POSITIVE TONE DRY DEVELOPMENT PROCESS FOR 0.25 µm LITHOGRAPHY

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The etching and resists stripping issues by using new safer silylation solutions for liquid phase silylation (LPS) of the positive tone diffusion enhanced silylated resist (DESIRE) process are presented. The silylation process and the composition of the silylation solution have been optimized. Characterizations of the silylation process have been performed using Fourier Transform Infrared absorption (FTIR), Rutherford Backscattering Spectroscopy (RBS), and a staining technique. A constant Si-depth vs. linewidth have been observed, resulting in a good linearity. Several solutions for the proximity effect reduction have been suggested. The dry development conditions have been optimized in the view of the reduction of the proximity effects. The thermal and chemical stability of the silylated resist have been studied. In order to explore the limits and the reduction of the proximity effects, this process has also been evaluated using off-axis illumination (OAI) and phase shifting masks (PSM).

1. Introduction

The demand for more dense ULSI devices has driven lithography into the 0.25 micron regime, which requires high resolution with wide process latitudes, good linewidth control over severe topography, reduction of proximity effects, and very precise overlay accuracy. Meanwhile a high throughput must be maintained and large field sizes must be achieved. The transition towards higher numerical apertures (NA) and shorter wavelengths has lengthened the lifetime of optical lithography. The first generation of 64 Mb DRAM devices has been realized using i-line lithography (λ=365 nm) using steppers with variable NA and partial coherence factors1. The resolution limitation has been alleviated by increasing NA and decreasing the wavelength. However higher NA lenses extend the limit of resolution at the expense of a rapid loss of depth of focus (DOF). On the other hand, the transition towards shorter wavelengths each time requires developments of all aspects of the technology. The most serious problem for shorter wavelength lithography (DUV) is linewidth control over topography due to interference effects caused by reflections of topographic features and non-uniform reflectivity on the multiple film layers over topography. Several techniques have been suggested to overcome these problems, such as phase shifting masks2, off-axis illumination techniques3, and top surface imaging4. Each technique has its advantages, drawbacks, and limitations. PSM enhance the resolution and DOF using the same exposure tools.

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Their main drawbacks are mask design and fabrication difficulties, mask inspection and repair of defects. However, the weak PSM (such as RIM, attenuated half tone) can be applied to real devices without special difficulties of layout, but they reveal poor resolution improvements for dense structures. Off-axis illuminations techniques have received a lot attention because the resolution limit and process latitudes for dense feature sizes are improved and because they are more easy to apply. The combination of weak PSM with weak OAI has proven to be useful for real process applications. Device production, however, additionally requires good control of Critical Dimension (CD) over topography. While maintaining single layer process simplicity, the DESIRE process has been suggested as an attractive solution to cope not only with limitations of resolution and process latitudes, but also with linewidth variations due to reflections over steps. The cost of DESIRE process has been reported to be attractive for DUV lithography. Therefore, surface imaging may become a mandatory process for patterning on topographic layers. The optimum combination of attenuated PSM, optimum OAI, and the DESIRE process is getting more important for the demand of the higher density devices and depends on the each specific layer. Attenuated PSM provide enhancement for the isolated patterns, while OAI improve the dense structures and the DESIRE process can be maintained the good CD control over topography even at shorter wavelengths (248 nm and 193 nm). However, these techniques have until now not received a wide acceptance as a production worthy process because conventional steppers and resists improvements have allowed to keep pace with industry needs so far. Moreover, tremendous efforts of exploring the limits of optical lithography might be proved the production worthy techniques, such as the commercial available defect free weak PSM, a suitable implementation of OAI with stepper configuration, and reproducible silylation and dry development equipment from a reliable supplier.

2. Experimental

The wafers were coated with a newly formulated resist (from JSR Electronic) which consist of a novolac based resin with a photo-crosslinker at 4500 RPM for 30 s and soft baked on a hot plate at 140 °C for 60 s, resulting in a resist thickness of 1.1 µm. Exposures were carried out on an ASM-L PAS 5000/70 (NA 0.42) deep-UV (λ=248 nm) stepper. Liquid phase silylation was carried out in a modified MTI track at room temperature using Bis(dimethylamino) dimethylsilane. The liquid phase silylation bath consists of silylating agent B[DMA]DS with PropyleneGlycol MethylEther Acetate (PGMEA) a resist solvent and n-decane as a safer solvent. After liquid phase silylation, the wafers were rinsed with n-decane, and subsequently baked on a hot plate at 90°C for 60 s before the dry development. Dry development was performed on an MRC MIE (Magnetron enhanced reactive Ion Etching) 720 etcher using a 1 step and a 2 step process or on a LAM Transformer Coupled Plasma (TCP) 9400. The linewidths were measured using a low voltage Hitachi S-6100 scanning electron microscope (SEM) and on cross-sectional views from a high voltage SEM (S-4100).
3. Results and Discussion

Liquid phase silylation

In the DESIRE process hexamethyldisilazane (HMDS) has typically been used in the gas phase as the silylating agent, although an alternative silylating agent, 1,1,3,3-tetramethyldisilazane (TMDS) has also been demonstrated some interesting advantages over HMDS. Liquid phase silylation using B[DMA]DS with N-methyl-2-pyrrolidone (NMP) in xylene with Plasmask 200-G for i-line exposures exhibited important advantages over gas phase silylation (GPS), such as (i) an improved silicon contrast, (ii) extremely high Si incorporation (up to 25 wt. %), (iii) room temperature silylation. Therefore, LPS can relax equipment requirements and cost. Liquid phase silylation was found to be useful for both i-line and DUV (248 nm) exposures. LPS for i-line exposures with Plasmask 200-G results in negative tone images. For DUV exposures, crosslinking is induced in the exposed areas leading to positive tone images. In the case of the DUV exposures, the positive tone DESIRE process has been reported using a newly formulated resist (which consists of a novolac based resin with a chemical photo crosslinker). DUV exposures convert the chemical photo-crosslinker to a crosslinked network in the exposed regions. This DUV induced crosslinking inhibits the Si-diffusion in the exposed areas. The liquid phase silylation is performed at room temperature. Dry development results in positive tone images. The liquid phase silylation for both i-line and DUV exposures used the B[DMA]DS with NMP as a diffusion promoter and xylene as a solvent. The positive tone DESIRE process using LPS has exhibited several advantages, such as an improved silylation contrast, an increased Si concentration, the use of room temperature silylation, a simpler process without post exposure baking steps, etc. Besides the lithographic performance, safety and cost issues have been studied to implement it into a manufacturing environment. We have reported the application of new safer solvents and a feasibility study of liquid phase silylation on a track. In earlier studies, for liquid phase silylation NMP was used as a diffusion promoter and xylene as a solvent. The NMP concentration had a strong influence on the diffusion behaviour of the silylating agent. Therefore the NMP concentration is very critical for the process. Because of safety reasons, xylene is not desirable for high volume production. We have been investigating safer solvents as an alternative for xylene. The PGMEA that is used as a safe resist solvent has been considered as a replacement for NMP. A relatively high soft bake temperature (140 °C for 60 s) has been used compared to conventional resist processing conditions. This temperature is needed to prevent dissolution of the resist by the silylation solution. This dissolution is mainly due to the solvent. We have investigated alternative aprotic (which do not react with hydroxyl groups) solvents from the viewpoint of safety, cost, dissolution of the resist, compatibility with the PGMEA, good carrier of the silylating agent. N-decane is an attractive alternative candidate. The new silylation solutions have been shown to exhibit several
advantages over xylene and NMP, such as, (i) safety, (ii) reduced dissolution rate of the resist, (iii) relaxation sensitivity to the silylation solution.

Characterization of silylation

Characterizations of the silylation reaction have been performed using FTIR, staining techniques, and RBS. FTIR spectroscopy has been used for the quantitative determination of the Si incorporation. The integrated absorbance of 1300-1230 cm\(^{-1}\) (Si-C bond deformation) was chosen as a quantitative measure for the built-in Si. Figure 1 shows the influence of the silylation agent concentration. This plot indicates that the optimum silylation concentration is 5-10% and by increasing the silylation concentration above 15% the Si content decreases again. Because by increasing the concentrations of the silylating agent, the resist will become insoluble and impenetrable and Si diffusion is retarded\(^{11}\). The concentration of the silylating agent is significant from the viewpoint of cost. This plot also shows that the exposed area does not contain any Si.

RBS spectroscopy was used to determine the Si atomic concentration and the Si-depth profile. Figure 2 shows that the Si concentration (6 atomic % or 18 wt. %) is larger than compared to that of the gas phase silylation in the negative DESIRE process (3 atomic % or 9 wt. %). This Si-concentration was observed to result in an increased dry development selectivity (25:1) using the same dry development conditions (compared to 14:1 in the case of TMDS [GPS]).
Figure 3 shows RBS measurements with various silylation agent concentrations using this process. This plot indicates that the Si atomic concentration is constant for silylation agent concentrations above 5%. The exposed areas do not contain any Si, because the exposed areas cross-link during the exposure. These results indicate that the optimum silylation agent concentrations are between 5-10% and the positive tone DESIRE process using the new safer solvents n-decane and PGMEA improves the silylation contrast and dry development selectivity. In order to optimize the composition of the silylation solution, the E-D (Exposure-Defocus) windows have been investigated by measuring a ±10% linewidth criterion.

(a) Silylation solutions (10:35:55)  
(b) Silylation solutions (5:45:50)

Fig. 4 Measured process windows showing the influence of silylating agents using transmission mask (σ = 0.58) at the various silylation solutions. (a) B(4MA)DS: PGMEA: N-decane (10:35:55), (b) B(4MA)DS: PGMEA: N-decane (5:45:50).
Figure 4 indicates that the influence of the silylating agents on process windows appears to be identical to the results of FTIR spectroscopy. This plots show that 2.0 µm DOF for 0.25 µm l/s of 10 % B[DMA]DS concentration is wider than that of 5 % B[DMA]DS concentration (1.6 µm DOF). Therefore 10% silylating agent concentration used as a standard process in the rest of the study.

**Linearity**

Linearity is one of the most critical issues for the positive tone silylation process. Figure 5 shows the non-constant silylation depth for various linewidths (as revealed by the SEM cross-section after delineating the silylated areas by an O₂ plasma) using a chemically amplified resist. Overflow of large silylated areas has been reported to result in non-linear performance in the SAHR process. A wet development step before silylation has been proposed in order to solve this problem, however this treatment is not practical because of increasing complexity of the process and the cost. We have investigated the linearity of positive DESIRE process with new silylation solutions using a staining technique and by measuring linewidths after dry development. We do not observe linearity problems with this positive tone DESIRE process. Figure 6 shows the constant Si-depth vs. linewidth, resulting in a good linearity (see Fig. 7). These SEM micro graphs illustrate the higher silylation angle (α) (see Fig 8a in the case of GPS) with small vertical swelling compared to that of the negative tone DESIRE process (i-line) using LPS with Plasmask 200-G (see Fig. 8 b). Linearity problems have been observed in the case of non-optimum process conditions (which means lower silylation contrast). Over-silylation on the larger areas can be avoided by using optimum process and resist conditions (such as soft bake conditions, optimum resists design, and high silylation contrast process).

**Fig. 5** Cross-sectional SEM micrograph of silylated profiles using a chemically amplified resist.

**Fig. 7** Experimentally measured linearity using the positive tone DESIRE process.
Fig. 6  
SEM micrographs of silylated profiles (248 nm, 0.42 NA) of the positive tone DESIRE process using liquid phase silylation (B[DMA]DS): (a) 1.0 µm dense lines, (b) 1.0 µm isolated lines, (c) 0.5 µm dense lines, (d) 0.5 µm isolated lines, (e) 0.3 µm dense lines, (f) 0.3 µm isolated lines.

Fig. 8  
SEM micrographs of silylated profile (1 µm lines): (a) negative tone DESIRE process using gas phase silylation (TMDS) (248 nm, 0.42 NA), (b) negative tone DESIRE process using liquid phase silylation (B[DMA]DS)(i-line, 0.48 NA).
Proximity effect

For the resolution enhancement techniques such as PSM, OAI, and the DESIRE process operating close to the resolution edge, local proximity effects are typically observed, showing up as small differences in linewidth between inner and outer lines of periodical structures and isolated lines. As minimum feature size is getting closer to the resolution limit, it becomes difficult to find an optimum single exposure dose that is satisfactory for different size and geometries (dense lines/spaces (l/s), isolated line and spaces, contact windows). For implementation on real devices, the proximity effect should be reduced. The proximity effect is influenced by optical parameters (NA, partial coherence, wavelengths, masks tone) and processing conditions (silylation and dry development).

Fig. 9  Measured E-D windows showing the influence of the proximity effects at DUV exposures (λ=248 nm, 0.42 NA, σ=0.58): (a) & (c) positive tone DESIRE process using liquid phase silylation, (b) & (d) negative tone DESIRE process using gas phase silylation.
The proximity effect is reduced by using a high silylation contrast process and/or by optimising the dry development process conditions (resulting in minimal micro loading effect) such as low operating pressures (for obtaining anisotropic etching) and high plasma densities (high etch rate and selectivity). In dry developed processes, a positive tone resist process exhibits less proximity effect compared to the negative tone process. This is due to the combined effect of aerial images and process conditions. During the dry development, silylated resist will be etched by physical sputtering, resulting in a linewidth loss (process offset). For the simulated aerial images of the positive tone resists, the isolated lines are wider than the dense lines for zero process offset. However, this difference in linewidth decreases with increasing process offset. However, this difference in linewidth decreases with increasing process offset. For quarter micron lines (resolution edge) in DUV stepper (λ=248 nm, N.A. 0.42), isolated lines become smaller than the dense structures under the high process offsets. We have reported a detailed study of proximity effects elsewhere. This proximity effect has been studied by measuring linewidths. Fig. 9 shows the results of the positive tone DESIRE using LPS and the negative DESIRE process using GPS. These E-D windows show that the positive tone DESIRE process exhibits a good overlap between dense and isolated patterns. For 0.25 µm patterns (see Fig. 10), the proximity becomes a serious problem mainly due to aerial images and partly due to used mask (the dense line is 0.02 µm wider than the isolated line). Several solutions have been investigated and proposed. The combination of OAI techniques with an attenuated PSM reduced the proximity effect between dense Is and isolated lines even for 0.25 µm feature sizes. This is because OAI improves the imaging for dense structures while an attenuating PSM improves the isolated features. It has been reported that the mask bias and the auxiliary pattern of sub-resolution type reduced the proximity effects. These optical tricks can reduce proximity for 0.25 µm feature size.

Dry development processing

The dry development conditions have been optimized using an MRC MIE 720 and LAM TCP 9400 with a 2 step process. In a first short step, a low concentration fluorinated gas mixture containing C₂F₆ is used to remove the top surface of the resist. This is followed by a 2nd step in pure O₂ to selectively etch the non-silylated resist. The linewidth and profiles between dense and isolated structure is strongly dependent upon the anisotropy and micro loading effects during the dry development. Fig. 11 show 0.3 µm and 0.35 µm dense and isolated lines for the various dry development process conditions. Loading effects are decreased by increasing the sputter etch component (power) at the expense of the etch selectivity. Fig 11 b & c show the smaller difference of linewidths and profiles between dense and isolated lines using optimum dry development conditions. Fig 11c is the results of LAM TCP 9400. These results show that the increased
Fig. 11  SEM micrographs of 0.35 μm and 0.3 μm dense and isolated lines: (a) using a standard process, (b) using a process with lower loading and increased anisotropy, (c) using an MRC MIE 720, (c) using a LAM TCP 9400 on the metal layer.

Fig. 10  SEM micrograph of 0.25 μm l/s using positive DESIRE process

Fig. 12  SEM micrograph of 0.3 μm l/s for 1 step O₂ standard process (MIE 720)
anisotropy and decreased loading effects result in vertical profiles and reduction of the proximity effects. Fig. 12 shows that the LPS can use 1 step pure O₂ plasma process (with MIE 720) without residues formation in the exposed areas due to the high silylation contrast.

Lithographic performance

We have evaluated the ultimate resolution limit using both conventional transmission masks and PSM. Under optimized conditions, 0.22 µm and 0.24 µm patterns (l/s) (see Fig. 13) have been obtained with conventional masks, and 0.18 µm patterns (l/s) (see Fig. 14) with an alternating shifter PSM on an ASM-L PAS 5000/70 DUV stepper (λ=248 nm, 0.42 NA). Figure 15 shows sub-100 nm isolated lines with a conventional mask using a mask bias.

Fig. 13 SEM micrographs of (a) 0.22 µm l/s (b) 0.24 µm l/s (λ=248 nm, 0.42 NA) after LPS (B[DMA]DS) using a conventional mask.

Fig. 14 SEM micrograph of 0.18 µm l/s using a PSM (248 nm, 0.42 NA).

Fig. 15 SEM micrograph of sub-100 nm isolated lines.
In optical lithography a positive tone resist process is strongly recommended for printing contact holes because a dark field mask can be used. In the case of a negative tone process, a light field has to be used, resulting in an inferior aerial image for contact holes and a higher sensitivity for defects. A dark field mask provides a higher aerial image quality than a light field one, especially for out of focus conditions. An attenuated PSM is most promising PSM techniques and especially suitable for contact windows. Fig. 16 shows the focus latitudes of 0.25, 0.3, 0.35, and 0.4 µm isolated contact windows at the different exposure doses (due to non-linearity of contacts) using an attenuated PSM. Fig. 17 shows cross-sectional SEM micrographs of the focus latitudes for 0.3 µm contact windows at the various focuses. Figure 18 shows the cross-sectional SEM micrograph of 0.25 µm contact holes with an attenuated PSM.

Fig. 16 Measured focus latitudes for the various contact sizes using an attenuated PSM.

Fig. 17 SEM micrographs of 0.3 µm contact holes of the positive DESIRE process at various focus settings.

Fig. 18 SEM micrograph of 0.25 µm contact windows obtained with positive tone DESIRE process.

Fig. 18 SEM micrograph of 0.25 µm contact windows obtained with positive tone DESIRE process.
As the wavelength is reduced, the control of C.D. variations over topography is becoming more difficult due to the higher reflectivity of most materials at shorter wavelengths. Therefore, top surface imaging techniques have received more attention not only to obtain the high resolution and the wider process latitudes, but also to control linewidth variations over topography. Figure 19 shows 0.3 µm poly gates of a shift register over topography in logic device applications. This SEM micrograph shows the perfect linewidth control over topography.

**Etching and Resist stripping**

To implement a positive tone DESIRE resist to a real device process, the etching process and stripping of the resist should be demonstrated in addition to high lithographic performances. The stripping of resist for the DESIRE process is one of the most critical process issues, because of SiOₓ cap formation and sidewall passivation during the dry development, which is mainly different from that of wet developable resist scheme.

Poly etching of 250 nm thick P-implanted polysilicon layer was carried out on a single wafer triode system using a low pressure HBr based etch process. The etching process in a triode system with a CFₓ/Clₓ/HBr chemistry was applied to the dry developable resist. The standard etch process of wet developable resist has been applied to dry developable resist to etch poly layer. One change in the standard etching process included a buffered HF dip before the etching. A buffered HF dip removed contaminants deposited on the sidewalls of the resist during the dry development. For stripping the resist after poly etching, the standard wet develop stripping process has been applied. After diluted HF dipping, the resist stripping has done in the standard wet develop stripping solutions (H₂SO₄/H₂O₂). Fig. 20 shows 0.25 µm poly patterns in 250 nm poly silicon layer after resist stripping.

![Fig. 19](image1.png)

*Fig. 19* SEM micrograph of 0.3 µm poly gates of shift register after LPS at DUV exposures (0.42 NA) over poly topography.

![Fig. 20](image2.png)

*Fig. 20* SEM micrograph of 0.25 µm poly patterns after poly etch and resist stripping.
The chemical and thermal stability of the silylated resists have been reported\textsuperscript{17,18}. It is important to obtain stable Si amounts and concentration after silylation, because the Si content influences the dry development. In early studies\textsuperscript{18}, we have reported that the unstability of the silylated resists in the case of GPS is due to the desilylation (hydrolysis) reaction, which can be enhanced by the presence of water in the environment and is increased by higher temperatures. We have investigated the out-diffusion of the resist in order to understand this mechanism and possibly apply to stripping of the resist.

**Fig. 21**  RBS measurements of Plasmask resist with a bake on a hot plate (2 min) for various bake temperature: (a) after silylation (HMDS), (b) after dry development.

**Fig. 22**  Out-diffusion with SiO\textsubscript{2} cap: Si content as a function of bake after dry development on a hot plate (1 min): (a) negative tone process using GPS (HMDS) (b) positive tone process using LPS (B\textsubscript{2}DMA)DS.
In the case of silylation (GPS) and subsequent baking, the Si amount as determined using FTIR and RBS, clearly shows a decrease of built-in Si with increasing temperature. When the silylated wafers (GPS) were dry developed and baked on the hot plate, the diffusion is retarded by the SiO₂ cap and the effect is less pronounced (see Fig. 21a). Fig. 22 is illustrated that in the case of the positive tone DESIRE process (b) the Si content is reduced by the baking even in the presence of a SiO₂ cap. This desilylation effect may be beneficial, because it could be used as a technique to remove the Si from the silylated regions, allowing dry stripping techniques to be used for resist removal.

4. Conclusion

We have investigated safer silylation solutions for application to the positive tone DESIRE process using LPS in DUV lithography. The proposed liquid phase silylation solution consists of B[DMA]DS with n-decane and PGMEA. The new silylation solutions have shown to exhibit several advantages, such as, (i) safety, (ii) reduced dissolution rate of the resist, (iii) relaxation sensitivity to the silylation solution. We have characterized the silylation process using FTIR, RBS, and a staining technique. A higher Si atomic concentration has been observed for the positive tone DESIRE process compared to that of negative tone DESIRE process using GPS (TMDS). A constant Si-depth vs. linewidth has been observed by using a staining technique, resulting in a good linearity. These silylated profiles exhibited a higher silylation angle with lower vertical swelling. Several solutions in order to overcome the proximity effects have been proposed such as (i) the higher contrast silylation process (LPS), (ii) the optical effects (positive tone, high N.A., and partial coherence factor, ..), (iii) optimum dry development conditions, (iv) combination with OAI and PSM techniques. The dry development conditions have been optimized. The poly etching and stripping issues have been studied. We have evaluated the etching and stripping process for 0.25 µm poly patterns. The desilylation reaction and the removals of SiO₂ cap have been suggested for the stripping of the dry developed resists. This new positive tone DESIRE process is considerably simpler as well as safer and easy to strip and results in a reduction of the proximity effect and in improved sensitivity as compared to GPS. A perfect linewidth control over topography in real device applications has been demonstrated. This positive tone DESIRE process has exhibited several advantages, such as high lithographic performance (resolution and process latitudes) and the implementation of the real devices process (stripping and proximity effect).

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