ArF Bi-layer Resist for sub-90nm L/S Fabrication

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The advent of 193nm ArF lithography opened new era of sub-90nm patterning in DRAM industry. ArF lithography in single layer scheme, however, has limitation in the substrate fabrication of sub-90nm L/S due to the decreased physical thickness of resist less than 3000Å and weak chemical structure of resist. Bi-layer scheme, composed of Si-containing top layer and thick organic bottom layer, is gaining attention for its capability of patterning and control of resist thickness as a substitute for single layer. Several resists were evaluated for bi-layer process in terms of resolution, dry development, bottom layer durability and SEM induced CD shrinkage. Resolution down to 80nm was achieved with Si content ranging from 8 to 9%. Etch selectivity in the dry development was a strong function of Si content and chemical structure of top layer with pitch size dependence based on O2/N2 gas chemistry in dual frequency plasma tool. Profile control after dry development was subject to change depending on the gas ratio (O2/N2) and power. Resist structure was proved to be a key factor in bottom resist durability at the substrate etch condition. Best combination of top and bottom resists in bi-layer scheme will be discussed.

Keywords: Bi-layer, dry development, ArF

1. Introduction

The application of 193nm ArF lithography paved the way for sub-90nm photo patterning [1-2], whereas single layer resist (SLR) faced a serious turning point for sub-90nm L/S fabrication in DRAM industry. Pattern collapse, which limits aspect ratio around 3 for 90nm L/S, resulted in the decreased physical thickness of resist less than 3000Å, which is critical point for stable substrate fabrication. Because of the transmittance problem, new chemical structures such as acrylate, cycloolefin maleicanhydride (COMA) hybrid, vinyether maleicanhydride (VEMA) hybrid replaced stable KrF resist based on polyhydroxystyrene [1-4]. And they are susceptible to degradation when they are exposed to plasma. Several different schemes have been proposed to overcome the limitation of single layer resist. Among them multi layer process (MLR) and bi-layer resist (BLR) process were regarded as most promising. However multi-layer resist scheme, composed of thin top resist and inorganic layer on top of i-line resist, failed to meet the demand of production line due to the complicated process. Another candidate, bi-layer scheme that consists of Si-containing top resist and bottom organic layer has been available since 90's in logic industry for the purpose of covering topography and is now turning to the DRAM industry. Fig. 1 shows the structures and process sequence of single layer and bi-layer for L/S fabrication. The structure of bi-layer is comparable to single layer since there is no BARC required. If in-situ process of dry development and substrate pattern transfer carries out, the sequence of bi-layer process is the same as single layer resist. And since cost of top and bottom resist is comparable to single layer resist, there is no increase in expenses. The application of bi-layer is to provide separate control of resist into the photo patterning (top Si containing resist) and dry etch resistance for substrate formation (bottom organic layer). Dry development is a key process to facilitate bi-layer scheme. Si content in top resist has a profound effect on the etch selectivity which determines the thickness of top resist, with trade-off in resolution and dry strip. Sidewall passivation

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limits anisotropic pattern transfer in organic bottom layer. While O₂/SO₂ based gas chemistry in high density plasma tool is believed to be the only one to provide vertical profile in organic etching [5], this chemistry produces integration issues such as corrosion-related pattern collapse and residues [6]. Conventional gas chemistry based on O₂/N₂ needs to be explored with practical plasma tool. The selection of bottom organic layer requires a lot of consideration depending on application step. As far as Si₃N₄ hardmask is concerned for substrate fabrication, durability as well as physical thickness of bottom organic layer plays important role for etch mask. With all these considerations combined, several types of bi-layer will be investigated in this paper.

ArF bi-layer top resist in the development is divided into 2 groups as shown in Table 1. First group is silsesquioxiane (SSQ) structure that contains Si in ladder like backbone. Second group has Si in its pendant group. While silsesquioxiane (SSQ) type has an advantage of high resistance to oxygen plasma due to high Si content inside backbone, resist synthesis and stable shelf life are still concerned. On the other hand, for second group, resist synthesis is comparable to single layer resist at the expense of easy decomposition of Si in the pendant during dry development.

![Fig. 1. Comparison of structure and sequences of single layer resist and bilayer resist.](image)

2. Experimental

Resists for top layer and bottom layer were supplied from several resist makers. Exposures were carried out on an ASML PAS 5500/1100, with numerical aperture (NA) settings of 0.75. Line slimming investigations during CD SEM measurements were carried out on a Hitachi 9220 CD SEM. CD slimming was measured using 50% threshold at an acceleration voltage of 800eV and beam current 6.2 pA. Dry development was performed in a dual frequency plasma tool based on O₂/N₂ based gas chemistry.

Relationship of Si content with resist performance is represented in Fig. 2. Si compound in the resist has a mixed face in bi-layer process. High content of Si can enhance etch resistance leading to large process window of dry development at the sacrifice of photo performance. SSQ type resist appears to be good candidate to contain high Si content without degrading contrast since it has hydrophobic Si inside backbone.

3. Results and discussion
Table 1. Comparison of chemical structures of ArF bi-layer top resists

<table>
<thead>
<tr>
<th>TYPE</th>
<th>Si in backbone</th>
<th>Si in Pendant group</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>SSQ</td>
<td>Acrylate</td>
</tr>
<tr>
<td>Chemical structure</td>
<td>[\text{R}_1\text{Si-O-Si}\text{R}_2]</td>
<td>[\text{R}_1\text{Si-O-Si}\text{R}_2]</td>
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Fig. 2. Relationships of Si content with resist performance

Bottom layer resist in ArF bi-layer process is required as an etch mask for substrate pattern transfer and an anti-reflective coating (ARC) layer. Typical material for etch mask is phenolic resin represented by novolak for high etch resistance. However, this is not available in 193nm bi-layer process directly due to the high reflectivity. It is reported that phenolic resin has high $k$ more than 0.5 leading to the reflectivity over 2% [7]. Fig. 3 shows dependence of reflectivity on absorption coefficient ($k$).

It is evident that $k$ should be less than 0.3 in order to achieve low reflectivity less than 1% at the thickness of more than 2000Å. Novel materials based on naphthalene type and amorphous carbon are in the development to meet the role of etch mask and anti-reflection layer.

Fig. 4 shows lithographic performances of several bi-layer resists in line and space (L/S) patterning. Si content in all samples is in the range of from 7% to 9%. Sample A, B, C were based on maleic anhydride-vinylalkyl type resin, SSQ type and acrylate type resin respectively. The resolution was almost comparable to ArF single layer resist although profile and exposure latitude were insufficient. Among them we’ve been focusing on SSQ type resist because of the stability in outgassing [8]. And recently the lithographic performance of SSQ was highly improved. Fig. 5 shows photo performance of modified SSQ type resist with high Si content of 15% on conventional 193nm ARC. 96nm L/S patterns were readily resolved using 0.75 NA ArF scanner. Depth of focus, exposure latitude and profile were almost comparable to those of ArF single layer resists. However the control of extinction coefficient ($k$) is still needed maintaining high dry etch resistance of current under layer. When we applied current under layer having 2% reflectivity, slight undercut was appeared as expected (Fig. 6) and this undercut affected profile during under layer etching.
Fig. 4. Lithographic performance of bilayer resists based on the different platforms.

Fig. 5. Lithographic performance of modified SSQ type resist on organic BARC; (a) profile and (b) process window.

Fig. 6. Lithographic performance of modified SSQ type resist on an under layer.
Dry development in bi-layer process is key step, which controls profile of bottom resist and selectivity of bottom resist over top resist. Fig. 7 shows the comparisons of etch rate and the resulting selectivity in the dry development depending on resist type. SSQ type with Si content of 9% showed best result with lowest etch rate. Higher Si content only is not capable of explaining the difference in etch rate since 8% Si in acrylate showed higher etch rate than 7% Si in PHS. Resist structure has a profound effect on etch rate as well as Si content. Fig. 8 represents images of top roughness after dry development. Top roughness limits notchig margin in the line and space patterning. SSQ type resist provided smoother top morphology than the other two types due to its sturdy chemical structure. So, it shows that selectivity and top roughness in the dry development are strong function of resist structure and Si content. Next issue in the dry development is to control the profile of bottom layer for etch mask in the pattern transfer of substrate. Fig. 9 shows dependence of bottom layer profile after dry development on process variables such as power and oxygen flow rate. First, profile improved with power at the oxygen flow rate of 6sccm, due to the increase of directionality of ions. Power controls ion energy in the plasma. High ion energy at high power can lead to the increase of ion damage with low selectivity and increased top roughness. On the other hand, low power (300W) for low ion damage should accompany low oxygen flow rate (4sccm) in order to suppress the isotropic reactions of oxygen radicals. However, lower etch rate of bottom organic layer at low power and low oxygen flow rate requires longer process time.

Selectivity in the dry development controls the thickness of top resist. For the thickness of top resist less than 1500Å for better lithographic performance, selectivity needs to be more than 3. It was reported that etch selectivity in the dry development was more than 5 in high density plasma (LAM TCP) above 130nm L/S pattern [9-10]. Selectivity is changeable at the different pattern size. Fig. 10 shows selectivity in the dry development as a function of pitch size. Selectivity decreases as pitch size decreases probably due to the enhanced sputtering yield of ions at the smaller pattern size. At the pattern size less than 100nm, selectivity dropped drastically to 2 leading to the increase of thickness of top resist more than 2000Å. So, selectivity in the dry development is limiting factor in the bi-layer process for sub-90nm L/S fabrication. Good combination of materials and process is required for high selectivity.

Fig. 11 shows the comparison of resist loss of several types of bottom layer resists. Novolak provided best durability almost double of acrylate type resist. Type A resist has an aromatic group in the acrylate backbone and did not show better durability than acrylate type resist. Fig. 12 displays vertical profiles of bottom layers left after they are
exposed to plasma at the etch condition of Si3N4 hardmask. Gas chemistry was based on CF4/CHF3/O2 in a dual frequency plasma tool. While acrylate type resist showed pattern degradation, which had been observed in ArF single layer resist, type A and novolak kept their original shapes. It is concluded that weak acrylate backbone structure induced pattern degradation in the pattern transfer. Some portion of acrylate type resin is expected to be included in under layer to make appropriate extinction coefficient below 0.3. However this can cause another problem in developing etch condition. New material having low extinction coefficient as well as good durability is needed.

**Pitch size dependence (acrylate type)**

![Graph showing pitch size dependence.](image)

Fig. 10. The change of selectivity in the dry development as a function of pitch size.

**Bottom PR loss**

![Graph showing bottom PR loss.](image)

**CF4/CHF3/O2/Ar gas chemistry**

Fig. 11. Comparison of bottom resist loss after exposure to CF4/CHF3/O2 plasma.

New etch process for BLR process is being developed with conventional O2/N2 chemistry. Fig. 13 shows the initial results for 40nm patterning with dry development and trimming. As shown in the figures, these results were obtained using the initial BLR having tapered profile. Better result is expected with the modified SSQ because it was much improved in terms of photo performance without reducing Si content.

One of issues in bi-layer process is CD shrinkage of top resist during SEM inspection. CD shrinkage has been a hot issue since the introduction of ArF resists. Fig. 14 compares several types of bi-layer resists and single layer resist in terms of SEM shrinkage. Bi-layer resists generally displayed worse result more than 10% compared to single layer resist of EPIC-V40, which shows 9%. SSQ type resist, on the other hand, has a record of only 2% which is comparable to KrF single layer resist. This is another reason for us to regard BLR process as production-worthy for sub-90nm device fabrication.

![Graph showing CD shrinkage.](image)

**Fig. 12. Profiles of different types of bottom resist after exposure to CF4/CHF3/O2 plasma.**

**Fig. 13. 40nm patterning with dry development and trimming (190 nm pitch).**

**Fig. 14. CD shrinkage of bi-layer resists and ArF single layer resist.**
4. Conclusions

Bi-layer resist appears to be good candidate for ArF process. It is simple process similar to single layer resist with BARC. Big issue of bi-layer process is immature material. Several types bi-layer resists based on different platforms were investigated in terms of photo performance, dry development, plasma durability and SEM shrinkage. SSQ type resist proved to be best structure as a top resist in terms of dry development with high resistance to oxygen plasma and smooth top morphology. Novolak provided best result in the plasma durability as bottom layer at the expense of relatively high reflectivity due to the high absorption coefficient. New material having low extinction coefficient as well as good etch durability is needed. SEM induced CD shrinkage can be reduced to 2% with SSQ type top resist, which is comparable to KrF single layer resist.

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References