Freezing Materials For Double Patterning

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Cost reduction of Double Patterning processes is one of the key areas of development for materials vendors. Among the various possible approaches, spin-on freeze coatings are particularly attractive since they can provide a combination of high imaging performance and high flexibility in terms of resist selection. This paper reports on the development of a new material for spin-on freeze double patterning, AZ® SOLID™ Coating. A suggested mechanism of action is proposed based on FT-IR studies, and the performance of the material in terms of structure quality, process window, impact on LWR, CD uniformity, and resist compatibility is described.

Keywords: photoresist, freezing, double patterning, ArF lithography

1. Introduction

The semiconductor industry faces a change in its usual modus operandi of reducing wavelengths in order to achieve higher lithographic resolution. It is the general consensus that EUV lithography will not be ready for the 32 nm node and probably also not for the 22 nm node. High NA, non-water based immersion lithography has effectively been abandoned as an alternative technology, mainly due to timing reasons and an insufficient increase in resolution to justify the cost of its development and introduction. Thus water-based 193 nm immersion lithography is the only option for the next nodes; however, its resolution limit at a maximum practical NA of 1.35 is around 40 nm for dense lines, or not enough even for the 32 nm node.

In this situation, double patterning has emerged as the semiconductor industry’s chosen method to continue shrinking feature sizes and remain on Moore’s Law. In one form of double patterning, known as Litho-Etch-Litho-Etch (LELE, see Figure 1), features are printed at a relaxed pitch that is within the capabilities of 193 nm immersion lithography, e.g., line/space patterns at 1:3 CD/pitch ratio. After etch transfer into the substrate and resist stripping, a second resist is applied, and a second exposure generates a 1:3 pattern that intercalates a new line into the space between the first features, thus leading to a dense line pattern at a resolution unobtainable by direct exposure.1

Figure 1: Schematic of a Litho-Etch-Litho-Etch (LELE) process for Double Patterning (double line process). 1: imaging and etch of first structure (1:3 L/S), 2 Coat and image 2nd resist, 3: 2nd etch step, 4: final dense line structure after stripping.
The LELE approach can in principle be applied to arbitrary patterns by appropriately splitting mask levels. While the LELE approach has been demonstrated to work in production environments, it has the disadvantage of doubling the cost of patterning for the critical layers. Another limitation is given by the effect of overlay error on the space CDs: overlay errors now translate directly into CD errors (Figure 2). This places severe demands on the overlay accuracy of future exposure tools. Self-aligned spacer approaches\(^2\) to double patterning avoid this issue; however, they are constrained in the type of feature they can produce.

While the overlay effects are inherent to the LELE scheme and cannot be eliminated by materials design, materials suppliers have been actively working to reduce the cost of LELE by eliminating one of the etch steps (Litho Litho Etch approach, LLE). To achieve this, the second resist coating must be applied on top of the first resist pattern without intermixing with or dissolving it. Approaches suggested for this include negative-tone resists\(^3\) that are inherently less prone to intermixing, and changing the solubility characteristics of positive-tone resists in what is colloquially referred to as “resist freezing.” The freezing capability can either be built into the resist itself, e.g. by adding functionality that crosslinks them in a bake step (“thermal freeze” process\(^4\)), or by using two resists with mutually incompatible solvent systems.\(^5\) However, adding these additional functions to high-resolution resist systems is not without problems, and this approach also severely limits the flexibility of selection of new or multiple resists that users would like to see for their production processes. The use of short-wavelength UV crosslinking\(^6\) has also been reported, but it requires additional equipment and causes changes in resist chemistry and dimensions.

An alternative approach is the use of a “freezing coat” that is applied between the first exposure and the second resist coat and that renders the first resist structure insoluble in the second resist.\(^1\) In its ideal form, the freezing coat will be compatible with a broad range of resist systems in order to maximize the flexibility of resist selection for the end user. A full list of desirable properties for such a coating is given in Table 1. A schematic overview of this type of freezing process is given in Figure 3.

### Table 1: Key Design Targets for Resist Freezing Overcoats

<table>
<thead>
<tr>
<th>Property</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD Stability</td>
<td>minimal CD change with processing, 2(^{nd}) imaging, etc</td>
</tr>
<tr>
<td>Low Defectivity</td>
<td>no scumming, good across wafer defectivity</td>
</tr>
<tr>
<td>Etch Consistency</td>
<td>equivalent etch performance between 1(^{st}) and 2(^{nd}) layers, no special OPC required</td>
</tr>
<tr>
<td>Broad PR Compatibility</td>
<td>material works well with any/all immersion resists</td>
</tr>
<tr>
<td>Top Loss</td>
<td>min. top loss for 1st image after processing &lt;10%</td>
</tr>
</tbody>
</table>

![Figure 2: Effect of overlay error OE on final CDs. Spaces S1 and S2 are related to the target space width S by S1 = S – OE and S2 = S + OE.](image)

![Figure 3: Process flow diagram of the dual imaging process using the resist freezing approach. The 2\(^{nd}\) resist image is interdigitated with the 1\(^{st}\) frozen resist image.](image)
2. Experimental

2.1. Materials
AZ® 300MIF, ArF 1C5D, MP thinner are commercially available from AZ Electronic Materials. AZ® EXP SOF-004 and EXP SOF-053 are SOLID™ (Spin On Liquid to Inhibit Dissolution) materials developed by AZ Electronic Materials. SOLID™ materials are applied from an aqueous medium.

2.2. Metrology and analytical instrumentation
B.A.R.C., resist, and SOLID™ film thicknesses were measured using a Nanospec 8000 tool. Material-dependent Cauchy constants were derived on a J. A. Woollam® VUV VASE® Spectroscopic Ellipsometer. CD-SEM measurements were done on Applied Materials NanoSEM. Cross-sectional SEM images were obtained on a Hitachi 4700. Defectivity inspection was carried out on KLA Tencor 2360 image inspection system.

2.3. Details of the 1st exposure
Lithographic exposures were performed on a Nikon NSR-306D (NA 0.85) interfaced with a Tokyo Electron Clean Track 8. 8in wafers were coated with AZ ArF-1C5D B.A.R.C. and baked at 200°C/60 sec to achieve 37nm film thickness. RESIST A was coated and subsequently pre-baked at 110°C for 60 sec to form 90nm film, and post exposure baked at 110°C for 60 sec.

A 6% attenuated PSM with a large area grating composed of 1:1 110nm L/S features was overexposed to image approximately 55nm lines using annular illumination (0.82 outer, 0.55 inner sigma). After PEB, the wafers were developed for 30 seconds with a surfactant-free developer, AZ®300MIF, containing 2.38% tetramethyl ammonium hydroxide (TMAH). For cross-grid contacts, 1:1 90nm L/S features were employed to print approximately 90nm lines using dipole illumination (0.82 outer, 0.42 inner sigma).

Resist B required higher baking temperatures with a PAB and PEB at 105°C/60”. Resist C was processed with a combination of PAB/PEB at 95°C/60”.

2.4. SOLID™ process for freezing resist images
SOLID™ material is coated at a film thickness of around 90nm on top of a wafer with a printed 1st image, and subjected to a soft bake at 120°C for 60 seconds thereafter. After developing with AZ® 300MIF developer for 30 seconds, the wafer is baked at an elevated temperature (“freezing bake” hereafter) for further consolidation of the freeze effect. A freezing bake at 160°C for 60 seconds is applied for EXP SOF-004, and 140°C/60” for EXP SOF-053, respectively.

2.5. Details of the 2nd exposure
2nd exposures use the same resist formulation and processing conditions as the first exposure. No B.A.R.C. coating is necessary since the B.A.R.C. from the 1st exposure remains. The same mask was used, but the field placement was incrementally shifted 14.7nm (220nm pitch /15 fields) across a row of fields so that a complete period of offsets was encompassed. In a worst case scenario, the alignment offset from the ideal position between 2 exposures would be 7.35 nm. In this paper, all 2nd layers apply same resist as 1st layers thereof, thus only one resist name is mentioned in the annotation of each figure.

2.6. Cross-grid contact hole
In one application of the freezing process, contact hole patterns can be implemented by imaging an area of horizontal line/space features over a frozen area of perpendicular line/space features. The scheme is shown in Figure 4.

Figure 4. Scheme for printing cross-grid contact hole patterns.

2.7. Defectivity tests
A flood exposure of the 2nd layer resist is carried out to mimic the double imaging process for defectivity tests.

The 1st image is printed as described in 2.3, then SOLID™ processing with EXP SOF-004 as described in 2.4 is carried out. The frozen 1st
image is then coated with a 2<sup>nd</sup> layer of resist A at a FT of 120nm. An open-frame flood exposure is applied to the films, followed by PEB and 300MIF development as mentioned in section 2.3. The wafer is then inspected with KLA Tencor 2360 for defects.

2.8. Dose tolerance tests

ArF-1C5D is coated on silicon wafer followed by a bake at 200°C/60". A 120nm of resist A coating is formed on top of B.A.R.C. film with pre-applied-bake at 110°C/60". Subsequently, the SOLID™ process described in 2.4 is employed to freeze the 1<sup>st</sup> layer resist coating. After the freezing bake, a 2<sup>nd</sup> layer of RESIST A is coated again with a PAB. The wafer is then subjected to open frame exposure at incremental energies, and the film thickness of dies exposed under each energy measured on a Nanospec 8000 thereafter. The dose to clear of the double coated film is considered as the tolerated dose.

2.9. Nomenclature

ADI: Image after resist development
ASI: Image after SOLID development
AFI: Image after SOLID freezing bake
Final: 1<sup>st</sup> image that underwent the complete double imaging process

3. SOLID ™ Composition and Mechanistic Studies

AZ® SOLID™ materials consist of a custom-designed copolymer and an additive (Figure 5). The copolymer contains one function optimized for maximum interaction with the resist surface (interaction group), and a second set of functionalities that maximizes solubility in the aqueous casting medium while reducing solubility in common resist solvents. Ratios of the respective monomers were optimized to meet the goals in Table 1, with particular focus on minimal or no CD change during the freezing process (AFI image). The additive types and loadings are adjusted to further optimize performance of the freezing process with respects to the targets of Table 1.

Stripping experiments of the AFI images showed a behavior that was inconsistent with bulk crosslinking of the resist. It was therefore hypothesized that the freezing process leads to the formation of a sheath of insoluble material around the first resist structures. Since minimal CD change is observed during the freeze process, this sheath was expected to be quite thin.

FT-IR studies were carried out in order to further study the nature of the sheath. This method was chosen because it can be easily carried out on (low-doped) silicon wafers and because it also provides sufficient sensitivity to the small signal provided by a thin surface layer. In order to simulate the resist sidewall, an acid feeder layer was coated from water on top of a resist film (the process scheme is given in Figure 6). After baking and TMAH development, the FT-IR indicated a reduction in the ester group signal and the presence of significant numbers of COOH groups on the resist surface, which was taken to indicate that this surface is a good model for the resist sidewall (Figure 7a).

As a side, the spectra also showed a significant decrease in the lactone signal. This effect has been observed in several IR studies of different 193 nm resists in our laboratories, although to our knowledge it has never been discussed in the literature. Lactones are known to undergo acid-catalyzed polymerization reactions, and it is presumed that such a phenomenon occurs during PEB. The impact of this effect on resolution and LWR of 193 nm resists is
unknown; however, for the purpose of the present study it is assumed to be incidental, except for the fact that the conversion of lactones into open-chain polyesters will lead to a corresponding increase in the ester band intensity. It is therefore assumed that more cleavable esters are lost during PEB and development than the decrease of the open chain ester band indicates.

The difference spectrum before and after SOLID™ treatment indicates a further decrease in the resist carbonyl vibrations; however, both lactone and ester bands are now decreased. There is a corresponding increase in a broad band around 1700 cm⁻¹ that we attribute to chemical and physical interactions of the resist surface with the spin-on freeze material.

No further changes in the FT-IR spectra are observed during the hardbake. We interpret this to mean that the hardbake does not change the chemical composition or nature of the interactions of the films. However, omission of the hardbake has a significant negative impact on the protection of the 1st resist. Our interpretation is that the hardbake only anneals the films; it results in a physical densification of the protective layer that increases its solvent resistance.

Based on the FT-IR evidence, we have arrived at a working hypothesis that SOLID™ processing generates a thin sheath of SOLID™ polymer around the resist structures that is bonded to the resist sidewalls by ionomeric interactions. Such interactions have been well documented in the chemical literature. The strength of these interactions is sufficiently large to make the ADI image impervious to the overcoating of the second resist from most common resist solvents as well as to subsequent TMAH development. A schematic view of this interaction is given in Figure 8.

Figure 7: Baseline-corrected FT-IR difference spectra for the process of Fig. 6. a) Top trace (right scale): difference spectrum for resist coat (1) minus coat after acid treatment, bake and development (2), corrected for film thickness loss. b) Bottom trace (left scale): difference spectrum of films before and after SOLID™ process. Upward direction indicates a decrease in the absorbance band.

Figure 8: Schematic view of the interaction of the ADI photoresist image and the SOLID™ components.

A criticism of this hypothesis is based on the observation that the SOLID™ freezing process also effectively protects large unpatterned areas. Such protection is of course indispensable for the practical application of any freeze process. As shown below, SOLID™ freezing performs well in this respect. We currently explain this effect by the assumption that chemical changes in unexposed resist during PEB, development, and SOLID™ processing generate a sufficient number of COOH groups even on nominally unexposed resist surfaces to lead to the formation of an effective protecting ionomer sheath in these areas.

4. Results and Discussion

Optimization of the copolymer components (Figure 5) resulted in a polymer that gave a high level of ionomer formation with only minimal CD change. The SOLID™ freeze material was further fine-tuned by the inclusion of additives into the formulation.

Figure 9 shows the relation between additive loading and freezing performance. Low CD growth is one of the most critical requirements for this type of materials. With increasing
additive loading, larger CD value of 1st image is observed. The CD growth can be fine-tuned through adjustment of the additive loading amounts.

Figure 9. Effects of additive loading on double imaging of RESIST A with EXP SOF-004

As shown in Figure 10, nested line features were printed through two isolated feature exposures separated by the freezing process. 55nm dense lines&spaces were achieved on a 0.85 NA dry 193nm scanner, a resolution that exceeds the resolution limit of the exposure tool. At 1 nm, CD growth is negligible, and top loss, another criterion for the material, is well below 10% of the resist height. Since the same photoresist is applied for both exposure layers, differences in etch selectivity is no longer an issue, as opposed to other approaches.

The effects of the freezing process on the process windows of 1st layer photoresist pattern are shown from Figure 11 to Figure 13. Figure 11 shows depth of focus (DOF) and exposure latitude (EL) throughout the process. The process margin of the 1st photoresist pattern is maintained, and the CD change is below 1nm.

Figure 12 shows the effects of soft bake temperatures on the final CD and exposure latitude. CD can be controlled via soft bake temperatures in a reasonable range. Higher soft bake contributes to some CD growth, while lower soft bake reduces the original CD slightly. This gives considerable flexibility in optimizing SOLID™ processing for different resists through processing temperature changes only. Figure 13 also lists LER/LWR numbers for the SOLID™ process: which shows no adverse impact on LER/LWR of the printed image.
Figure 12. Exposure latitude vs. soft bake temperature of SOLID™ material (RESIST A / EXP SOF-004).

Figure 13 shows the effects of freezing bake on lithographic performance. To effectively protect the 1st image from the 2nd resist process, a freezing bake higher than 155°C is required for this particular photosresist and SOLID material combination. Similar to the results of Figure 12, LER and LWR are not sensitive to variations in the freezing bake temperatures.

Figure 13. Exposure latitude vs. freezing bake temperature of SOLID material (RESIST A / EXP SOF-004)

CD uniformity is one of the most critical issues for this type of cutting edge process. Table 2 shows the CD uniformity data measured for ADI and post double-imaged patterns. CD uniformity of 1st image kept on final pattern is comparable to the value on ADI. The 2nd image also shows satisfactory uniformity and LER/LWR numbers.

Table 2. CD uniformity (RESIST A / EXP SOF-004)

In photolithography, resolution and process margins of contact hole patterns is much more limited than that of line/space patterns. Freezing schemes provide a new approach to print contact holes by utilizing the larger process windows of line/space features. The so-called cross-grid contact process prints two set of lines at 90° orientations to obtain contact pattern. This step requires an intermediate freezing process to avoid any erosion of the 1st image. Figure 14 shows cross-grid contact printed with AZ EXP SOF-004.

Defectivity is often a showstopper for lithographic materials, given the increasing demand for feature shrinking. A defectivity map is shown in Figure 15. The test is carried out as described in section 2.7 to mimic the real case for double imaging except pattern printing on 2nd layer. The methodology is described in the experimental section. The defect density is as low as 0.4 pcs/cm².

Figure 14. Cross-grid contact hole printed with RESIST A frozen by EXP SOF-004
Figure 15. Defectivity inspection. Defect density 0.4pcs/cm² (RESIST A / EXP SOF-004)

Figure 16. Dose tolerance to 2⁻nd resist layer exposure (RESIST A frozen with EXP SOF-004)

Figure 16 shows dose tolerance of frozen 1⁻st resist coating to the 2⁻nd resist exposure which indicates the degree of protection. The relation between soft bake temperatures and dose tolerance is plotted in Figure 16a. With increasing baking temperature or time, additive diffusion is enhanced to a higher level, therefore a higher degree of protection is achieved to withstand higher exposure dose on the 2⁻nd resist layer.

Wide resist compatibility is highly desired by the industry; however, many currently prevalent freezing materials require special resist platforms, especially 2⁻nd layer resists. Those materials are able to freeze only particular combinations of photoresists which are exclusively developed for freezing process. We have therefore tested a number of resists with different polymer platforms to determine the breadth of applicability of the AZ® SOLID™ materials.

EXP SOF-004 is evaluated and works well with RESIST B as shown in Figure 17. RESIST C is a 193nm immersion photoresist which is widely used by semiconductor manufac-

turers. As it is composed of polymer(s) with a low glass transition temperature, it is not compatible with current freezing materials from major material vendors. EXP SOF-053 was formulated to be capable of freezing RESIST C. A lower bake at temperature of 140°C is applied in the freezing process. As shown in Figure 18, double imaging is achieved with negligible CD growth. The profile of the 1⁻st image is maintained comparable to the ADI image.

5. Conclusion
We have described double imaging with a newly develop resist freezing material, AZ® SOLID™ Coating, and have proposed a working hypothesis for its mechanism based on ionomer formation in a thin sheath around the first resist image. The SOLID™ freezing process has been shown to have no impact on 1⁻st resist process windows. The CD of the 1⁻st resist pattern in the final doubled image is tunable through adjusting soft and freezing bake temperatures. Various commercial available photoresists have been evaluated with two SOLID™ formulations, EXP SOF-004 and EXP SOF-053, and the SOLID™ materials have been found to exhibit wide resist compatibility. Defectivity was found to be low,
and the first resist image was found to be well protected from overexposure in the second imaging step.

As the same photoresist can be used for both 1st and 2nd layers, the differences in etch rates which complicate many other freezing process are no longer an issue.

We therefore conclude that AZ® SOLID™ materials will provide a reliable and flexible platform for the implementation of resist freezing processes for double patterning.

5. References
7. a) AZ Electronic Materials presentation at Nikon Lithovision Forum 2009 (San Jose, February 2009); see also corresponding Nikon eView article, in press; b) G. Wakamatsu et al., Proc SPIE 7273 (2009), in press; M. Hori et al, Proc. SPIE 6923-17 (2008); c) see ref. 4.