Etch Properties of 193nm Resists: Issues and Approaches


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Polymer chemistries for 193nm resists are more or less defined and their lithographic performance is quite good to implement 100nm design rules. In spite of the use of high carbon containing adamantane or norbornene moieties in the polymer design, there exists etch selectivity as well as surface roughness issues after treatment with etch plasma. It is very much necessary to modify the etch plasma used for 193 nm resists to improve the surface roughness. Etch rates of several acrylate, methacrylate and hybrid type polymers are measured and compared. While the problem still exists, acrylates in general seem to offer better surface properties than methacrylates. On the process side, e-beam curing of 193nm resists offers improvement in both etch selectivity as well as surface roughness. It was found from the IR spectra of before and after e-beam cured films that e-beam curing reduces the carbonyl groups and compacts the resist film leading to etch improvements. Effects of three different e-beam curing processes (Standard, LT and ESC) on the methacrylate & hybrid type 193nm resists were studied with respect to resin chemistry changes, resist film shrinkage, pattern profiles, etch rates, and CD SEM stability. Etch rate, selectivity and resist surface roughness after etch of both methacrylate and hybrid resists were improved using the e-beam curing process. E-beam curing drastically reduces (from ca. 15% to 2 - 5 %) the CD SEM shrinkage; however, considerable shrinkage occurs during the curing process itself.

Keywords: 193nm resists, etch issues, e-beam curing

1. Introduction

Starting from last quarter of 2001, installation of high NA (>0.68) 193nm exposure tools are on-going at major DRAM and logic chip manufacturing companies targeting design rules of 130 nm and below. Several process issues of 193nm resists are also being addressed at the same time. One of the issues that faces the etch engineers is the unsatisfactory etch stability of 193nm resists. The problem is two fold. First the etch selectivity compared to 248 nm resists is lower and the second issue is surface roughness after the etch process. Since the polymers used in the 193nm resists are non-aromatic and cleave differently to the etch plasma than that of 248nm resists, modification of the etch process is necessary. Resist chemists are engaged in improving the etch issues by modifying the polymer backbone. As modification of polymer backbone often results in big differences in the lithographic performance, only minor modifications are being carried out. On the process side, e-beam curing of 193nm resists is found to offer improvement in etch as well as elimination of surface roughness issues[1-4]. In this paper we report the etch characteristics of several 193nm polymers/resists as well as the benefits of e-beam curing on the etch characteristics, CD SEM stability. Chemical changes in the resist during e-beam curing was also followed through FTIR analysis.

2. Experimental

2.1 Polymers and resist solution preparation:

Two types of 193nm polymers and resists viz. methacrylate and hybrid type, were chosen for the electron beam curing studies. Details of monomer and polymer synthesis are given else where[5-8]. Methacrylate resists were prepared by dissolving

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the polymer, 2 wt % triphenylsulfonium nonaflate photoacid generator (PAG) and 20 mol % triethyl amine base with respect to the PAG in ethyl lactate. The hybrid resist was formulated in a similar way but in propylene glycol monomethyl ether acetate (PGMEA), using the hybrid polymer.

2.2 Resist patterning:
Patterning of the resists were carried out as follows: the resist solutions were spin coated on organic B.A.R.C. (AZ® ArF-1C5D) coated silicon wafers, and softbaked (115°C for 60sec for methacrylate and 130°C for 60sec for the hybrid) to obtain a typical film thickness of 0.33 µm using a Tokyo Electron Clean Track Mark 8. The film thickness was measured with a Nanometrics Nanospec® 8000. The coated wafers were exposed using a Ultratech ArF excimer laser stepper, ArF Microstep™ 193L (NA 0.60, σ 0.70). Post exposure bakes (110°C for 60sec for methacrylate and 110°C for 90sec for hybrid) were generally carried out within 10 minutes after exposure. The baked wafers were developed with AZ® 300MIF, a surfactant-free developer containing 2.3 8% tetramethylammonium hydroxide (0.26 N), and rinsed with water. Inspection of the pattern profiles was performed using a Hitachi S-4000 scanning electron microscope (SEM).

2.3 Etch rate measurements:
Blanket etch rates of polymers or resists were measured on LAM etch machine. Poly-Si and oxide etch was carried out, respectively, using O₂/N₂/Cl₂ /HBr and O₂/N₂/C₂F₆ gas mixtures, unless specified otherwise.

2.4 Electron beam curing:
Electron beam curing was done using an ElectronCure™ electron beam process chamber (Electron Vision Corporation) at 3.75 keV and 6mA. The electron beam system utilizes a flood electron beam source that provides a uniform exposure over the entire area of the wafer being processed. A dose level of 2000 µC/cm² was used in this study. The principles of the electron source and details of operation can be found elsewhere[9]. Three different processes, namely standard (uncontrolled wafer temperature), LT (low temperature) and ESC (medium temperature) were conducted. Film thickness before and after e-beam curing was measured using an ellipsometer from J.A. Woollam Inc. using 21 map points. The FTIR spectra were collected using a Magna-IR 760 from Nicolet Instruments.

2.5 Line width slimming measurements:
Line width slimming was measured on a KLA 8100 CD SEM installed with a KLA-Tencor software version 3.1.4. The linewidth change over a period of time was measured using a 50% threshold at acceleration voltage 400 V and beam current 10 pA. The electron beam continuously irradiated the line throughout the measurement. Magnification was set at 100 k. Focus was adjusted on one line and the linewidth of a different, e-beam-unexposed line was measured at 6 sec intervals up to 120 sec. After 120 sec, CDs were measured every 30 sec up to 10 min. An average of three top-down measurements was taken for 0.15 µm CDs, and the linewidth change with respect to time was plotted.

Etch measurements were carried out on a LAM etch machine. Poly-Si and oxide etch was carried out using O₂/N₂/Cl₂/HBr and O₂/N₂/C₂F₆ gas mixtures, respectively.

3. Results and Discussion
3.1 Etch Rates of Methacrylate, Acrylate and Hybrid Type Resists:
Oxide etch rates of methacrylate resists A, B, C, acrylate resist D and hybrid resist E are provided in table 1. The methacrylate resist A, B and C consists of poly(2-methyladamantyl methacrylate /mevalonic lactone methacrylate), poly(2-methyladamantyl methacrylate/y-butyrolactone methacrylate), and poly(2-ethyladamantyl methacrylate/3-hydroxyadamantyl methacrylate/ norbornenelactone methacrylate), respectively. Acrylate resist D was formulated from poly(2-ethyladamantyl acrylate/3-hydroxyadamantyl acrylate/ norbornenelactone acrylate) and the hybrid resist E was formulated using poly(t-butylnorbornene)carboxylate /Maleicahydride/2-methyladamantyl methacrylate/mevalonic lactone methacrylate. Since the etch rates are measured under identical conditions, a direct comparison may be made.

<table>
<thead>
<tr>
<th>Resist</th>
<th>Etch rate(nm/min)</th>
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<tbody>
<tr>
<td>Methacrylate A</td>
<td>75.9</td>
</tr>
<tr>
<td>Methacrylate B</td>
<td>83.3</td>
</tr>
<tr>
<td>Methacrylate C</td>
<td>79.9</td>
</tr>
<tr>
<td>Acrylate D</td>
<td>85.9</td>
</tr>
<tr>
<td>Hybrid E</td>
<td>99.3</td>
</tr>
</tbody>
</table>
The difference between resist A and B is the lactone monomer. Six member lactone seems to be slightly better than five member lactone in terms of etch rate. No obvious difference was found between methacrylate resist C and acrylate resist D. Hybrid resist has high etch rate during oxide plasma compared to methacrylate or acrylate type.

3.2 Surface roughness issues of 193nm resists:

Figure 1 shows the surface SEM pictures of methacrylate resist B, acrylate resist D and hybrid resist E after etch treatment using an aggressive oxide etch plasma.

While the acrylate resist D seems to be better in terms of roughness, all the resists show severe surface roughness and hence it is necessary to use mild and optimized plasma conditions or other processes to improve the surface roughness.

3.3 Effect of e-beam curing on the etch rate and surface roughness after etch

E-beam curing process has been reported to improve the etch rates of 248 and 193nm resists [1-4]. Three different processes of e-beam curing namely standard (uncontrolled wafer temperature), LT (low temperature) and ESC (medium temperature) were studied to understand the influence of the curing processes on the etch rate, surface roughness and pattern profiles. After accounting for the film shrinkage during the curing process (see following paragraphs on the shrinkage during e-beam curing), the e-beam curing process offers about 25% improvement in the etch for the methacrylate resist A and about 20% improvement for the hybrid resist E. (Fig. 2)

Since the e-beam curing showed not only improvement in the etch resistance but also in the surface roughness, it was of interest to check the chemical changes in the resist.
3.4 Chemical changes of e-beam cured 193nm resists:

Figures 4 & 5 show the FTIR spectra of methacrylate and hybrid resists before and after various e-beam curing process of a resist film coated wafer. Scheme 1 and 2 provides the resist chemistry before and after exposure and PEB for typical methacrylate and hybrid resists.

![FTIR spectra of methacrylate resist](image1)

![FTIR spectra of hybrid type resist](image2)

The polymers before exposure and PEB are insoluble in resist developers. During exposure, acid is generated from the PAG and a catalytic cleavage of the acid sensitive groups of MAAdMA, MLMA and BNC occurs leading to a developer soluble polymer. This reaction leads to the solubility contrast in the exposed and non-exposed areas thus enabling the patterning process of lithography.

It has been reported that 193nm resists of the kinds shown in Scheme 1 undergo a loss of carbonyl groups upon e-beam curing and moderate changes in the C-H, C-H2 and C-H3 bonds in the 3000-2800 cm⁻¹ region [3-4]. In this study, the influence of three different processes, viz., standard, LT and ESC, on the level of carbonyl loss in the FTIR were observed. E-beam curing eliminates the two carbonyl peaks present between 1800 and 1700 cm⁻¹. The various e-beam curing processes do not show significant differences. The same observation was found for the hybrid type resist as well (Figure 5) indicating similar chemical changes (loss of carbonyl groups).

3.5 Effect of e-beam curing on the film shrinkage

More than 20 % film shrinkage occurs during the e-beam curing processing due to the compaction (free volume loss) as well as the loss of material mass (chain scission and cross-linking reactions). Methacrylates show 22-24 % while hybrid resists show 23-27 % film shrinkage under same e-beam curing conditions (Figure 6). Kim et al.⁴ have reported that resists based on poly(norbornene derivative/maleic anhydride) or "COMA" type shrink more (30 %) compared to methacrylate (18 %) using the same standard e-beam curing process as the current study. Although a direct comparison is not possible as the acid sensitive groups are different, it is reasonable to assume that the hybrid type would have shrinkage between that of COMA and pure methacrylate. The high shrinkage of the hybrid type resist compared to the methacrylate type may be due to formation of high volatile by-products during e-beam curing for low molecular weight (Mw = 6500 vs. 11500 for methacrylates) resins. Between the three processes, the difference in the film shrinkage is not significant at the e-beam dose studied. Standard process shows about 2-3 % higher film shrinkage than the LT process. The small difference can be attributed to the

![Scheme 1](image3)

![Scheme 2](image4)
differences in the temperature (highest for the standard and lowest for the LT process).

3.6 Effect of e-beam curing on the pattern profile

The contact hole profiles of the methacrylate resist before and after e-beam curing processes are shown in figure 7.

Upon e-beam curing, the contact hole CD size increases (hole widening), a phenomenon similar to the line width slimming of the line patterns during CD SEM observation[1]. For example, the CD size is 155 nm (measured on the top) before e-beam curing and it increases to 173 nm upon e-beam curing. Another observation is that the top of the profiles widens at a much higher rate than the bottom of the profiles. Between the three processes, the top and bottom CD difference (ACD) after e-beam curing is 18, 8 and 6 nm for the standard, LT and ESC processes, respectively. Since the ACD is least for LT and ESC processes, these two processes may be preferred over the standard process.

The line profiles also undergo rounding (top loss) phenomena, i.e., the top of the resist shrinks more than the bottom (resist-wafer interface) of the resist. Similar to contact holes, the ΔCD change is less for the LT and ESC process than for the standard process (figure 8). However, the ΔCD change trend is not so clear when the pitch is 1:3 and 1:5, as shown in Figure 9. When slightly T-topped profiles were e-beam cured, the T-tops are eliminated after the e-beam cure due to the top loss mentioned above, and no rounding is seen (figure 9).

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3.5 Influence of e-beam curing on the CD slimming of 193nm resists

A considerable decrease in the line width (CD slimming or hole widening) occurs during the CD measurement of 193nm resists. The slimming process can be fitted well with a triple exponential rate law, indicating three different processes contributing to the CD slimming [10].

The CD slimming after the e-beam curing was measured for both methacrylate and hybrid resists (figures 11 & 12). Perhaps due to the shrinkage during the e-beam curing process itself, the e-beam cured resists show drastic decrease in the shrinkage during CD measurement. The slimming was only about 2.5 % for the
methacrylate resist vs. 15 % before e-beam curing at similar conditions.

The decay constants calculated based on the following equation are provided in table 2 and 3.

**Triple Exponential Decay** ($\tau =$ half life)

$$CD = a_1 e^{\ln2 t} + a_2 e^{\ln2 t^2} + a_3 e^{\ln2 t^3}$$

Table 2 Decay constants for the methacrylate resist before and after e-beam (ESC process) curing

<table>
<thead>
<tr>
<th></th>
<th>Before EB curing</th>
<th>After EB curing</th>
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<tbody>
<tr>
<td>$a_1$</td>
<td>7.97</td>
<td>0.00</td>
</tr>
<tr>
<td>$a_2$</td>
<td>7.92</td>
<td>2.30</td>
</tr>
<tr>
<td>$a_3$</td>
<td>84.11</td>
<td>97.70</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>1.12</td>
<td>1.00</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>17.86</td>
<td>8.38</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>9.76E+13</td>
<td>6.80E+10</td>
</tr>
</tbody>
</table>

Analysis of the decay constants indicates that the fastest and most troublesome decay process is completely absent after e-beam curing, and the linewidth change can be described by a double exponential decay. The amplitude associated with the second decay constant ($\tau_2$) is considerably smaller after e-beam curing. The second decay process has been assigned to the evaporation of residual solvents. It is to be expected that during the e-beam curing process the residual solvent and other volatiles are mostly eliminated, a drastic decrease leading to almost no change in the CD during CD SEM measurements.

4. Summary

Dry etch characteristics of polymers and resists applicable for 193nm exposures as well as the issues are highlighted. It is very much necessary to optimize the etch conditions to minimize the surface roughness after etch of the 193nm resists. Acrylates seem to be slightly advantageous than the methacrylates. E-beam curing process eliminates the surface roughness issue. The influence of three different e-beam curing processes on methacrylate and hybrid type resists was studied with respect to resin chemistry changes, resist film shrinkage, pattern profiles, etch rates, and CD SEM stability. Methacrylate and hybrid type 193nm resists lose carbonyl groups with possibly a reduction in the free volume leading to improved etch resistance/selectivity. Methacrylate resist films shrink ca. 22-24% and hybrid resist films shrink ca. 23-27 % during e-beam curing. The LT process shows the least shrink compared to the ESC and standard processes. The ESC and LT processes were found to stabilize the patterns uniformly compared to the standard process. Etch rate and selectivity of both methacrylate and hybrid resists were found to be improved using the e-beam process. Perhaps the greatest advantage of using the e-beam curing process is the elimination of the surface roughness during
the etch process. All three processes used do not show the surface roughness after etch. E-beam curing drastically reduces (from ca.15% to 2-5 %) the CD SEM shrinkage; however, considerable shrinkage occurs during the curing process itself.

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References