RESIST DESIGN CONSIDERATIONS FOR DIRECT WRITE AND PROJECTION ELECTRON-BEAM LITHOGRAPHY TECHNOLOGIES

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The deep-UV positive acting chemically amplified resists referred to as CAMP6 and ARCH were evaluated for use in direct write and projection electron-beam lithography technologies. In the evaluation we compared the lithographic characteristics of each resist under electron-beam exposure using primarily a JEOL JBX-5D11 system operating at 50 KeV and a Scattering with Angular Limitation Projection Electron-Beam Lithography (SCALPEL) tool operating at 100 KeV. Both resists exhibited contrast values > 5 and resolution well below 0.20 µm. CAMP6 was however plagued with excessive film loss after the process post-exposure bake step and required a protective coating on the film to improve process latitude. A series of ARCH formulations were observed to eliminate any film loss caused by either heating during exposure or the high vacuum environment of the exposure tool. When exposed on the direct write tool, 0.09 µm wide features at a dose of 11 µC/cm² were delineated. Sub-0.25 µm images were obtained using the projection system at a dose of 19 µC/cm².

I. INTRODUCTION

The drive towards increasing circuit pattern density and reduced tolerances of the critical dimension (CD) of the pattern, has resulted in the investigation of numerous advanced lithographic technologies. Direct write electron-beam lithography has been the technology of choice when attempting to minimize the CD of a device or test structure being fabricated. It is, however, not the appropriate technology for volume production of any integrated circuit. The use of an electron-beam as the exposure source in projection systems should provide high throughput coupled with the resolution capability of direct write tools. One such system is termed Scattering with Angular...
Limitation Projection Electron-Beam Lithography (SCALPEL). This system contains features that distinguish it from previous projection electron-beam approaches namely a step and scan writing strategy and a scattering mask. The experimental system as described by Berger et al. [1] works at a 100 keV accelerating voltage. The principle of operation of the SCALPEL tool is illustrated in Figure 1.

![Figure 1. Schematic depicting the principle of operation of the SCALPEL tool.](image)

As electrons pass through a mask, which consists of a low atomic number material patterned with a high Z material, scattering occurs resulting in different angular distributions of electrons from the patterned and unpatterned regions. In the back-focal plane of the projecting lens system the electrons are distributed according to their angle of scatter. An aperture placed in this plane acts as an angularly limiting filter. The contrast obtained is governed by the size of the aperture. A small field of view tool which uses the SCALPEL approach has been built to investigate the capabilities and the limitations of this new projection electron beam technology [2].

To meet the high throughput (30 - 200 mm wafers/hr.) and resolution (< 0.10 µm) requirements dictated by potential users of the electron-beam technology, resists in which the radiation induced chemistry is based on chemical amplification are viewed as the most viable materials. Two families of CA resists have been investigated for use in electron-beam lithography and are referred to as CAMP6 and ARCH. Both have been extensively characterized in Deep UV (λ = 248 nm) lithography [3]. The CAMP6 formulation required the use of a protective coating to provide any process stability [4]. Elimination of the coating and improvements in the overall lithographic performance over the CAMP6 resist was obtained with the development of the ARCH materials. The
ARCH formulation is a multi-component dissolution inhibition type material which has exhibited superior resolution when exposed to direct write electron-beam and x-ray radiation [5]. This material provided a path to the identification of a resist capable of < 0.10 µm resolution. Details of the evolutionary development and processing performance of the CAMP6 and ARCH materials when exposed on both a 50 KeV direct write and a 100 KeV projection electron-beam exposure systems will be presented.

II. EXPERIMENTAL

CAMP6 and ARCH resist films of thickness ranging from 0.35 - 1.0 µm were spin coated onto hexamethyldisilazane primed silicon substrates at spin speeds ranging from 1500 - 4000 rpm. No overcoat material was used with ARCH and all substrates were pre-exposure hot plate baked at temperatures ranging from 105 - 125 °C for 1.0 min.

Direct write electron-beam exposures were performed on a JEOL JBX 5DII system operating at 50 KeV and 10 nm spot size, an Etec shaped beam vector scan exposure system operating at 50 KeV or a Cambridge EBMF model 10.5 vector scan system operating a 40 KeV, 2.048 nm field size, 1.0 nA spot current and 0.05 µm address. The basis of the SCALPEL tool is a transmission electron microscope. The machine also has a wafer stage with x,y,z and θ movement which allows for step and repeat printing across an area of 20 mm x 20 mm. A Faraday cup has been installed in the experimental tool to enable us to measure incident exposure currents accurately.

One square millimeter masks which consist of a 1000 Å thick silicon nitride membrane supporting patterns of 500 Å thick tungsten were used in all SCALPEL exposures. The SCALPEL tool demagnifies the mask by a factor of two. It consists of 6 areas of 450 µm X 300 µm as seen Figure 2. Each area of the mask has specific patterns to evaluate CD control and the proximity effects on the resist.
It is important to note that this mask has 37.3% of clear area. It means that during exposure with the SCALPEL experimental tool 37.3% of the 450 X 450 µm area on the wafer is in fact exposed. This is a correction factor that is taken into consideration when comparing doses from conventional e-beam systems to the SCALPEL projection electron-beam tool.

Exposed resist films were either immediately removed from the exposure tool or allowed to sit for a specified delay time in the environment of the tool or in the clean room prior to the process post-exposure bake (PEB) step. All samples were subsequently post-exposure baked on a hot plate at temperatures ranging from 105 - 130 °C for 1.0 min. The samples were immersion developed in 0.13-0.26 N tetramethyl ammonium hydroxide (TMAH) for 1.0 min and rinsed in de-ionized water for 1 - 2 min and spin dried. Mask and patterned wafer metrology was performed on an Hitachi S-6000 scanning electron microscope (SEM). Resist resolution performance was evaluated using an Hitachi 2400 SEM.

III. RESULTS AND DISCUSSION

III.1 Direct Write Electron-Beam Exposure of CAMP6 and ARCH Resists

CAMP6 is a chemically amplified resist consisting of poly(4-acetoxy styrene-co-4-t-butoxycarbonyloxystyrene-co-sulfur dioxide) PASTBSS and a nitrobenzyl ester photoacid generator
The overall aromatic monomer to sulfur dioxide ratio in the polymer was 3:1 and a 60:40 proportion of acetoxy styrene to 4-t- butoxycarbonyloxystyrene.

The direct write electron-beam sensitivity of the two component resist was strongly dependent on the process post-exposure bake condition and for a PEB temperature range of 115 to 130 °C, the sensitivity could be improved from 25 to 7 µC/cm² @ 40 KeV. The affect of the post-exposure baking conditions on imaging of 0.25 and 0.50 µm line and space patterns is depicted in Figure 3. Resist wall profile degradation is observed at the extreme PEB temperature of 130 °C and represents a condition providing only marginal process latitude.

![Figure 3. Change in resist image profile as a function of process conditions; a) PEB = 115 °C, Dose = 25 µC/cm², b) PEB = 130 °C, Dose = 7 µC/cm²](image)

Improvements in resolution were achieved through the use of an Etec shaped beam vector scan electron-beam exposure tool operating at 50 KeV. Figure 4 is an SEM photomicrograph of 0.20 µm line and space patterns in 0.30 µm thick resist. A dose of 14 µC/cm² and PEB conditions of 115 °C for 1 min was used to generate the patterns.

![Figure 4. SEM photomicrograph of 0.20 µm lines and spaces in 0.30 µm thick CAMP6 resist.](image)
To improve the post exposure delay time latitude of CAMP6 an overcoat/topcoat is required. The top protective coating has provided stability when exposed to 248 nm radiation on the order of ~10 min. Use of the topcoat for films exposed to electron-beam radiation has resulted in degradation of the line edge quality of the resist pattern. The difference in edge quality for samples exposed to 248 nm and electron-beam radiation are shown in Figure 5. The increased edge roughness in the case of the electron-beam exposed sample is attributed to the partial crosslinking of the topcoat film when exposed to electrons.

![Figure 5. SEM photomicrographs of electron-beam (a) and deep-UV (b) exposed CAMP6 samples containing a topcoat.](image)

The elimination of the use of a topcoat to improve time delay latitude as well as improving the resolution capability of CAMP6 beyond 0.20 \( \mu \)m has produced the newer generation chemically amplified ARCH resist formulation.

A typical electron-beam exposure response curve for ARCH resist exposed at 50 KeV containing a 6 % loading of the photoacid generator is displayed Figure 6. The baking conditions for both the prebake and post-exposure bake steps were 115°C for 1 minute The resist contrast was calculated to be greater than 7. Under these conditions and for an initial film thickness of 0.50 \( \mu \)m, the measured sensitivity is 11 \( \mu \)C/cm\(^2\).
For exposures performed on JEOL electron-beam exposure system patterns on the order of 0.10 µm and in 0.30 µm resist thick films were resolved. Dark field images at 0.10 µm dimensions are shown in Figure 7.

Figure 6. Exposure response curve for ARCH resist at 50 KeV.

The excellent resolution of the resist can also be seen in Figure 8 where 0.09 µm bright field lines and spaces are resolved in 0.30 µm thick resist. Depending on the process post-exposure bake condition the dose required to generate these patterns ranged from 9-15 µC/cm² @ 50 KeV.

Figure 7. SEM photomicrograph of coded 0.10 µm line/space pairs obtained at 50 keV.
The well known trade-off of higher sensitivity and reduced process latitude is evident in the data given in Table 1. The data also suggests that achieving the goal of a 10 µC/cm² @ 100 KeV resist with acceptable process latitude has not been obtained. This is unlike what has been observed for ARCH when exposed to 248 nm radiation where no change in a 0.30 µm CD over an 8 °C temperature range at a dose of 30 mJ/cm² was observed. The difference observed when the resist is exposed to electrons can be attributed to the non-optimized acid formation efficiency process compared to what occurs when the material is exposed to deep-UV radiation.

The evaluation of ARCH as a positive acting, electron-beam resist also consisted of determining what effect heating during exposure and the high vacuum environment of the exposure tool could have on the lithographic performance of the material. Samples were exposed at a dose range of 8-20 µC/cm² @ 40 KeV and removed from the tool to determine if a partial relief image of

Table 1. Effect of PEB conditions on ARCH exposure dose latitude

<table>
<thead>
<tr>
<th>*PEB Temp. (°C)</th>
<th>ΔCD/(µC/cm²) (nm)</th>
<th>% Exp. Dose Latitude</th>
<th>*Sensitivity (µC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>5.5</td>
<td>18</td>
<td>12</td>
</tr>
<tr>
<td>120</td>
<td>12</td>
<td>14</td>
<td>9</td>
</tr>
<tr>
<td>125</td>
<td>&gt;20</td>
<td>~0</td>
<td>7.5</td>
</tr>
</tbody>
</table>

*Time = 1.0 min, *50 KeV

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the pattern in the resist was observed. Evidence of film evolution from the exposure step is an indication that the activation energy for the acid catalyzed deprotection reaction is low enough to cause partial removal of the film in the exposed areas. For ARCH which contains a carbonate protecting group no exposure induced film evolution was observed. This is contrary to what has been observed for an experimental resist which contained an acetal protecting group and an acid generator of nearly equivalent strength to that used in the ARCH formulation. Figure 9 is a plot of % film loss after exposure as a function of varying the component containing the acetal protecting group in the resist. The dose used to generate the plot was 10 µC/cm² @ 40 KeV.

![Figure 9. Effect of heating during exposure on the extent film loss for a resist containing an acetal protecting group.](image)

It has been calculated that during exposure a modest temperature rise to 40 - 50 °C can be realized. For those materials where the deprotection reaction occurs at temperatures below 40 °C, film loss in the exposure chamber will lead to unwanted contamination of critical working parts of the tool. This example therefore represents a type of CA resist which is incompatible for use in electron-beam lithography.
Figure 10 represents a plot of the change in the size of a nominal 1.0, 0.5, and 0.30 µm wide ARCH resist feature as a function of varying the time an exposed sample is maintained in the electron-beam tool prior to removal and post-exposure baking. For feature sizes ranging from 0.30 - 1.0 µm, there is no noticeable size change over a 15 hr delay period. It can be concluded that the components of the resist and radiolysis products do not volatilize in the vacuum environment of the tool as well as at the elevated temperatures the wafer reaches during the exposure. In addition there is no measurable diffusion of the radiation generated acid at room temperature over the delay period investigated. These results were used in evaluating the ARCH resist when subjected to 100 KeV projection electron-beam exposures.

III.2 ARCH Projection Electron-Beam Exposure Results

Initial evaluation of the lithographic characteristics of the ARCH containing a 3 % acid generator loading produced images shown in Figure 11 a and b. Exposure dose requirements depended on the feature type and tone. Coded 0.25/0.35 µm lines/spaces features from bright and dark fields of the mask were resolved at a dose of 26 and 42 µC/cm² @ 100 KeV, respectively. The rounding of the images is due to the inherent astigmatism of the experimental exposure tool. The difference in dose to
resolve the images in bright and dark field is due to the difference in back scattered electron dose as discussed by Watson elsewhere [6].

When the ARCH formulation containing the 6 % acid generator loading was used, a 35% increase in sensitivity of the resist system was observed. 0.25 µm lines/spaces were resolved in bright and dark field at doses respectively of 19 and 22 µC/cm². Further enhancement in the sensitivity of ARCH as well as improving the performance of the experimental projection e-beam tool are in progress.

IV. CONCLUSIONS

The development and evaluation of the positive acting chemically amplified resists CAMP6 and ARCH have provided a path to the identifying a material which is acceptable for use in both direct write and projection electron-beam lithographies. Both materials exhibited high contrast and resolution. The observance of both properties are essential when attempting to insert an advanced lithography technology on to the National Lithography road map.

The compatibility of the resist formulation and the observed radiation induced chemistry during the standard operating conditions of an electron-beam exposure tool has reduced the number of CA resists which can be used in this technology. The high desire of using a commercially available
DUV resist in electron-beam lithography is therefore not a given. Exposure induced heating affects of film when present in the high vacuum environment of the electron-beam exposure tool eliminates the use of resists in which the acid catalyzed deprotection reaction is characterized by a low activation energy process. Resist film evolution in the exposure tool represents a totally unacceptable characteristic and precludes the use of a resist in which this is observed.

For the two families of resists evaluated in this study, the higher level of film loss after the process post-exposure bake step and the need to use a top protective coating to enhance process latitude has made the CAMP6 resist less desirable. The unforeseen crosslinking reaction occurring in the overcoat film during electron-beam exposure again exemplifies that careful consideration must be taken before a material which is applicable for use in photo-lithography can be used in the higher energy exposure based tools.

It was shown that introduction of the multi-component resist ARCH vastly reduced the film loss (3 %) observed after the PEB step and significantly improved the process control of these materials. High contrast was evident and provided the ability to simultaneously print bright and dark field images at feature sizes below 100 nm. It is envisioned that the printability of features below 50 nm is possible if the aspect ratio of the resist is scaled appropriately and optimization of the process post-exposure bake step is performed. Under SCALPEL exposure, the sensitivity of ARCH containing 6 % photoacid generator varied from 19- 22 µC/cm² depending of the tone and type of SCALPEL mask features. The sensitivity of the resist system under SCALPEL exposure needs to be improved even in bright field areas to reach the target dose of 10 µC/cm² @ 100 keV. The observed resist sensitivity and resolution should increase as mask design, exposure dose control and radiation induced acid formation process are improved.

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REFERENCES


