Materials and Processes of Negative Tone Development for Double Patterning Process

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A new negative tone imaging with application of new developer to conventional ArF immersion resist materials is proposed to form narrow trench and contact hole patterns, which is promising for double patterning process, since it is difficult to obtain sufficient optical image contrast to print narrow trench or contact hole below 60 nm pattern size with positive tone imaging. No swelling property in the developing step realized low LWR number at 32 nm trench patterns. Uniform de-protection ratio through the depth of resist film reduced cuspy resist pattern profile causing micro-bridges at narrow trench pattern, and low frequency LWR number down to 2.4 nm. High resolution potential was demonstrated with 38 nm dense S/L under 1.35 NA immersion exposure. Better CD uniformity and LWR number of trench pattern were obtained by negative tone development (NTD) process with comparison to positive tone development (PTD) process. Excellent defect density of 0.02 counts/cm² was obtained for 75 nm 1:1 S/L by combination of 0.75 NA dry exposure and NTD process combination. NTD process parameters impacts to defectivity were studied.

Keywords: Negative tone imaging, 193 nm immersion lithography, Double patterning, Fine trench imaging, CD uniformity, Defectivity

1. Introduction

Double patterning process with ArF immersion exposure is getting the only candidate for the 32 nm half pitch lithography in the mean time, followed by extension down to 22 nm half pitch lithography[1,2]. As well known, there are several methods in double patterning, such as double exposure process, spacer defined process, double line process, litho-process-litho-etch (freezing) process, double trench process, and dual tone development process. Spacer defined process is now ready for manufacturing flash memory devices below 40 nm half pitch design rule[3, 4]. However, it is difficult to obtain complex layout of line patterns with this process since only sidewalls of line patterns can define the pattern layout, therefore, this process can not be applied to logic devices in which there are a lot of complex pattern layout for each layers. On the other hand, double line and double trench process are good candidates for the lithography of complex pattern layouts[5]. Many studies of freezing process are still continued as the alternative process of double line process[6-9], however, there are some difficulties in defining CD-offset and defect control.

Double line process is indeed good candidate for the low coverage ratio layers, since narrow line pattern can be easily obtained due to the enough optical image contrast for the optical lithography. However, as well known, it is very difficult to obtain enough optical image contrast in narrow trench pattern with positive tone imaging, therefore, there is no lithography solution for high mask coverage ratio layers such as metal wiring layers and via hole layers that dual damascene process is applied in the case of positive tone imaging. On the other hand, it is easy to obtain enough optical image contrast for high coverage ratio layers with negative tone imaging[10].

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There are two methods for negative tone imaging. The one is the combination of the resist material that works as negative resist (e.g., cross-linking resist, lactone-ring closing resist) and alkaline positive tone developer [11]. The other is the combination of the conventional positive tone resist material that the protection group can be cleavable with acid-catalyzed reaction, and new negative tone developer (NTD) [10]. The polarity of conventional positive tone resist material is increased with the de-protection reaction, in which the high polar resist material gives slower dissolution rate to the new negative tone developer compared to the low polarity material. Thus, the dissolution contrast of the latter method comes from the polarity change of resist material.

Very low or no swelling properties were confirmed with QCM analysis with NTD process [10]. In combination of alkaline positive tone development (PTD) and conventional ArF positive tone resist materials, some swelling properties are usually observed, since the partially de-blocked polymers that do not have enough dissolution rate to developer allow alkaline chemicals to penetrate into film, then, generate ionized polymers that have high polarity. Finally, such high polarity chemicals induce swelling properties with penetration of aqueous solution. In NTD process, there’s no ionization step, therefore, penetration rate should be much slower than that of PTD process. This should be the reason why the swelling properties were not observed in NTD process.

Better narrow trench resolution and LWR number were demonstrated with the first resist platform of FAiRS-9521A01 and NTD process compared with PTD process [12]. These results should come from not only better optical image contrast, but also ideal dissolution character of very low or no swelling properties in development step. The first platform of FAiRS-9521A01, although, has an issue of surface micro-bridging at narrow trench pattern, therefore, LWR number should be improved if the issue could be removed. We have only demonstrated better lithography performance in narrow trench pattern, but not demonstrated manufacturability performance such as CD uniformity and defectivity.

Recently, this NTD process is studied for several special double patterning processes in addition to the application of double trench process. First example is the application of fine contact hole imaging with combination of vertical and horizontal lines double exposure process and NTD process [13]. Second example is pitch frequency doubling with combination of just one exposure process and dual tone development process [14, 15]. Therefore, manufacturability performance such as CD uniformity and defectivity should be confirmed.

2. Experimental

2.1. Materials

Adamantane-based alicyclic methacrylate copolymers having an acid-decomposable group were synthesized using free radical polymerization in order to employ in this study. An organic solution, containing each of the adamantane-based copolymers and a triarylsulfonium type photo acid generator (PAG) and an amine as a base, was prepared for resist samples.

2.2 Lithographic conditions

The resist solution was filtered and spin-coated on silicon wafer that was coated with a bottom anti-reflection coating (BARC), and baked at 100 °C for 60 sec, and giving film thickness of 100 nm as standard process. The wafers were exposed through reticle using an ASML PAS5500/1100 ArF laser scanner with 0.75NA, a TWINSCAN™ XT:1700i ArF laser immersion scanner with 1.20NA, or a TWINSCAN™ XT:1900i ArF laser immersion scanner with 1.35NA, dipole or annular illumination system. After the exposure, the wafers were baked (PEB) at 105 °C for 60 sec, and developed with a 2.38% aqueous trimethylammonium hydroxide (TMAH) solution at 23 °C for 30 sec or a new negative tone developer composed of an organic solvent. Detail conditions of development process are described in each section.

2.3 SEM measurement conditions

A Hitachi S-9380II or a KLA Tencor eCD-II scanning electron microscopy (SEM) was used to measure pattern width and LWR. The LWR was defined as a 3σ of line width distribution. The threshold algorithm and a threshold level of 50 % were employed for detecting the pattern edges of line in top-view images obtained at the magnification of 150000. To quantify LWR, a 350 nm area of line patterns was divided into 32 regions, then, the line widths of the 32 equally divided areas were measured.

2.4 Defectivity evaluation conditions
There are two methods for negative tone imaging. The one is the combination of the resist material that works as negative resist (e.g., cross-linking resist, lactone-ring closing resist) and alkaline positive tone developer\textsuperscript{[11]}. The other is the combination of the conventional positive tone resist material that the protection group can be cleavable with acid-catalyzed reaction, and new negative tone developer (NTD)\textsuperscript{[10]}. The polarity of conventional positive tone resist material is increased with the de-protection reaction, in which the high polar resist material gives slower dissolution rate to the new negative tone developer compared to the low polarity material. Thus, the dissolution contrast of the latter method comes from the polarity change of resist material.

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2.4 Defectivity evaluation conditions
Line and space patterns with 150 nm pitch 1:1 duty were printed on an 8-inch wafer and inspected in 87 cm² area. A KLA Tencor 2360 bright field defect inspection tool was used for the defect inspection with array mode and 0.25 µm pixel. Detected defects were reviewed with a SEM of Applied Materials SEMVisionG3.

3. Results and Discussion
3.1 Material solution for micro-bridging issue

The first resist platform, FAiRS-9521A01, for NTD process has an issue of micro-bridges with narrow trench patterning (Fig. 1). These micro-bridges were observed only at resist surface area, but not at bottom of resist pattern. There’s no line width dependence, but trench width dependence. Many micro-bridges were observed in finer trench pattern below trench width of 40 nm.

(a) 

(b)

Fig. 1. Trench pattern profile of FAiRS-9521A01, (a) trench CD is 45 nm, (b) trench CD is 32 nm.

Two hypothesis can be proposed, the one is dissolution rate decrement at resist surface due to the highly de-blocked polymer localization at the surface after PEB, and the other is swelling of resist pattern due to the penetration of developer or rinse water into resist pattern. No or very low swelling property was already confirmed by QCM analysis during development and rinse step of NTD process, in comparison to the PTD process, therefore, un-uniform dissolution rate distribution through depth of resist film is suspected. Since dissolution rate contrast in NTD process arises from polarity change of polymers by the de-protection reaction, de-protection ratio through depth of resist film was analyzed with TOF-SIMS method on the surface of slantingly sliced resist films that were exposed with different dose for each (Fig. 2). No de-protection reaction was observed with the resist film that non-exposed and exposed at 2.0 mJ / cm². De-protection reaction was completed almost at 6.4 mJ / cm² through depth of resist film. The polymers at resist film surface were completely de-protected at 4.2 mJ / cm², but the polymers inside of resist film were partially de-protected from 4.2 mJ / cm² to 5.6 mJ / cm². Especially, most of protection groups of inside of the resist film are still un-decomposed at 4.2 mJ / cm². These facts suggest that there’s un-uniform dissolution rate distribution through depth of resist film at half-exposed area to provide slow dissolution rate of resist film surface at such area, although that of inside of resist film could be dissolved faster. To realize uniform dissolution rate distribution through depth of resist film, the de-protection ratio distribution through depth of resist film should be uniform for every exposure doses.

![Fig. 2. TOF-SIMS analysis result of protection unit on the surface of slantingly sliced resist films that were exposed with different dose for each other.](image)

From these analytical results, it should be important to realize the uniform acid distribution generated from PAG through depth of the resist film during the de-protection reaction step, since the de-protection reaction is acid-catalyzed reaction. The uniform PAG distribution through depth of the resist film after coating has already been confirmed, therefore, the generated acid may be concentrated to resist film surface during PEB step. PAG and generated acid concentration was analyzed by ESCA method at resist surface before and after PEB step, and the ratio of these concentration numbers are described as relative acid concentration ratio. This number was measured for several PAGs and PEB temperatures, and the results were summarized in Fig. 3. The conventional PAG that was applied to FAiRS-9521A01 showed higher relative acid concentration ratio numbers at every PEB temperatures compared to PAG-A, B, and C. This results means that the generated acid from conventional PAG is easily concentrated around resist film surface during PEB step to de-protect polymer around resist surface easily, compared to that of inside of the resist film. On the other hand, PAG-A and B are hardly to be concentrated to resist surface during PEB step compared to the
conventional PAG and PAG-C, therefore, microbridges should be suppressed with these PAG-A or B application.

Fig. 3. ESCA analysis results of PAG and generated acid concentration at resist surface. Relative acid concentration ratio indicates the ratio of the concentration after PEB to that before PEB.

The suppression of micro-bridges was demonstrated with 1.2 NA immersion exposure process on sample-A that PAG-A applied and sample-B that PAG-B, where 32 nm trench with 128 nm pitch were applied to print on the wafer (Fig. 4), and sample A was focused on to study lithography performance in detail. Sample A showed 88 nm pitch resolution at the same dose for 32 nm trench patterning with 64 nm 1:1 mask although 96 nm pitch could not be resolved with FAiRS-9521A01 (Fig. 5). Although high frequency LWR numbers at 32 nm trench were 4.1 nm for sample A and 4.2 nm for FAiRS-9521A01, low frequency LWR numbers at same pattern were 2.4 nm for sample A and 4.2 nm for FAiRS-9521A01 (Fig. 6). These results suggest that sample A has better resolution compared to FAiRS-9521A01. Furthermore, sample A showed 38 nm half pitch resolution with large exposure latitude of 29% and large bridge margin of 33% on 1.35 NA immersion exposure process (Fig. 7).

Fig. 4. 32 nm trench pattern profile for (a) FAiRS-9521A01, (b) sample-A, (c) sample-B.

Fig. 5. Mask linearity data for (a) FAiRS-9521A01 and (b) sample-A at the dose for 32 nm trench patterning with 64 nm 1:1 mask

Fig. 6. Top down view and LWR number of (a) FAiRS-9521A01 with normal scan, (b) FAiRS-9521A01 with rectangle scan, (c) sample-A with normal scan, (d) sample-A with rectangle scan of 32 nm trench with 128 nm pitch.

Fig. 7. (a) Top down and (b) cross-section view of sample-A at 38 nm 1:1 dense pattern.

3.2 CD and LWR uniformity

Sample A was employed for the CD and LWR uniformity study with NTD and PTD process. A dynamic dispense unit that is a trial unit was applied for NTD, and a static dispense unit that is a production unit was applied for PTD. Although the unit and process have not been optimized for NTD, good intra-wafer CD uniformity number of 3.3 nm at semi-isolated trench pattern of 45 nm with 128 nm pitch was already obtained with NTD process, while PTD process gave worse CD uniformity around 4.0 nm within the wafer even under optimized dispense unit and process. Still CD local distribution was observed on the wafer with NTD process (narrow trench size at left-bottom area on the wafer (Fig. 8a), such local distribution should be process-induced because dispensed developer attacked this area at the beginning of developer dispense. Therefore, this typical CD distribution could be fixed by optimization of dispense unit and development process to improve CD uniformity.
CD uniformity numbers at dense trench pattern of 43 nm CD with 90 nm pitch were 1.6 nm for NTD and 1.4 nm for PTD so that it is said there was no big difference between these processes at dense pattern (Fig. 9). Intra wafer LWR number distribution at dense trench pattern with NTD process was 4.8 nm, which was smaller number by 0.5 nm than that of PTD process (Fig. 10).

3.3 Defectivity
Sample A was also inspected defectivity over 75 nm 1:1 line and space pattern areas, where evaluation conditions were as follows; a dynamic dispense unit for development step, 20 second development time, and 0.75 NA ArF dry scanner for exposure step (Fig. 11). Only two defects were observed in 87 cm² inspection area, thus, the defect density number was only 0.02 counts / cm², of which detected defect type was classified as particle. Large resist pattern area and large substrate area were also inspected, and the total defect densities were 0.10 counts / cm² for large resist pattern area and 1.04 counts / cm² for large substrate (BARC) area (Fig. 12), respectively. The type of defects on large resist pattern was fall-on type particle (0.10 counts / cm²), and those on large substrate were blob type (0.31 counts / cm²) and typical particle type (0.73 counts / cm²).

Process parameter, such as development time, rinse time, paddle or paddle-less in development step, and exposure dose, were studied to understand how these parameters would influence to defectivity on large resist pattern and large substrate. Most of these parameters did not influence to defectivity, although, long development time of 60 seconds with dynamic development resulted higher defect density of blob type (0.60 counts / cm²) and particle (1.38 counts / cm²) on large resist patterned area, and particle (2.08 counts / cm²) on large substrate area, respectively. Even though the development unit and processes have not been optimized, these defectivity were good enough on early stage of process development, however, it is considered that defectivity performance can be improved with materials of developer, rinse, and resist, process optimization with developer or rinse nozzle, development cup, or process parameter in development recipe.
4. Conclusion

NTD process with organic developer is good candidate for litho-etch-litho-etch double patterning process, especially for high mask coverage ratio layers such as metal wiring layers and via hole layers that dual damascene process is applied, since the enough optical image contrast can be easily obtained compared to positive tone imaging. The root cause of the micro-bridging issue in the first resist platform for NTD process was studied, where control of the generated acid distribution through depth of resist film during de-protection reaction of polymers realized uniform de-protection through depth of resist film. New platform of sample-A (named as FAiRS-9521A02) showed not only no micro-bridge issue but also better lithographic performance in LWR and resolution. Besides, NTD process showed advantages in CD-uniformity of isolated trenches and LWR compared to PTD process. Very low pattern defect density of 0.02 counts / cm² was obtained even without fully optimized hardware and recipe of development step. Further improvement will be investigated with material, hardware, and process optimization in CD-uniformity and defectivity.

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