Development of Materials and Processes for Double Patterning toward 32 nm Node ArF Immersion Lithography

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A new negative tone imaging with application of new developer to conventional ArF immersion resist materials is proposed for narrow trench pattern formation, which is effective to the double trench process that is one of the candidates of double patterning process for 32 nm node semiconductor devices. No swelling property was realized in the developing step, in which the dissolution mechanism was discussed. Significantly better line width roughness (LWR) and resolution on narrow trench pattern were observed with this negative tone development compared to positive tone development. These results suggest that this negative tone development process is one of the promising candidates for double trench process.

Keywords: negative tone imaging, ArF immersion lithography, double patterning

1. Introduction

Double patterning process with ArF immersion exposure tool is now positioned as the best candidate of 32 nm node device manufacturing^[1]. Several special processes are proposed to relax difficulty to achieve the minimum pitch in one exposure step. Spacer-defined process is a good method to obtain simple 1:1 line and space dense pattern, and considered to be applied to flash memory devices^[2]. This process has a self-aligned patterning step, which is spacer (sidewall) formation besides the first etched hard mask. Therefore, it is not possible to obtain complex pattern layout like gate layer in logic devices with spacer-defined process. Double line process (litho-etch-litho-etch process) is useful for such complex pattern layout since there is not restriction in pattern type^[3]. However, two hard mask layers are necessary for double line process, and it is difficult to apply this process to layers that have small area to be opened, for example, metal layers in logic devices. Double trench process is better candidate for such layers, and there's no necessity to use two hard mask layers^[4]. Therefore, double trench process has an advantage in the viewpoint of cost and throughput.

As well known, it is very difficult to open narrow trench with conventional positive imaging process using conventional resist whose dissolution rate increases with the action of acids generated from PAG. It is considered that this poor imaging performance on narrow trench patterning comes from the poor optical image intensity that leads to poor under dose margin. Although a dark mask is necessary for trench patterning with positive tone imaging process, a bright mask, which can afford strong optical intensity and better image contrast, can be applied to trench patterning with negative tone imaging.

There are two methods obtaining negative tone image, the one has a combination of new negative tone resist^[5] and conventional alkaline developer, and the other is a process with a conventional resist material and new negative tone developer. In the former case, the negative tone resist material usually needs polar and hydrophilic units to perform high dissolution rate to alkaline developer and such units may stay after exposure, since the pattern formation is realized by the cross-linking reaction which may not destroy polar and hydrophilic units. Water and alkaline molecules

in the developer can easily penetrate into the resist film having those units during development step, followed by pattern swelling to result large line width roughness (LWR), bridging margin, and high defectivity. Therefore, we started to study the latter negative imaging process, which includes conventional ArF immersion resist material and new negative tone developer, as the dedicated process to double trench process for 32 nm node device manufacturing.

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.

2.1. 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 s, and giving film thickness of 100–160 nm. The wafers were exposed through reticle using an ASML PAS5500/1100 ArF laser scanner with 0.75NA or a TWINSCANTM XT:1700Fi ArF laser immersion scanner with 1.20NA, dipole or annular illumination system. The wafers were baked (PEB) after the exposure and negative tone development composed of an organic solvent. A Hitachi S-4800 or S9380II scanning electron microscopy (SEM) was used to measure pattern width and LWR. The LWR was defined as a 3 σ of line width distribution. The threshold algorithm, the threshold level of 50 % w 105 °C for 60 s and development with a 2.38% aqueous trimethylammonium hydroxide (TMAH) solution at 23 °C for 30 s were employed, for detecting the pattern edges of line in top-view images obtained at the magnification of 150,000. 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.

2.3 QCM analysis

The mass variation of a resist film in development step was measured by quartz crystal microbalance (QCM) method with Litho Tech Japan QCM AZ-3. The resist solution was filtered and spin-coated on QCM substrate. The

coated substrate was baked at 100 °C for 60 sec to give film thickness of 150 nm. The substrate was exposed with 193 nm using Litho Tech Japan IMEC-5000 ArF laser exposure tool without any reticle, and baked at 105 °C for 60 s. The prepared substrate was finally used for the mass variation measurement at 23 °C for 100 s.

3. Results and Discussion

3.1 Dissolution property

In the case of positive tone imaging process with a conventional resist material and alkaline developer, the acid-sensitive polymer generates alkaline-developable units of ArF resist, which are usually carboxylic acids. In the case of negative tone imaging process on this study, the resist material is basically the same as the conventional resist, so that, the dissolution contrast is derived from the polarity or hydrophobicity change of the polymer by the de-protection reaction with the acid generated from PAG. Thus, it is supposed that hydrophobicity or polarity parameter of developer liquid is key to control dissolution contrast. Dissolution rates of a polymer protected with acid-labile units or a de-protected polymer were measured for many organic solvents as developer chemical, and the results were summarized in Fig. 1. Since the four kinds of solvents having the hydrophobicity parameter^[6] around 3–4, and polarity parameter^[6] the protected polymer, but poor solvent to the de-protected polymer, these solvents can be good candidates for the negative tone developer.

Fig. 1. Dissolution character with organic solvents. White dots indicate both protected and de-protected polymer films were dissolved within 30 s. Black dots indicate both polymer films were not dissolved within 30 s. Gray dots indicate only protected polymer film was dissolved within 30 s.

Fig. 2. Film thickness data for an ArF resist, a) after PEB indicated as gray dots, b) after positive tone development indicated as black dots, c) after negative tone development indicated as white dots.

As increasing exposure dose, the film thickness started to decrease at around 4 mJ/cm^2 and the film was dissolved completely at around 6 mJ/cm^2 with the alkaline developer as shown in Fig. 2. This result suggests that the polymer reacts with the acid over 4 mJ/cm^2 to generate alkaline-developable units. On the other hand, the film thickness started to increase at 4.5 mJ/cm^2 and the film was not dissolved over 7 mJ/cm^2 during negative tone development. The change of dissolution rate occurred at practically same dose between the two development processes, positive development with the alkaline chemical and negative development with organic chemical. This fact suggests that the dissolution contrast in the negative tone development process is derived from the de-protection reaction of polymer.

Although most of the ArF resist have somewhat swelling property under alkaline developer, we expected low swelling property with this negative tone development, since the developer of organic chemical has much more hydrophobic property than alkaline developer. The swelling property in this negative tone development process was confirmed with QCM analysis and the results were summarized in Fig. 3. The film was exposed from 1 mJ/cm^2 to 6 mJ/cm^2 , followed by PEB to dip into organic developer within 20 seconds, and the dissolution rate became slower and slower with increase of dose. The delta frequency did not go to minus value under exposure during $1\text{-}6 \text{ mJ/cm}^2$.

This results supports that there is no swelling property both in the film composed of polymer protected with acid-labile unit and in the film composed of de-protected polymer, soaked in the organic negative tone developer. A film

Fig. 3. QCM measurement results with a negative tone developer and exposed ArF resist films.

exposed with a little dose energy contains a partially de-blocked polymer having hydrophilic and acidic unit, even the dissolution rate of the film is slow enough to retain patterns after developing step with alkaline developer. The hydrophilic and acidic unit is neutralized and ionized with alkaline chemical during positive tone development to make resist matrix hydrophilic to accelerate water sinking through the film. Although the local hydrophilicity becomes larger by the neutralization, average hydrophilicity is still insufficient to develop in the case of low dose, since most of the protecting units in the polymer are not converted to acidic unit yet. The dissolution steps of a film consist of developer penetration, solvation of polymer, and diffusion into developer. Since the solvation rate is very low with low dose area by insufficient de-protection, the dissolution rate depends on the solvation rate during development process with alkaline chemical. On the other hand, there is no neutralization step in the negative tone development process with organic developer so that it is considered that this property gives in the low swelling property. Additionally, since the molecular size of water is very small, water molecules easily penetrate into the film, but most of the organic solvents have much larger molecular size, therefore, penetration rate of organic solvent to the film is presumably much slower than that of water. Therefore, penetration step may determine the dissolution rate in the negative tone development process. Actually, faster dissolution rate was observed with organic solvent having small molecule size than larger one.

As commonly well known, every organic chemical has its own dissolution rate to an organic

solvent, therefore, the dissolution contrast depends on the chemical structure, molecular weight, and arrangement of monomer unit in polymer. A molecular weight dependency to the dissolution contrast was studied and summarized in Fig. 4. In the case of a polymer of low molecular weight below 6,000, the dissolution contrast was too small to obtain even rough pattern, although the de-protected polymer has very high dissolution rate to the organic developer. The dissolution rate of the exposed film, which contains highly de-protected polymer, became significantly slower with increase of molecular weight of polymer, however, the dissolution rate of unexposed film became slightly slower compared to the exposed film with increase of molecular weight of polymer. Sufficient dissolution contrast was obtained with the polymer having above molecular weight of 9,000.

Fig. 4. Dissolution rate and dissolution contrast of an ArF resist with negative tone developer, (a) unexposed film, (b) exposed with 15 mJ/cm², (c) dissolution contrast.

Fig. 5. Dissolution rate comparison of an ArF resist with (a) negative developer and unexposed film, (b) negative developer and exposed film, (c) positive developer and unexposed film, (d) positive developer and exposed film.

From these dissolution studies, we selected an organic solvent as developer from the four gray dotted candidates in Fig. 1, and a polymer having molecular weight of 9,000 as the resist material for further study in this paper. The dissolution rates of exposed film with 15 mJ/cm² and unexposed film to the both positive alkaline developer and negative organic developer were summarized in Fig. 5, of which the resist has dissolution contrast of 1.3×10^3 to the negative tone developer, and 1.3×10^5 to the positive tone developer, respectively. This dissolution contrast supposed to be large enough to obtain fine pattern for semiconductor devices.

3.2 Lithographic performance

This negative tone development process gave fine trench patterns with 1.2 NA immersion exposure tool, dipole illumination, and a 6% half tone mask. LWR values with this negative tone development process were compared to those with positive tone development process at 45 and 32 nm trench patterns, and the results were summarized in Fig. 6. The same resist, exposure tool, and mask were applied also to positive tone development processes. Manual dipping process was applied to negative tone process. LWR values of 45 nm trench pattern with negative tone process were 3.2 nm, and that with positive tone process were 4.3 nm. In addition, 32 nm trench patterns were nicely opened with negative tone development process, although this pattern could not be opened with positive tone development. It can be considered that the better LWR with

Fig. 6. Trench patterning result of ArF resist with 1.2 NA immersion exposure and (a) negative tone developer, (b) positive tone developer.

Fig. 7. Illustration for explanation of pitch frequency doubling mechanism with double development. (a) The area to be opened with positive tone development. (b) The area to be opened with negative tone development. (c) The area to be remained as resist pattern after double development. (d) Mask. (e) The threshold of de-protection ratio for dissolution into a positive tone developer. (f) The threshold of de-protection ratio for dissolution into a negative tone developer.

negative tone process was derived from no swelling property in the dissolution step.

These results suggest that the negative tone imaging process with organic developer has enough potential to apply to semiconductor device manufacturing, especially in the layers that need narrow trench patterning, for example, metal layers and implant layers of logic devices, the layers that double trench process should be applied in 32 nm node.

3.3 Feasibility of pitch frequency doubling with double development

If the de-protection ratio thresholds for dissolution between the positive alkaline development and negative organic development are different with each other as shown in Fig. 7, there arises the possibility of pitch frequency doubling using double development with positive and negative developer^[7]. The sensitometry results, shown in Fig. 2, support the possibility of pitch frequency doubling, since the doses to open between the positive and negative development are different with each other. The less exposed areas are developed with negative developer and much exposed areas are developed with positive developer. Finally, the pattern configuration after double development is completely the same as the case of spacer-defined process as shown in Fig. 8.

Fig. 8. Illustration for explanation of process steps for spacer-defined process and double development process. (a) Cross-section view for each step of spacer-defined process. (b) Overview of line end for each step of spacer-defined process. (c) Cross section view for each step of double development process. (d) Overview of line end for each step of double development process.

Spacer-defined process requires the steps of spacer deposition on hard mask etched with first pattern, etch back step, and etching hard mask, on the other hand, the double development process does not require such steps, as shown in Fig. 8. Therefore, double development process has advantages in throughput and cost compared to spacer-defined process although it is still difficult to apply to a complex pattern layout.

Double development feasibility was demonstrated with the condition of 0.75 NA ArF

dry exposure tool, 1 : 1 120 nm 6% half tone mask, first development with negative tone developer for 15 second, and second development with 0.048% TMAH alkaline developer. As shown in Fig. 9, 120 nm pitch line and space patterns were obtained, and the quite low k_1 number of 0.23 was obtained with calculation on Rayleigh's equation (1).

$$(\text{Resolution}) = k_1 \times (\text{wavelength of light source}) / (\text{numerical aperture}) \quad (1)$$

Quite high resolution of 33 nm is expected from this low k_1 number of 0.23 with 1.35 NA ArF immersion exposure process.

Fig.9. Top-down SEM image of resist pattern of 120 nm pitch line and space after processing with double development with negative tone development and positive tone development.

4. Conclusion

New negative tone development process with organic developer was proposed for fine trench pattern formation with ArF exposure process, since larger optical image contrast can be applied with negative tone imaging compared to positive tone imaging. The dissolution contrast comes from the polarity or hydrophobicity change by the acid-catalyzed de-protection reaction of polymer, similar to positive tone process. No swelling property was observed in dissolution step with negative development process, and the dissolution contrast is 1.3×10^3 , which is smaller than that of positive tone development, but enough to fine pattern. Better LWR and resolution on trench pattern, compared to positive development

process, was realized with the good optical image and no swelling dissolving property. These results suggest that this negative tone development process is one of the promising candidates for 32 nm node below device manufacturing with double trench process. Feasibility of pitch frequency doubling with application both positive and negative tone development process was studied, and quite low k_1 number of 0.23 was obtained.

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