Understanding of Strategic Design of Resist Formulation Through Studying of Quencher-Functional Component and Those Contributions to High Resolution Patterning

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Utilizing Line and Space (L/S) application on high resolution patterning to critical dimension (CD) below 42nm line thru typical ArF PTD process sees severe problems of trade-off or lack of correlation among linewidth roughness (LWR) and dose response (Esize), which are critical performers for delivering decent patterning ability toward Multiple Pattering Process (MPP). For improving those critical functional performances and reducing those trade-off, it has been carried out a study of various types of Quencher-functional component (QFC) as acid diffusion controller with understanding different gradients in resist matrix and those working models. When incorporated with more surface-active type or not-uniformed distribution type of QFC, it showed higher LWR at 45nm half pitch and all pattern fallen at both 38nm and 37nm half pitch. For the case of QFC having homogeneous gradient or less distribution to surface, it showed more contributions to control of roughness at exposed edge area on line patterns, and extended its functionality to the improvement at 37nm HP. For those different types of QFC as acid diffusion controller, they showed all different level of contribution to LWR and Esize response at 45nm HP to 37nm HP, and followed different efficiency with various concentrations in resist formulation.

Keywords: ArF, Lithography, Line Width Roughness, Dose Response, Esize, Quencher-functional component, Photoacid Generator, Acid diffusion controller, Acid concentration

1. Introduction

Improving Line-Width Roughness (LWR) remains a significant challenge in all resist materials toward advanced lithography. As reported many times, LWR is a quite complexed result having significant relevance with various conditions or parameters from physics and chemistry such as illumination, light intensity, resist polymer property, PAG photo efficiency, acid concentration and many others in/from/to resist [1-6]. It is significantly necessary to understand how to control those parameters, particularly for acid concentration or diffusion, pertaining to good patterning with lower roughness at even for higher resolution with smaller CD area.

To simply reach to lower roughness, it has been used strong basicity quencher or surface-active type of base component to resist formulation. However, this approach may bring other concerns such as slower sensitivity of dose of light, worse dose response, and difficulty of profile control from severe heavy top profile and others, even though ignoring to consider photo-speed control difficulty in perspective of photo-resist product manufacturing.

For achieving lower LWR with fast dose response on printing narrower CD feature as like 38nm or 37nm half pitch in single exposure without sacrificing other performances, it was designed a few specific quencher-functional components to bring better distribution in resist matrix and weak basicity impacting to acid control, and compared with other typical quenchers having properties as described in previous paragraph.

2. Experimental
2.1. Sample preparation

The photoresists were formulated with 193nm photoresist polymer, PAG, acid diffusion controller, and solvents. Due to the proprietary nature of these materials the details of their composition are not disclosed. The solutions were filtered through 0.02 μm PTFE filter prior to evaluation.

2.2. Material selection

Various types of Photoacid Generator (PAG) and Quencher-functional component (QFC) to control acid concentration or diffusion were selected as based on their different nature as shown in Table 1 below. For QFC, it was considered with basicity and distribution in resist matrix such as surface-active property as major properties for these experiments.

| Table 1. PAG and QFC Selection. |
|---------------------------------|
| **PAG** | 1 | 2 | 3 | 4 | 5 |
| Absorbance @ 193nm | High | High | Mid | Low | Low |
| Hydrophobicity - Cation | Low | Low | Mid | High | High |
| Diffusion | Fast | Slow | Slow | Slow | Fast |
| Acidity | Strong | Weak | Weak | Weak | Strong |
| QFC | 1 | 2 | 3 | 4 |
| Basicity | Low | High | High | Low |
| Distribution to Surface | Low | Mid | High | Low |
| Photo-Reactivity | Low | none | none | High |

2.3. Lithographic evaluation

Each Resist formulations were coated by spincoater for 90nm film thickness on 200 mm Si wafer to check Dose to Clear (Eth) and processed for ArF bulk exposure with ASML1100 ArF scanner. For lithographic patterning, resist films were prepared by spin coating for 90 nm thickness on an antireflective coating (ARC) film layered on HMDS primed 300mm wafers using a TEL CLEAN TRACK LITHIUS i+. Films were exposed on an ASML 1900i for Line and Space (L/S) patterning under PSM reticle and various illumination conditions as shown in Table 2. After development process with TMAH 2.38 wt% solution, post-lithographic patterns were inspected with Hitachi CD-SEM CG-4000 for measuring optimal exposure dose (Esize) to print and Line Width Roughness (LWR) for L/S half-pitch 45 nm, 38 nm and 37 nm, respectively. It was processed cross-sectional inspection for pattern profile with Hitachi S9380.

| Table 2. Lithography/exposure process condition. |
|---------------------------------|
| **Substrate** | 300mm Silicon |
| ARC LAYER | Dupont Organic BARC |
| Resist FT | 900A |
| PAB / PEB | 90C / 95C, all 60s |
| Exposure / Illumination | PSM, Dipole-35Y, X-pol |
| | 1.35, 0.986/0.896 for HP 38nm, 37nm |
| | 1.30, 0.86/0.61 for 45nm HP |
| Develop | TMAH 2.38wt% |
| PIR | Yes |

3. Results and discussion

3.1. Variation of dose to clear (Eth)

From process of ArF bulk exposure, it was compared Eth variation of QFC types with various PAG types as shown in Fig 1. It varied with loadings of QFC to resist formulation from relatively low as 0.75× to high as 1.25×, and applied all same moles from each QFCs for this Eth comparison. When compared with those Eth variations thru different QFC loadings in resist and normalized those variations to QFC 1 as seen in Fig. 1, all QFCs showed different behavior of Eth thru different PAG types having different level of property, particularly for an absorbance @ 193nm wavelength. About QFC with acid diffusion, QFC 2 followed different Eth variation through a property of anion diffusion when compared with PAG 4 and PAG 5. For this variation of QFC 4, it was shown as similar behavior with QFC 3, but unlikely with other QFC 4 which showed similar or lower variation to QFC 1.

![Fig 1. Normalized Eth variations of QFC vs PAG.](image-url)
QFC’s function to Eth variation followed its strong basicity as critical to control photo-acids. For the case of QFC 2, it showed almost double level of Eth variation from applied with PAG 4 as compared to other PAG 2 and PAG 3, which had relatively higher absorbance of 193nm light. It was thought QFC’s function might be varied with Eth variation from different environment of acid concentration occurred from different level of photo-efficiency of PAG, or different ratio of PAG/QFC in resist matrix. Regarding this behavior upon different level of QFC loading ratio to PAG, it is shown in Fig. 2 with comparison of PAG 2, 3 and 4.

Fig. 2. Eth variations comparison of QFC loading thru PAG type (a) with PAG 2 (top), (b) with PAG 3 (mid), (c) with PAG 4 (bottom).

3.2. Optimal dose to print (Esize) contribution

It was carried out to monitor Esize of each Line and Space (L/S) pattern on all half pitch 45 nm, 38 nm and 37 nm, and summarized into Table 3 and below.

As shown in Table 3, all QFCs showed their Esize contributions to print 3 CDs of L/S pattern area as similar to Eth variation as following a relationship between QFC type and loading with PAG type. This relationship was also presented in Fig. 3 as normalized to QFC 1. Compared to QFC 1, QFC type 2 and type 3 having a relatively higher basicity showed high contribution of Esize to print at all type of CDs, regardless of PAG type.

Table 3. Esize comparison of QFC type/loading vs PAG type.

(a) Esize at 45nm HP

| QFC type/loading to PAG Type | 45nm Esize [mJ/cm²] |
|-----------------------------|---------------------|
|                            | PAG 1  | PAG 2  | PAG 3  | PAG 4  | PAG 5  |
| QFC 1                       |        |        |        |        |
| 125%                        | 22.9   | 26     | 26     | 31.3   | 31     |
| 75%                         | 15     | 17.2   | 17.2   | 21.8   | 20.8   |
| QFC 2                       |        |        |        |        |
| 125%                        | 34.8   | 38.2   | 39.6   | 62.6   | 58.4   |
| 75%                         | 18.7   | 20.8   | 21.6   | 31.3   | 29     |
| QFC 3                       |        |        |        |        |
| 125%                        | 31.4   | 34.6   | 35.8   | 56.8   | 51.6   |
| 75%                         | 18     | 22.4   | 21.1   | 31.6   | 28.1   |
| QFC 4                       |        |        |        |        |
| 125%                        | 19.2   | 21.8   | 21.1   | 26.9   | 25     |
| 75%                         | 13.2   | 15.4   | 14.8   | 19.4   | 17.3   |

(b) Esize at 38nm HP

| QFC type/loading to PAG Type | 38nm Esize [mJ/cm²] |
|-----------------------------|---------------------|
|                            | PAG 1  | PAG 2  | PAG 3  | PAG 4  | PAG 5  |
| QFC 1                       |        |        |        |        |
| 125%                        | 18.4   | 21     | 21     | 23.6   | 24     |
| 75%                         | 12     | 13.6   | 13.6   | 17     | 16.6   |
| QFC 2                       |        |        |        |        |
| 125%                        | 26.4   | 29.8   | 31.2   | 47.2   | 44.4   |
| 75%                         | 14.5   | 15.9   | 16.8   | 23.6   | 23     |
| QFC 3                       |        |        |        |        |
| 125%                        | 23.7   | All pattern fallen | 34.2 |
| 75%                         | 13.8   | All pattern fallen | 19.1 |
| QFC 4                       |        |        |        |        |
| 125%                        | 15.2   | 17     | 17.5   | 21.4   | 20.1   |
| 75%                         | 10.2   | 11.8   | 12.4   | 14.6   | 13.8   |

(c) Esize at 37nm HP

| QFC type/loading to PAG Type | 37nm Esize [mJ/cm²] |
|-----------------------------|---------------------|
|                            | PAG 1  | PAG 2  | PAG 3  | PAG 4  | PAG 5  |
| QFC 1                       |        |        |        |        |
| 125%                        | 24.7   | 27     | 27     | 30.2   | 31     |
| 75%                         | 15.6   | 17.8   | 17.2   | 21.8   | 20.8   |
| QFC 2                       |        |        |        |        |
| 125%                        | 32.4   | 34.6   | 36.8   | 56     | 52.8   |
| 75%                         | 18     | 20.1   | 20.8   | 29.1   | 28     |
| QFC 3                       |        |        |        |        |
| 125%                        | All pattern fallen |        |
| 75%                         | All pattern fallen | |
| QFC 4                       |        |        |        |        |
| 125%                        | 21.6   | 23.4   | 22.9   | 28     | 26.4   |
| 75%                         | 14.4   | 16     | 16     | 19.4   | 18.7   |

In case of QFC 4, it showed lower level of Esize contribution than QFC 1 and mostly constant at 45nm HP as remarkably different to QFC 3 and 4. Considering of specific environment with relatively higher photo-efficiency PAG or higher acid concentration, weak basicity or less diffusive type of QFC didn’t contribute actively to control acids as compared to other types of QFC. It was also
observed in same case at even at higher normalized image log slope (NILS) condition such as 45nm HP. However, when moved to print narrower L/S CD area, 38nm HP and 37nm HP, QFC 4 showed a change of Esize contribution to higher at even with lower 193 absorbance PAG as like PAG 4 and 5.

3.3. Line width roughness (LER) contribution

Line Width Roughness (LWR) is a quite complicated measurement parameter relevant to complexed physical condition impacted from exposure optics, light intensity, resist film thickness and other temperature/time process condition, and, also to chemical properties such as resist polymer activation energy, PAG photo efficiency, photo-acid concentration, acidity, diffusion, dissolution rate and other related functional parameters. Focusing to control of acid concentration and/or diffusion, it is significantly important to understand a contribution of QFC with different types of PAG to LWR. Continued same approach as previous Eth and Esize variation with QFC’s type and loading with PAG types, it was measured LWR contribution at all half pitch of 45nm, 38nm and 37nm respectively, and described in Table 4 and Fig. 4. QFC 3 was eliminated from the comparison of LWR at both 38nm HP and 37nm HP due to all fallen out of line pattern.

As seen in Table 4, QFC 1 showed mostly 2.3 nm~2.7 nm range of LWR variation through loadings and PAG types on both 45nm HP and 38nm HP, and 2.9 nm~3.4 nm at 37nm HP. Compared to QFC 2 and QFC 4 shown in the table, it observed QFC 1 had all lower LWR values through different pitch conditions and particularly showed much better and lower roughness at narrower CD area 37 nm. Considering NILS on 37nm HP, it typically brought poor aerial image and harder to print patterns than the condition of 45nm or 38nm HP. QFC 1 reached a level of LWR 2.9~3.3 nm at 37nm HP as ~1.5 nm lower remarkably from that of QFC 2. For the case of LWR variation from QFC loading, it almost went to lower when applied higher QFC loading or less variation within 0.1nm range. However, QFC 3 behaved differently to LWR variation from other QFCs as shown in Table 4. At 45nm HP, QFC 3 increased LWR to higher as 0.2 nm~0.6 nm variation range with increasing its loading. QFC 3 had a nature of surface allocation highly than other QFCs and impacted hugely to change a profile on top area of line pattern, as shown in Fig. 5, and it was thought to induce line pattern fallen at narrower CD area.
Table 4. Line Width Roughness (LWR) Variation from QFC type/loading with PAG type on half pitch 45 nm, 38 nm and 37 nm.

(a) QFC 1 - LWR

| Loading | CD Feature [half pitch] | PAG 1 | PAG 2 | PAG 3 | PAG 4 | PAG 5 |
|---------|-------------------------|-------|-------|-------|-------|-------|
| 125%    | 45nm                    | 2.6   | 2.5   | 2.5   | 2.4   | 2.4   |
| 75%     | 45nm                    | 2.7   | 2.7   | 2.7   | 2.6   | 2.6   |
| 125%    | 38nm                    | 2.6   | 2.4   | 2.4   | 2.3   | 2.3   |
| 75%     | 38nm                    | 2.7   | 2.6   | 2.6   | 2.5   | 2.5   |
| 125%    | 37nm                    | 3.3   | 3.2   | 3.1   | 3.0   | 2.9   |
| 75%     | 37nm                    | 3.5   | 3.3   | 3.2   | 3.1   | 2.9   |

(b) QFC 2 - LWR

| Loading | CD Feature [half pitch] | PAG 1 | PAG 2 | PAG 3 | PAG 4 | PAG 5 |
|---------|-------------------------|-------|-------|-------|-------|-------|
| 125%    | 45nm                    | 3.1   | 3.0   | 3.1   | 3.2   | 3.2   |
| 75%     | 45nm                    | 3.2   | 3.1   | 3.1   | 3.2   | 3.2   |
| 125%    | 38nm                    | 3.3   | 3.0   | 3.2   | 3.2   | 2.9   |
| 75%     | 38nm                    | 3.3   | 3.1   | 3.2   | 3.2   | 3.0   |
| 125%    | 37nm                    | 4.6   | 4.3   | 4.5   | 4.8   | 4.4   |
| 75%     | 37nm                    | 4.5   | 4.3   | 4.2   | 4.7   | 4.3   |

(c) QFC 3 – LWR

| Loading | CD Feature [half pitch] | PAG 1 | PAG 2 | PAG 3 | PAG 4 | PAG 5 |
|---------|-------------------------|-------|-------|-------|-------|-------|
| 125%    | 45nm                    | 3.8   | 3.8   | 4.0   | 3.7   | 3.8   |
| 75%     | 45nm                    | 3.2   | 3.4   | 3.4   | 3.3   | 3.6   |
| 125%    | 38nm and 37nm : all pattern fallen |   |   |   |   |   |
| 75%     | 38nm and 37nm : all pattern fallen |   |   |   |   |   |

(d) QFC 4 - LWR

| Loading | CD Feature [half pitch] | PAG 1 | PAG 2 | PAG 3 | PAG 4 | PAG 5 |
|---------|-------------------------|-------|-------|-------|-------|-------|
| 125%    | 45nm                    | 3.2   | 2.9   | 2.9   | 2.8   | 2.8   |
| 75%     | 45nm                    | 3.3   | 3.0   | 3.0   | 3.0   | 3.1   |
| 125%    | 38nm                    | 3.2   | 2.8   | 2.8   | 2.7   | 2.8   |
| 75%     | 38nm                    | 3.2   | 2.8   | 2.8   | 2.7   | 2.8   |
| 125%    | 37nm                    | 3.8   | 3.6   | 3.7   | 3.5   | 3.3   |
| 75%     | 37nm                    | 3.9   | 3.8   | 3.9   | 3.6   | 3.4   |

From Fig. 5, it was shown QFC 3 which was surface active type had a strong top profile as independently from PAG types, while other QFCs showed a change of top profile from PAG 2 to PAG 4 as following those absorbance level. This could support a result of LWR increment to higher with QFC 4 as observed in Table 4. Additionally, it observed QFC 1 had the lowest LWR at each CD areas of line pattern, and lower variation of LWR from changing its loading in resist formulation, which meant to have more stable and less sensitive from changing of concentration ratio between QFC and acids generated from PAG at the edge of exposed/unexposed area. This advantage of QFC 1 also contributed to print narrower CD features without drastic change of LWR performances compared to other QFCs - specifically QFC 2 as shown in Fig. 6, from its natures of efficient distribution in resist matrix rather than allocating mostly to surface and relatively weak basicity to avoid a huge change of acid concentration.
4. Conclusion

In this experiment, it was carried out to take a comparison of various Quencher-functional component (QFC) as matching with different types of PAG, through seeing Line Width Roughness (LWR) contribution from relatively larger CD 45nm half pitch to smaller 37nm half pitch. For better understanding of LWR variation from QFC loadings and LWR contribution to narrower CD area, it was investigated with QFC’s response to Dose such as Dose to Clear (Eth) and Optimal Dose to Print (Esize).

From reviewing of results, QFC 1 was strongly recommended for applying to high resolution patterning as likely to 38nm or 37nm HP patterning in single exposure as lower NILS environment, since was able to achieve better and lower LWR without sacrificing of Dose response performance and fast Esize contribution, rather than other types of QFC such as surface-active property or highly strong basicity type.

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