Inactivation Technology for Pitch Doubling Lithography

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We propose novel inactivation technologies which improve resolution. Base generators have been developed, which inactivate acid by thermal treatment or exposure. This thermal inactivation technology realizes simple litho-inactivation-litho-etch (LILE) process with good fidelity. After 1st patterning, acid is inactivated by amine released from the thermal base generator under low temperature baking of less than 150°C. Just adding one simple low temperature bake process, LILE has two advantages; i) keeping high throughput, and ii) avoidance of pattern deformation. 32nm line and space (l&s) pattern is successfully delineated by pitch split double patterning. The inactivation technology has been expanded to frequency doubling. Photo base generator (PBG) is used to inactivate acid generated by exposure. Acid concentration in both of low and high exposed area is precisely controlled by base generation efficiency of PBG. The dual tone resist, which has positive tone dissolution property at low dose region and negative tone at high dose, splits a line in two and successfully delineates 32.5nm l&s pattern using 65nm l&s mask with single exposure.

Keywords: Inactivation, Base generator, Double patterning, LILE, Dual tone resist, Frequency doubling

1. Introduction

In order to push forward the finer IC manufacturing, both the minimum critical dimension and the pattern pitch of the circuit feature must be reduced. Immersion lithography contributed to accelerate 45nm node device production. The coming of extreme ultraviolet (EUV) lithography is desired to realize beyond 22nm node, however it has many technical issues to overcome. Post 40nm technology is facing thresholds beyond which conventional photolithography process cannot transcend.

Double patterning technology is one of the candidates to break the wavelength brick wall¹⁾. Over the past few years a considerable number of studies have been carried out to apply double

patterning. Self-aligned double patterning (SADP) of sidewall spacer is approaching manufacturing stage of flash memory devices. Litho etch litho etch (LELE) double patterning has been investigated for DRAM and logic devices. Litho litho etch (LLE) including additional freezing step have been proposed such as coating materials cure, HBr/Ar plasma cure, ion implantation cure and vacuum ultra violet (VUV) irradiation cure.^{2), 3), 4), 5)} Simpler LLE processes have been developed employing thermal freezing chemistry in 1st resist⁶⁾ or freezing free Posi/Posi process with alcohol solvent of low PEB temperature 2nd resist⁷⁾.

Cost of ownership is a major concern for double patterning. Therefore, process simplicity is

desired for increasing productivity and decreasing process cost. Double exposure concept have been brought by non-linear resist and contrast enhancement layer (CEL).^{8), 9)} The simplest process is a frequency doubling in the conventional process of single exposure and single development; positive-negative hybrid dual tone resist has been proposed.¹⁰⁾

In this paper, we report rational freezing free materials for LLE application. We also report novel dual tone resist, which realizes frequency doubling by single exposure and single development. The concept, mechanism and optimization of dual tone resist are discussed on simulation and experimental patterning results.

2. Method

2.1 Materials

Polymethacrylate derivative, which has acid labile and lactone adhesion units, was used for 1st resists (Self hypnosis ArF resist for double patterning: SHAD). Base polymer, photo acid generator (PAG), quencher and thermal base generator (TBG) were mixed in propylene glycol 1-monomethyl ether 2-acetate (PGMEA) / cyclohexanone solvent. Carbamate derivatives were used for TBG. Polymethacrylate derivative, including acid labile and hexafluoroalcohol adhesion units, was used for 2nd patterning resists (Joist for ArF double exposure: JADE). Base polymer, PAG and quencher were mixed in alcohol solvent.

Double Frequency ArF resist: DFAR was formulated with PAG, quencher, PBG, polymethacrylate derivative and PGMEA/cyclohexanone solvent. Triphenylsulfonium salt derivative was used for PAG.

2.2 Lithography process

A CLEAN TRACKTM LITHIUSTM i+ (Tokyo Electron Ltd.) was used for SHAD, JADE DFAR apply, bake and development. A Nikon immersion scanner (NSR-S610C) was used for pattern formation of SHAD, JADE and DFAR.

SHAD, JADE and DFAR development was carried out in 2.38wt% tetramethylammonium hydroxide (TMAH) aqueous solution as developer with single puddle for 30sec.

2.3 Measurement

Film thickness was measured with Lambda ACE VM-3010 (Dainippon Screen Manufacture Co. Ltd.). Photo resist line width was measured with a CG-4000 (Hitachi hi-technologies Co.) and cross section pattern was observed with a S-4300 (Hitachi hi-technologies Co.).

Photo acid and base generation were measured on quartz wafers on absorbance at 522nm of coumarin 6, with ArF exposure tool of an ArFES (Litho Tech Japan Ltd.).

2.4 Simulation

Optical simulation was carried out on PROLITHTM (KLA-Tencor Co.) and resist profile simulation was run on Shin-Etsu in house simulator¹¹⁾.

3. Results and Discussion

3.1 LILE Process Flow

A positive resist (SHAD) containing thermal base generator (TBG) for 1st patterning and an alcohol solvent positive resist (JADE) for 2nd patterning are employed (Figure: 1). After 1st patterning, inactivation bake treatment is carried out by acid neutralization with amine from the thermal base generator.

Figure1: LILE Process flow

3.2 Materials and process

3.2.1 Pattern Retention Ability of Self Hypnosis Resist (SHAD)

A 70nm l&s SHAD pattern was formed on BARC (Figure 2a). Figure 2b shows the SHAD pattern after the steps of inactivation bake (130°C/60s), JADE coat, flood exposure (30mJ/cm²), PEB and development. JADE dissolved and SHAD pattern appeared after development. Skipping inactivation bake, the

SHAD pattern disappeared (Figure 2c). The result indicates that the addition of TBG and the inactivation bake treatment is effective to keep 1st pattern shape.

Figure 2: 1st pattern retention ability after 2nd development

3.2.2 Hole fabrication by cross line of double patterning

A delineation of hole pattern by double patterning of X-Y cross line has been proposed¹²⁾. The combination of dipole illumination and polarization creates very high optical contrast, it is promising technology to fabricate $0.3k_1$ hole.

1st SHAD was printed in vertical line on a 100nm film thickness and 2nd JADE was cross over horizontal line on a 65nm film thickness. Illumination condition was NA1.30, dipole, polarization, 6% half-tone phase shifting mask (HT-PSM). Figure 3 shows 40nm hole pattern with constant exposure dose on 1st SHAD and variation dose on 2nd JADE. No CD variation in 1st pattern was observed with variation of 2nd exposure dose. This result indicates that acid on 2nd exposure is efficiently inactivated by TBG.

Figure 4 shows 40nm hole with constant exposure dose and different focus position. A square hole pattern was formed and more than $0.2\mu\text{m}$ depth of focus (DOF) margin was obtained.

Figure 3: 40nm hole with variety of 2nd exposure dose

Figure 4: 40nm hole with variety of focus position

3.2.3 Pitch Split by Double patterning

Pitch split by double patterning is attractive approach to breaking through the diffraction resolution limit at k_1 value of 0.25.

128nm pitch of 1st SHAD pattern was printed on 70nm thickness and 2nd JADE was printed with 32nm shift position on 65nm thickness. Illumination condition is NA1.20, polarization, 6% HT-PSM. 32nm l&s pattern was delineated by pitch split double patterning (Figure 5).

Figure 5: 32nm l&s pattern by pitch split double patterning

3.2.4 Dual Tone Concept by Photo Inactivation

Dual tone resist has two thresholds and split a line in two. It has possibility of frequency doubling by single exposure (Figure 6). Dual tone resist is the most attractive approach to realizing pitch split without additional freezing process and exposure.

Steven J. Holmes et al. showed dual tone resist by hybrid of positive-tone and negative-tone.¹⁰⁾ The hybrid of positive and negative had been formulated partially acid labile protected polyhydroxystyrene, PAG and cross linker. However, in case of polymethacrylate based ArF resist, it is inconsistent with reality in negative tone, because of low reactivity in cross-link reaction of carboxylic acid.

Figure 6: Aerial image and photo resist profile; conventional positive resist (a) and dual tone resist (b)

The photo base generators have been developed^{13, 14), 15)} and their applications^{16, 17)} were reported for negative tone and image reversal. For tone inversion, the idea of acid inactivation by base generators is reasonable approach.

Figure 7 (a) shows calculation result of acid, base and active acid concentration with different base generation efficiency. Acid or base from PAG or PBG is calculated in eq.1. The ϕ is expressed by Dill's C parameter. The active acid is calculated in eq.2.

In the case that the following two conditions are satisfied, 1) PBG efficiency is lower than that of PAG, and 2) a total molar amount of PBG and additive quencher is 10~80% higher than PAG, both of an active acid increased region and an active acid decreased region versus dose are appeared. These regions with increase and decrease of the active acid provide positive-tone and negative tone patterns, respectively.

Simulations of dissolution rate curves are shown in Figure 7 (b). The simulation model is based on parallel reaction of acid-base and acid catalyst deprotection¹¹⁾. A set of PAG ($\phi=0.05$) and PBG

($\phi=0.01$) shows steeper active acid slope in convex curve (a-2), slower dissolution rate and higher gamma in negative-tone (b-2) than a set of PAG and PBG of small efficiency difference (b-1) and large efficiency difference (b-3). Moderate gap between acid and base generation efficiency is necessary to improve negative contrast. The dissolution contrast of negative-tone is lower than that of positive-tone, which is expressed in higher dissolution rate and slow gamma in negative-tone even in the optimum PAG and PBG efficiency.

$$\text{Acid or Base generation} = 1 - \exp(-\phi * \text{Dose}) \quad \dots \text{eq.1}$$

ϕ ; acid and base generation efficiency

$$\text{Active acid} = \text{Acid from PAG} - \text{Base from PBG} - \text{Additive quencher} \quad \dots \text{eq.2}$$

3.2.5 Effect of Positive-Negative Dose Gap on Resists Pattern Profile Simulation

Positive and negative exposure dose can be variable by changing amount of additive quencher or PBG. Positive and negative exposure dose gap becomes narrow with an increase of the quencher amount or PBG. Figure 8 shows relationship of positive and negative dose gap and resists profiles. In Figure 8, optimum PAG ($\phi=0.05$) and PBG ($\phi=0.01$) efficiently, which is result from Figure 7, and different quencher amount are used for simulation parameter. The resists profiles were calculated on NA1.35, dipole Illumination, 44nm l&s 6% HT-PSM. Z-axis in right pictures is reciprocal number of dissolution rate; it shows resist pattern profile. In the case that negative/positive dose ratio is 8, negative pattern do not appear. That dose ratio of 3 gives wide negative pattern. Optimum dose ratio is 5. This result suggests that it has a possibility to print 22nm l&s pattern from 44nm mask. The line width of negative seems wider and dissolution rate is a little higher than positive. The profile difference between positive and negative is caused by low contrast of negative-tone. The simulation was carried out on the parameters, in which neutralization rate constants of acid-quencher and acid-generated base are the same. If the rate constant of acid-generated base is changed to

Figure 7: Acid, base and active acid concentration calculation result with different base generation efficiency (a) and dissolution contrast curves (b)

Figure 8: Simulation of contrast curves with different positive-negative exposure dose gap (a) and resist profiles (b)

Figure 9: Simulation of frequency doubling resist profiles with variety exposure dose

higher, the negative contrast would be increased.

A contrast enhancement of negative-tone in resist materials development is necessary to harmonize positive and negative profiles.

3.2.6 Dose Variation on Resist Profile Simulation

Resist profile simulation with variety of exposure dose is shown in Figure 9. The resists profiles were calculated on NA1.35, dipole Illumination, 44nm l&s 6% HT-PSM. Positive-tone line becomes slim with an increased exposure dose, while negative-tone line becomes fat. Exposure latitude of negative is narrow, compared to positive.

3.2.7 Acid and Base Generation Efficiency Measurement

Coumarin-6 is an acid sensitive dye that exhibits a change in the visible absorption when protonated. The intensity of the peak at ~522nm corresponds to the amount of protonated coumarin-6 and is therefore a measure of the amount of acid in the film.

PAG, coumarin 6 and polymethacrylate were mixed in PGMEA/PGME/ γ -Butyrolactone mixture solvent. For base detection, camphorsulfonic acid, PBG, coumarin 6 and polymethacrylate are mixed in the solvent above.

PAG or PBG containing solution were spun coat on quartz substrate and baked at 100°C/60s. After ArF exposure, 522nm absorbance was measured with a spectrophotometer. Normalized acid or base concentrations were calculated by the 522nm absorbance. The measurement results, fitting curves and C-parameters ϕ of acid generation from triphenylsulfonium salt and base generation from PBG-1 are illustrated in Figure 10. The base generation efficiency is one fifth of the acid generation, and this value is better for negative-tone contrast, as mentioned above.

Figure 10: Measurement result of acid and base generation efficiency

3.2.8 Optimization of Positive-Negative Dose Gap on Patterning Property

Patterning pictures and contrast curves with different positive-negative dose gap are shown in Figure 11. The positive-negative dose gap was changed by different quencher amount.

60nm thickness of DFAR was spun coat on BARC. Illumination condition was NA1.05, dipole, polarization and 6% HT-PSM.

The gamma of negative was slower and the film loss of negative was bigger than that of positive. In case of negative dose divided by positive dose equals 5; it gave frequency doubling of 50nm line from 100nm mask. The simulation result was proved by experimental patterning.

Figure11: Contrast curves and patterning result of dual tone resist

3.2.9 Patterning Result of Frequency Doubling Resist

Figure 12 shows patterning result of dual tone resist with 100, 80 and 65nm mask. 60nm thickness of DFAR was spun coat on multi layer of spin on glass and spin on carbon. Illumination condition was NA1.05, dipole, polarization and 6% HT-PSM.

Negative lines appeared at positive space and increased width wider with an increase exposure dose. 50nm and 40nm line patterns were printed by single exposure with 100nm and 80nm mask and partially printed at 32.5nm line pattern with 65nm mask. There is a possibility for resolving 32nm l&s and finer by material improvement.

Figure12: SEM pictures of frequency doubling resist at various exposure dose and mask size

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