EVALUATION OF MATERIALS FOR 193-nm LITHOGRAPHY

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The explosive growth in performance of microelectronic devices has been made possible by steady advances in microlithography and photoresist technologies. Tremendous efforts to extend optical lithography beyond the 0.25 micrometer boundary, as currently obtainable with KrF-excimer lithography, are ongoing. Although some similarities exist between the imaging chemistries involved in the 248 nm and 193 nm lithographies, different materials are needed due to the distinct difference in optical absorbance requirements.

Resist systems which can be developed with aqueous base would be preferred. However, it might well turn out that the targeted requirements can only be fulfilled by resist systems which involve some type of dry etch steps. This paper will focus on a positive tone resist system, which is based on novel silicon containing methacrylate polymers. Due to a unique combination of monomeric building blocks, polymers with high silicon concentrations and, at the same time, high thermal stability are obtained.

1. Introduction

It is due to steady advances in microlithography and photoresist technology that the explosive growth in performance of semiconductor devices, as it is observed today, has been made possible. Although being unclear for quite a while, it is generally accepted today that optical lithography will continue to be the dominant technique for the mass fabrication of advanced semiconductor devices. Strong efforts for pushing the limits of optical lithography to higher performance are observed. It is widely believed that 193-nm lithography (ArF-excimer) is the most

Received April 16, 1996
Accepted May 31, 1996
likely candidate for becoming the technology of choice to approach the ambitious sub-0.2 µm resolution target [1-3].

There are considerable differences in design of resist materials for 193-nm as compared to the materials used in deep-UV (248-nm) lithography. In both cases, resist systems involving some type of chemical amplification mechanism are believed to be required in order to achieve the targeted sensitivity range. However, different materials will be needed, since polyhydroxy styrenes, which are typically used for deep-UV photoresists, are too much absorbing at 193 nm for being used in single layer systems at this wavelength. Therefore, the synthesis of new polymers with tailor-made physical properties is required.

In this paper we wish to report on the progress made on our approach for a positive tone bilayer resist system [4]. We believe that the bilayer technology might turn out being a good compromise between process complexity and overall performance, since the good dry etch resistance of aromatics can be obtained without the need for a silylation process. The approach is outlined in Scheme 1. It involves new silicon containing methacrylate polymers bearing acid labile side groups. Due to a unique combination of monomeric building blocks, polymers with high silicon concentrations and, at the same time, high thermal flow stability, could be successfully prepared.

**Scheme 1:**

Process sequence involved in the image forming process:

A: Expose through mask;
B: Development in aqueous base;
C: Dry etching in oxygen plasma.

![Scheme 1 Diagram](image-url)
2. Experimental

Materials

The methacrylate polymers used in this study were prepared by standard free radical solution polymerization. Molecular weights were controlled by the nature and the concentration of the initiator, polymerization solvent and temperature, and finally by the use of a chain-transfer agent.

Lithography

Resist solutions were spin-coated onto an appropriately hardbaked planarizing layer. Resist applied substrates were exposed through a chrome/quartz mask, using a Lambda Physics LPF 205 excimer laser operated in ArF-mode (contact printing), and by using a SVGL Microscan prototype (193 nm) instrument for stepper exposures. After a post-exposure bake (PEB), the wafers were developed in dilute tetramethyl ammonium hydroxide solution (TMAH). Dry etching in oxygen plasma was performed in an Alcatel CF 2P instrument or on a Lucas Labs Helicon. Resist film thicknesses were determined after softbake by a Zeiss Axiospeed instrument, using a refractive index of 1.47, or with a Tencor Alpha Step 100 tool. Resist film dissolution rates were determined on an in-house built interferometric tool.

3. Results and Discussion

General

It has been realized before that bilayer resist concepts hold a big potential for the design of ultrahigh resolution imaging systems for 193 nm lithography [5-8]. We believe that this technology might well turn out to be the method of choice due to a balanced trade-off between process complexity and overall performance. A highly absorbing planarizing layer can be considered as a bottom antireflective coating. Our new resist approach is based on a new combination of methacrylate monomers. The monomeric building blocks lead to polymers with tailor-made properties and are easily incorporated into the resist polymers. MPTS is a versatile monomer, since it has unique physical properties due to an extremely high silicon content of 27 wt.-%. MAA, on the other hand, is known for introducing high Tg and is controlling the dissolution kinetics during development. If the MAA and MPTS monomers are combined with a third monomer, bearing an acid labile blocking group, which is responsible for creating an acid
induced polarity change, resist polymers with widely tunable physical properties become accessible (Scheme 2). In order to obtain polymers for a high performance resist, the ratio of each monomer in the polymer needs to be carefully balanced. In addition, also the nature of the acid labile blocking group is highly critical.

Scheme 2: Terpolymers involved in the bilayer resist system

**Thermal Analysis of Polymers**

The possibility to combine specific monomers opens an elegant way for the synthesis of polymers with widely tunable physical properties. Reversibly blocked methacrylic acid monomers (BMAA) are easily accessible: TPMA and EEMA by reaction of methacrylic acid with the corresponding vinyl ether, BUMA by combining methacryloyl chloride with tert.-butanol. In order to ensure sufficient dry etch stability, MPTS monomer ratios between 0.15-0.3 were used, leading to polymers with silicon contents of 10-15 wt.-%. The MAA monomer ratio was kept as low as possible to avoid adhesion problems on the planarizing layer, but at the same time needed to be sufficiently high to prevent thermal flow of the structured resist during the etch processes.
The TGA curves of terpolymers bearing acetal and ester type blocking groups are shown in Fig. 1. It is worthwhile to note the considerably higher decomposition temperature of the ester as compared to the acetal type polymers, which as a consequence have only a limited process window.

![Fig. 1: TGA traces of acetal (a) and ester (b) type terpolymers](image1)

![Fig. 2: Relationship between polymer composition and glass transition temperature](image2)

**Table 1:** Physical data of BMAA containing methacrylate polymers

<table>
<thead>
<tr>
<th>Polymer in Feed</th>
<th>wt-% SI MAA</th>
<th>Mole Fraction MAA</th>
<th>Mole Fraction BMAA</th>
<th>Mole Fraction MPTS</th>
<th>Yield (%)</th>
<th>GPC Mw (Mn)</th>
<th>Tg (C)</th>
<th>TGA wt.-loss between 160-300°C (% 10°C/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.1</td>
<td>0.10</td>
<td>0.75 (a)</td>
<td>0.15</td>
<td>91</td>
<td>11'800 5'300</td>
<td>2.22</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>10.3</td>
<td>0.20</td>
<td>0.65 (a)</td>
<td>0.15</td>
<td>90</td>
<td>13'500 6'100</td>
<td>3.35</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>9.9</td>
<td>0.30</td>
<td>0.55 (a)</td>
<td>0.15</td>
<td>88</td>
<td>14'200 6'200</td>
<td>2.28</td>
<td>110</td>
</tr>
<tr>
<td>4</td>
<td>9.8</td>
<td>0.35</td>
<td>0.50 (a)</td>
<td>0.15</td>
<td>89</td>
<td>11'750 5'500</td>
<td>2.14</td>
<td>134</td>
</tr>
<tr>
<td>5</td>
<td>10.3</td>
<td>0.40</td>
<td>0.45 (a)</td>
<td>0.15</td>
<td>81</td>
<td>15'500 6'400</td>
<td>2.42</td>
<td>139</td>
</tr>
<tr>
<td>6</td>
<td>15.3</td>
<td>0.30</td>
<td>0.43 (a)</td>
<td>0.27</td>
<td>83</td>
<td>14'500 3'900</td>
<td>4.07</td>
<td>80</td>
</tr>
<tr>
<td>7</td>
<td>15.2</td>
<td>0.40</td>
<td>0.35 (a)</td>
<td>0.25</td>
<td>89</td>
<td>16'100 6'300</td>
<td>2.58</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>0</td>
<td>1 (a)</td>
<td>0</td>
<td>85</td>
<td>11'100 4'700</td>
<td>2.36</td>
<td>153</td>
</tr>
<tr>
<td>9</td>
<td>11.6</td>
<td>0.3</td>
<td>0.5 (b)</td>
<td>0.2</td>
<td>95</td>
<td>13'100 4'800</td>
<td>2.74</td>
<td>&gt;100**</td>
</tr>
</tbody>
</table>

*) a = BUMA, b = TPMA; **) Onset of thermally induced removal of THP blocking groups,
A series of ester blocked terpolymers was prepared with various monomer ratios. The physical properties of these polymers are listed in Table 1. The data show that the glass transition temperature is strongly dependent on the polymer composition. MPTS has a strong plastizising effect, which needs to be compensated by the incorporation of MAA. The correlations between MAA concentration in the polymer and the glass transition temperature for two series of polymers, containing 10 wt.-% and 15 wt.-% silicon respectively, are plotted in Fig. 2. No anhydride formation, which would lead to matrix crosslinking, is occurring in the temperature range that we observed, since the correlation is quite linear.

**Dissolution Properties**

There are some distinct differences in the dissolution characteristics of materials based on phenolics and materials which contain carboxylic acid moieties. One needs to keep in mind the different acid strength of the two functionalities, leading to a different dissolution behavior in TMAH based developers.

![Graph 3a](image1.png)  
**Fig. 3a:** Dissolution rates of films from polymers 2-5 in TMAH developers of various concentrations

![Graph 3b](image2.png)  
**Fig. 3b:** Influence of MAA mole fraction on the dissolution rate in TMAH developers of various concentrations
In order to gain some insight about the dissolution properties of our polymers in developer solutions, the dissolution rates of a series of MAA/BUMA/MPTS polymers (1-5) were measured in aqueous TMAH solutions of various concentrations (Fig. 3a,b). It is obvious that the dissolution rates of the unexposed bulk films are strongly dependent on the molar fraction of MAA in the polymer and on the developer normality. Assuming that a complete deblocking of the ester moieties is feasible, the resulting total mole fraction of MAA would be 0.85. As a consequence, a tremendous difference in the dissolution speed between nonirradiated and irradiated zones of the resist film should be induced, leading potentially to resist materials of extremely high contrast.

Oxygen Plasma Etching

The etch selectivity between a novolac planarizing layer and a TPMA containing terpolymer 2 (mole fraction MAA=0.3, TPMA=0.5, MPTS=0.2) with a Si-content of 12% is plotted in Fig. 5. It is found that the etch selectivity is strongly influenced by the etching conditions. As expected, the etch selectivity is increased at elevated oxygen pressures. Etch ratios of >20 are feasible at oxygen pressures >3 Pascal. At these pressures, the novolac etch rate lies in a reasonable range of 170 nm/min (Fig. 4).

![Fig. 4: Etch rates of novolac and Si-polymer 2](image1.png)  ![Fig. 5: Dependency of etch selectivity on oxygen pressure measured on polymer 2](image2.png)
Lithographic Evaluation

Resist formulations were prepared by dissolving the polymers, along with various amounts of a photoacid generator, typically triphenylsulfonium triflate (TPST), in PGMEA. The total solid content was in the range of 16 wt.-%, leading after spin-coating and softbake to resist films of 0.25-0.3 micrometer thickness. The UV absorbance spectra of resist films containing various TPST loadings were measured on quars disks and are depicted in Fig. 6. Since the contribution coming from the pure polymer is measured to be only $A_{193}=0.038$, the total absorbance is mostly controlled by the TPST concentration in the lithographic film.

First imaging experiments were performed on a resist formulation mainly consisting of polymer 9 (99 parts) and TPST (1 part), dissolved in PGMEA. Films of 1/4 micron thickness were obtained by spin-coating ontop of a hardbaked layer of pure novolac at a speed of 5000 rpm and a subsequent baking step at 100°C for 1 minute. The lithographic evaluation started with contact exposures performed on our in-house tool. The resist system was exposed at 193 nm with a dose of 25 mJ/cm², subsequently post-exposure baked at 100°C for 1 minute and developed in a solution of 0.003 N TMAH, leaving behind a finely patterned surface. Pattern transfer down to the silicon substrate was then performed on our Alcatel etcher (oxygen plasma, 40 sccm, 50 Watt, 7 minutes). The material was able to resolve 0.5 micrometer line/space patterns, the smallest
features of our mask, with vertical sidewall profiles (Fig. 7a). Also the formation of “grass” has not been observed (Fig. 7b). In addition, it has already been reported that patterns of polymer 9 based resist have a thermal flow stability of at least 120°C, since no small and large pad line deformations have been observed [4].

A more detailed investigation of the same resist material was performed on the experimental SVGL Micrascan 193 nm exposure tool, which has a numerical aperture of 0.5. A hardbaked DNQ/novolac resist of 0.6 µm thickness was used as the planarizing layer in this case. If doses of 24 mJ/cm² were applied, the sub-0.2 micrometer resolution potential of our bilayer resist approach was demonstrated (Fig. 8a,b).
The dependency of variations in developer normality and PEB temperature on the resist contrast have been analyzed. Films of a resist which is based on a acetal type polymer were casted on top of bare silicon and processed. It is worthwhile to note that the resist contrast ($\gamma$) is virtually unaffected by the developer normality and is determined to be 10 (Fig. 9). For this particular

\[ \begin{align*}
\text{Fig. 8a:} & \quad 0.175 \ \mu m \text{ line/space pattern of resist from Fig. 7a, imaged at the Micrascan exposing tool (NA = 0.5).} \\
\text{Fig. 8b:} & \quad 0.20 \ \mu m \text{ line/space pattern of resist from Fig. 7a}
\end{align*} \]

\[ \begin{align*}
\text{Fig. 9:} & \quad \text{Dependency of sensitivity curves of acetal based resist on developer normality} \\
\text{Fig. 10:} & \quad \text{Sensitivity curves of acetal type resist at various PEB temperatures}
\end{align*} \]
formulation, standard 0.262 N TMAH developer can be used without dark erosion of nonexposed zones of the resist film. The use of dilute developers results in a small loss in resist sensitivity. The dissolution rates of exposed resist films are very high and virtually independent from the developer normality. As expected, also the PEB temperature has an influence on resist sensitivity (Fig. 10). Some loss of resist contrast is observed if the resist is baked at an elevated temperature of 120°C. This phenomena might be caused by some undesired side reactions of the leaving group, eventually leading to nonvolatile products which reduce the dissolution rate of the exposed resist film.

Also the imaging performance of resist materials based on BUMA containing polymers was elaborated. The switch to these materials seems attractive due to their higher stability against thermal decomposition. In addition, it has been demonstrated that the BUMA monomer can be successfully used in polymers for deep-UV lithography [9,10]. Preliminary lithographic results show that imaging is also possible with a resist material consisting of polymer 3 and TPST. We encountered difficulties in generating the same promising lithographic results as were found with the original formulation based on polymer 9. The ester type polymers that are obtained if similar monomer mole fractions are used (BUMA as compared to TPMA) are quite different with respect to glass transition temperature (Tg) and dissolution properties. We also found considerable differences in the morphology of the resist films, leading in some cases to nonhomogeneous films and, as a consequence, to nonuniform dissolution behavior of the irradiated zones of the films. In addition, BUMA is introducing a much stronger dissolution inhibiting effect than TPMA. We feel that the change from the acetal type to the ester type blocking group chemistry seems to introduce the need for significantly rebalancing the molar composition of the resist polymer, and also the use of alternative monomers might be worthwhile considering.

4. Conclusions

A positive tone bilayer resist system has been presented, which is based on novel methacrylate polymers bearing acid labile and silicon containing side groups. Due to a unique combination of the monomeric building blocks, polymers which combine high silicon concentration and high thermal flow stability were successfully accessed. If applied on top of a hardbaked novolac planarizing layer, the sub-0.2 micrometer resolution potential has been demonstrated. The lithographic performance is strongly dependent on the physical properties of
the silicon containing polymers, namely the nature of the acid labile blocking group. Therefore the monomer ratios in the polymers need to be carefully balanced.

5. Acknowledgments
The authors wish to thank Carlo Mertesdorf and Norbert Muenzel for the helpful discussions, and Niklaus Bühler, Reinhard Schulz and James Popplewell for supporting this work.

6. References