 N TMAH developer was measured to be 80 nm/sec, confirming the naphthol group is an acidic group as designed. Although it is well-known that naphthalene is more transparent than benzene at 193nm, PNAMA is still quite absorbing at 193nm. The optical density of PNAMA is measured to be 3.1 \( \text{m}^{-1} \) at 193nm, much higher than those of HFA and FSM homopolymers.

Terpolymers with MADMA, NLM, and NAMA were synthesized. Table 6 summarizes the optical properties of MADMA/NLM/NAMA terpolymers with different NAMA concentrations. As expected, the optical density of the terpolymers increases as the NAMA concentration in the polymer structure increases. Despite the relatively high OD of the MADMA/NLM/NAMA terpolymers, a resist based on the terpolymer with 4
mol% of NAMA demonstrated good lithographic performance under a PC illumination condition (0.75 NA, att. PSM, Resist thickness: 2000 nm) (Fig. 14).

Table 6. Optical density of MADMA/NLM/NAMA terpolymers with different NAMA concentrations

<table>
<thead>
<tr>
<th>Polymer</th>
<th>OD (μm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MADMA/NLM/NAMA with 4 mol% NAMA</td>
<td>0.6</td>
</tr>
<tr>
<td>MADMA/NLM/NAMA with 7 mol% NAMA</td>
<td>0.72</td>
</tr>
<tr>
<td>MADMA/NLM/NAMA with 15 mol% NAMA</td>
<td>1.56</td>
</tr>
</tbody>
</table>

75nmL/200nmP

Figure 14. Top-down SEM pictures of 70nm lines in 200nm pitch with a NAMA resist.

Conclusions

In an effort to reduce/eliminate the swelling behavior associated with typical 193nm methacrylate resists, we have incorporated a series of acidic functionalities into the polymer structure and studied their impact on the material properties and lithographic performance of the resulting polymers. Polymers with the carboxylic acid functional group have demonstrated a swelling behavior in the partially exposed area, similar to the typical 193nm methacrylate resists. The incorporation of the HFA and FSM groups into the polymer structure could completely eliminate the swelling behavior and dramatically improve the dissolution properties of the resist polymers. Both HFA and FSM groups are transparent at 193nm and thermally stable.

Resist polymers with the FSM group generally exhibit a high $R_{\text{max}}$ in the aqueous base developer. The relatively acidic FSM group also profoundly affects the deprotection chemistry of the protecting groups on the resist polymer. As a result, resists based on FSM-containing polymers have shown excellent lithographic performance for line, trench and contact hole levels under the 45nm exposure conditions. Particularly, the FSM resists have demonstrated a superior bright field and dark field compatibility. In addition, due to the reduced fluorine content, resists with the trifluoromethyl sulfonamide group have improved etch resistance over the resists based on the FSM group. Furthermore, the FSM resists are totally immersion compatible. Thus, the FSM resist system offers a viable resist solution for 45nm node and beyond applications. Finally, we have demonstrated that the naphthol group could be used as an alternative non-fluorine-containing acidic group in the design of high performance 193nm resists.

Acknowledgement

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References


