Understanding of Interactive Behaviors between Resist Film and Under-layer

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We tried to understand major impacted factor induced missing via defect as important challenge in EUV process and figure out favorable solution to avoid fundamental root cause. Main focal point in this study was interaction between resist film and surface condition of under-layer. As the result, it was found that higher polarity under layer has capability to enhance de-scum effect with NTD type resist combination. Opposite trend between exposed/unexposed region is ideal condition for resist scum removal without pattern peeling and its condition was achieved under NTD type resist with higher polar under-layer.

Keywords: EUV, Adhesive work, Interfacial energy, Missing defect, Scum

1. Introduction

EUV process was actually inserted to HVM as realistic photolithographic scaling driver relieving from Multiple-patterning. However, defect issue in this process must be considerable, especially missing type error on hole pattern is serious problem. In our previous work, the existing of latent defect around hole bottom was examined and effective solution for defect suppression utilizing robust etching technique was introduced [1]. Additional de-scumming process before etching of under SoG layer has wider capability to suppress the missing hole defect, however, photolithographic relevant factor, material design, chemical reaction or dimensional restriction, has to be investigated.

In this study, assuming that the origin of not-opened hole might be insolubilized potion in photo-resist film, we examined mainly interfacial reaction between photo-resist and under-layer. Historically, adhesive work ($W$) have been studied to prevent the peeling or collapsing of resist pattern mainly [2-4]. In order to understand the reason to be insoluble the solubilized region despite exposed, de-protected and polarity changed.

This paper would introduce our examination results about the infliction of resist adhesive work with modified under-layer surface and mention about our explorations of insolubilized mechanism.

Unexpected and probabilistic patterning error, represented by missing via hole defect in EUV process (Fig. 1), is most headache problem, because it has direct impact to devise manufacturing yield, especially missing via hole case. As shown in Fig. 2, defect cloud covered on CD distribution peak [5]. The number of defect count in this defect cloud includes latent defect. Based on the result of defect count in nominal ADI, it seemed that etching process induced missing defect (Fig. 3). However, these increased defects were reduced utilizing de-scum treatment before pattern transfer to under layer (Fig. 4). According to this result, it can be understood that Latent missing defect exactly existed and it might be hardly detected by current top-view type inspection tool. Major factors inducing latent missing defect incompletely opened hole may be indicated as resist dissolution delay at pattern bottom area or inhibition of solubility as shown in my imagined pattern profile (Fig. 5).

Fig. 1. Missing hole type defect image.
In order to understand behavior of latent defect, which incompletely opened hole, we focused on the interfacial behavior between resist and under-layer, assuming that missing mode error is similar to bridging type defect on line pattern (Fig. 6) [6]. We found before that inhomogeneous layer existed around interfacial region with under-layer and it was obviously different from bulk region in resist film (Fig. 7) [6]. Based on previous result, we tried to identify the relevant behavior of resist residue with under-layer’s property utilizing concept of adhesive work calculation and examination results would be introduced in this paper.

2. Experimental

Experimental condition is summarized in Table 1. Various resist materials were used in suitable case individually. EUV resist with 193nm-sensitivity was used under 193nm immersion exposure in fundamental study and under EUV exposure for fine patterning.

| Table 1. Experimental condition. |
|----------------------------------|
| Exposure tool                  | 193 imm. TWINSCAN XT:1900i | NA 1.35 |
| EUV                             | TWINSCAN NXE-3300           | NA 0.33 |
| Resist processing Coater       | CLEAN TRACK™ LITHIUS Pro 193 |
| Resist stack Film stack structure | PR/Sub/SoC/Bare-Si           | SoC: 35nm |
| Resist                          | UEV PTD Resist 193 exposure | FT: 50nm |
| Resist                          | UEV NTD Resist 193 exposure | FT: 50nm |
| Resist                          | EUV Exposure                | FT: 25nm |
| Resist                          | E UV PTD Resist EUV Exposure | FT: 25nm |
| Metrology                      | CD-SEM Verity SEM® 5i      |        |

3. Explanation of resist adhesive work

3.1. Surface free energy

Adhesive work was estimated by Young-Dupre equation (1) [8] based on raw date of contact angle measurement in DIW and diiodomethane each [9].

\[
\gamma_{RL} = \gamma_R + \gamma_L - 2 \times (\gamma_d^R \times \gamma_d^L)^{1/2} - 2 \times (\gamma_h^R \times \gamma_h^L)^{1/2}
\]

\[
\gamma_{SL} = \gamma_S + \gamma_L - 2 \times (\gamma_d^S \times \gamma_d^L)^{1/2} - 2 \times (\gamma_h^S \times \gamma_h^L)^{1/2}
\]

\[
\gamma_{RS} = \gamma_R + \gamma_S - 2 \times (\gamma_d^R \times \gamma_d^S)^{1/2} - 2 \times (\gamma_h^R \times \gamma_h^S)^{1/2}
\]
Probability of resist pattern peeling has to be considered with relation between surface free energy of resist ($\gamma_R$), substrate ($\gamma_s$) and developer solution ($\gamma_L$) on polar and disperse component matrix as shown in Fig. 8.

![Fig. 8. $\gamma$-Value triangle in resist processing.](image)

### 3.2. Peeling estimation with adhesive work

In this session, the relation between $\gamma$-value triangle ($\gamma_R$, $\gamma_s$, $\gamma_L$) and pattern peeling on the matrix of polar and disperse components (Fig. 7). For example, in the case that inscribed circle with $\gamma_R$ and $\gamma_s$ is enough small and distance between $\gamma_L$ and the circle is longer (Fig. 9a), pattern adhesion force is enough big to prevent peel. In the opposite case (Fig. 9b), surface energy between resist and substrate become bigger and affinity with TMAH become higher, so eventually pattern peeling might be induced [8].

![Fig. 9. Peeling trigger in $\gamma$-value variation.](image)

### 3.3. Relation of desorption and adhesive work

We tried to estimate de-scumming property utilizing same calculation as adhesive work. When adhesive work must be calculated, surface energy of resist($\gamma_R$) might be used for estimation of pattern peeling estimation. On the other hand, $\gamma_R$ has to be used with same formula when resist desorption property is expected as shown in Fig. 10b (right side). I supposed that in the case that adhesive work is smaller, oppositely desorption force will be accelerated and de-scumming capability will be increased.

![Fig. 10. $\gamma$-Value balance on exposed region.](image)

### 4. Results and discussion

#### 4.1. Examination of resist profile variation

As I mentioned in previous section, inhomogeneous layer existed around pattern bottom area and it had footing profile. Classifying resist film in surface (atmosphere side), Bulk and interfacial (under-layer side), $T_g$ of surface region is relatively lower and interfacial region is higher, because of polymer rigidity. So acid diffusion length in chemically amplification is different between surface and interfacial region as shown in Table 2. If main cause of footing profile (Fig. 6) resulted from shortened acid diffusion, resist profile of NTD resist must be necking oppositely (Table 3).

Comparison result between PTD and NTD [11] type resist profile is represented in Fig. 11. Footing profile came out in both cases. It seems that acid diffusion length must not be dominant factor of footing profile based on this result.

| Depth region | Polymer flexibility | $T_g$ (relative) | Acid diff. length |
|--------------|--------------------|-----------------|------------------|
| Surface      | Flexible           | Lower            | Longer           |
| Bulk         | Theoretical        | Theoretical     | Theoretical      |
| Interfacial  | Rigid              | Higher           | Shorter          |

Table 2. Relation of $T_g$ and acid diffusion.

#### 3.3. Relation of desorption and adhesive work

![Table 3. Impact of acid diffusion length.](image)

![Fig. 11. Footing profile on PTD and NTD. 193nm sensitive EUV resist: 88nm Pitch. Exposure: 193immersion.](image)
4.2. Adhesive work of resist pattern

Historically, adhesion property of resist pattern has been studied for pattern peeling prevention. Dependency of pattern peeling was related to several under-layer and adhesive work was calculated in each case. PTD type resist material was used in this case. Threshold of pattern peeling can be supposed around 15 dyn/cm in this process condition (Fig. 12).

4.3. Approach of desorption force control

In order to desorption property in exposed region for descumming enhancement, adhesion work variation was examined on various kind of under-layer. 3 kind of under-layer were prepared as same as pattern peeling prevention check. These were nominal SoG, Silica-rich type, organics. Both adhesive work on exposed/ unexposed region are represented in Fig.13. When adhesive work ($W$) was made small on silica-rich type under-layer, adhesive work decreased on not only exposed region but also unexposed region (Fig. 13, middle column). On the other hand, both $W$ increased on organic under-layer (Fig. 13, right column).

We now try to explain the results of Fig. 12 in detail. Focusing on the arrow length between inscribed circle and TMAH in Fig. 14A-1(on SoG) is longer than A-2 (on silica-rich under-layer) and same result came out on exposed region. This trend has to be opposite in order to get individually controllable opposite properties that adhesive work ($W$) on SoG is higher and $W$ on modified under-layer is lower.

4.4. Negative impact of HMDS priming

HMDS priming treatment has been used widely to prevent resist pattern peeling especially on inorganic or metallic under layer historically. Influence of HMDS priming would be explained in this session, because various metallic materials were introduced for under-layer of EUV resist patterning in order to enhance resist sensitivity or modify resist profile [12]. In fact, resist peeling is hardly prevented without HMDS priming on inorganic under layer, because inorganic material has higher polarity closed to TMAH aq.

![Fig. 12. Collapse trend on adhesion work.](image)

![Fig. 13. Adhesive work relation.](image)

![Fig. 14. γ-Value variation by surface modification.](image)

![Fig. 15. Pattern peeling on contrast curve.](image)
As shown in Fig. 15, resist film peeled on contrast curve making without HMDS priming. It can be understood that HMDS priming on inorganic under-layer is effective to avoid pattern peeling. Estimation result of adhesive work is represented in Fig. 16. Adhesive work did not increase only on unexposed/line region, but also on exposed/space region obviously, it can be characterized that resist dissolution property was getting worse, in other word, resist scumming was induced. Actually, resist scum increased drastically by HMDS priming (Fig. 17).

![Fig. 16. Adhesive work variation by HMDS.](image1)

![Fig. 17. Increasing trend of resist residue EUV PTD resist under 193 exposure. Pattern; 88nm-pitch.](image2)

4.5. Approach in NTD type resist process

NTD type resist processing is promising technique to obtain higher image contrast on hole pattern, therefore, we also examined its property regarding relation to under-layer surface condition.

In the relative comparison (Fig. 18), NTD type resist has wider adhesive force on various kind of under-layer. Base on this result, we checked the adhesive work on unexposed (soluble) region and desorption property on exposed (insolubilized) region.

We prepared three types under-layer which nominal SoG, silica-rich film and organic BARC as same as PTD evaluation, and EUV resist, which has 193 sensitivity, was patterned under 193-immersion exposure. Adhesive work comparison result is represented in Fig. 19, and favorable result was found on silica-rich under-layer case. Adhesive work on unexposed/soluble region was getting lower and it became higher on exposed/insolubilized region oppositely. It means that de-scum effect was enhanced without pattern peeling.

![Fig. 18. Stability on various under-layer.](image3)

![Fig. 19. γ-Value variation in the case of NTD.](image4)

As mentioned in session 4.3, adhesive work ($W$) variation by surface control is favorable to get mutually opposite trend between exposed and unexposed region. In detail, it is better that $W$ of exposed/insoluble region become higher to avoid pattern peeling and become lower in unexposed/soluble region to enhance de-scum effect. Modifying surface condition to higher polarity, desirable combination was viable as shown in Fig. 19 (right column).

Comparison result in exposed/unexposed region with NTD type resist is represented in Fig. 20. As compared with PTD case, favorable result came out on silica-rich under layer case. Focusing on the distance from inscribed circle to developer solution (Fig. 20), the arrow length became shorter on unexposed region after changing under-layer from nominal SoG (Fig. 20a) to surface modified one (Fig. 20b). On the other hand, it became longer on exposed region changing UL from c to d case in Fig. 20. It means that de-scum capability was enhanced in soluble region and adhesive force was strengthened in insolubilized region. It can be
understood that resist residue related defect would be reduced without pattern peeling in higher polarity under-layer condition.

Subsequently, variation of pattern profile was observed on control and modified under-layer. Footing profile was obviously captured on nominal SoG under-layer, and removal effect was recognized on modified surface which had higher polarity (Fig. 21). It can be understood that resist scum might be relevant to interfacial free energy of under-layer.

5. Summary

We tried to understand major impacted factor induced missing via defect as important challenge in EUV process and figure out favorable solution to avoid fundamental root cause. Main focal point in this study was interaction between resist film and surface condition of under-layer. As the result, it was found that higher polarity under layer has capability to enhance de-scum effect with NTD type resist combination. As shown in Table 5, opposite trend between exposed/unexposed region is ideal condition for resist scum removal without pattern peeling and its condition was achieved under NTD type resist with higher polar under-layer.

### 6. Conclusion

In this study, we investigated the resist desorption behavior from under-layer to understand the relation between missing type defect and resist scum/residue. Finally, difference property in PTD and NTD type resist was clarified and feasible solution in NTD type resist combined with surface modified under-layer was figured out. It might not be difference of resist type (PTD/NTD), but difference of developer solution property which is aqueous solution (TMAHaq) or non-aqueous solution (nBA).

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