Progress in Resists Development for EPL (Electron Beam Projection Lithography)

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Electron beam (EB) lithography, together with ArF, F₂ and EUV (Extreme Ultra-Violet), is one of the most promising candidates for the next generation 65nm node and below from the viewpoint of resolution and DOF (depth of focus). However, since EB lithography has a disadvantage in throughput compared with optical lithography, it is generally used for mask and ASIC (Application Specific Integrated Circuits) device manufacturing. The application for it in mass production has been a difficulty. Recently, EPL (Electron Beam Projection Lithography) and LEEPL (Low Energy Electron Proximity Lithography) are being developed to improve the throughput problem of EB. In this paper, we investigated the subject of high sensitivity for imaging resist, which is one of the current topics of EPL. We resulted in an imaging resist which has high sensitivity and small line edge roughness by applying a specific additive and specific resin. Furthermore, we also developed an imaging resist which has high sensitivity and excellent resolution by applying the acid generator which controlled the strength of acid, and diffusion.

Keyword : EPL, resist, sensitivity, line edge roughness, resolution

1. Introduction

As the design rule going down to 65nm node and below, ArF, F₂, EUV, and EB are considered as the candidates for the next generation lithography. However, there are still many problems for each lithography, as described below.

ArF Lithography has the issue of high cost for mask with a complicated OPC (Optical Proximity Correction). For ArF imaging resist, problems such as DOF degradation by high NA, line edge roughness, and defect have been addressed. F₂ Lithography has the matter of soft pellicle. For F₂ imaging resist, development of high transparency materials such as fluorine-substituted resins and applying thin resist film are considered as subjects [1]. As to EUV lithography, since there is no existing material which photo of this wavelength can penetrate through, more sophisticated source, optics, and mask are required. Also, applying of a multilayer film is needed. This kind of technical establishment has been thought as future tasks. For EUV imaging resist, resist thickness is limited due to the atomic absorbance in the

film [2].

About EB lithography, improvement in throughput is recognized by the equipment development of EPL which utilizes high accelerated energy electrons and 4 time mask [3, 4, 5], in addition, development of LEEPL which utilizes low accelerated energy electrons and one time mask [6, 7]. For EB imaging resist, since there are no restrictions of transparency, various materials is applicable. For example, application of Poly hydroxyl styrene type resin which has an actual result by KrF Lithography and mask making is possible. However, EB lithography has the issues of complementary mask and inspection tool of stencil mask. Furthermore, imaging resist of high sensitivity is required for EPL which adopts high accelerated EB. Thin film thickness of imaging resist is required for LEEPL which adopts low accelerated EB [8]. In this paper, we report our work on high sensitivity resist for EPL.

2. The subject of imaging resist for EPL

EPL has excellent resolution by adoption of high

acceleration voltage of 100KV and a very small semi-angle of the EB. However, since electronic permeability is high, acid generation efficiency is very low. This is disadvantageous to high sensitivity of chemical amplified resist system. The development of high-sensitivity imaging resist for EPL is very important to reach high throughput. However, as shown in Figure1, high sensitivity often compromises with poor resolution and line edge roughness, which has been thought as a critical issues for EB resist.

Resolution

Line edge roughness

Figure1; Resolution and Line edge roughness of Resist A, B Resist A and B are positive tone and chemical amplified type resists which consist of resin, acid generator, quencher and casting solvent. Resist B is derived from Resist A with less quencher loading. 300nm film thickness, equal lines and spaces and exposed by 50kV DWEB (HL700D).

3. Experiments

3.1. Imaging Resist

3.1.1. Resist System

The imaging resist samples consist of resin, acid generator, quencher, and casting solvent. All samples were positive tone and chemical amplified type resist system.

3.1.2 Resin

In chemical amplified resist system, the loading level of acid generator is an important factor to sensitivity. The difference between the radiation chemistry, which is associated with EB exposure, and photochemistry has been reported by product analysis [9, 10]. The secondary electrons released from resin matrix are considered playing a key role in the acid generating reaction for EB resist. From the viewpoint of acid generating efficiency, dissolution speed to developer, and etching resistance, polyhydroxystyrene has been selected as the base resin.

3.1.3. Acid generator,

Triphenyl sulfonium salt was selected from sensitivity, heat stability and chemical stability as a base acid generator.

3.1.4. Quencher

Various Amines was used.

3.1.5. Solvent

Ethyl Lactate was mainly used from the solubility of resin, acid generator and quencher.

3.2. Evaluation conditions

3.2.1. Exposure

Exposure was performed by Hitachi direct writing electron system with variable shaped beam. The acceleration energy was 50kV. EPL imaging was conducted at Nikon using an experimental column, where the acceleration was 100kV.

3.2.2. Resist Process

The resist sample was coated on the bare-Si at each targeted film thickness by adjusting spin speed. The softbake was carried at the temperature of 130°C for 90 seconds. The exposed resist was then post exposed baked at 130°C for 90 seconds and developed for 60 seconds in 2.38wt% aqueous tetramethylammonium hydroxide solution.

3.2.3 Molecular weight distribution of Resin

The molecular weight distribution M_w (weight average molecular weight) / M_n (number average molecular weight) of resin was measured by GPC (gel permeation chromatography) calibrated over styrene conversion.

4. Results and Discussions

4.1. Line Edge Roughness (LER)

4.1.1. The image of LER aggravation

The main components of resist are resin, acid generator, and solvent. In resist solution, since solvent exists in large extra quantity, it is thought that resin and acid generator are distributed uniformly. However, after film formation by soft baking process, it is considered that acid generator is not distributing uniformly in resin matrix due to the difference between the structure, polarity, viscosity of resin and acid generator. Furthermore, for resist with high sensitivity, high level loading of acid generator is expected, so that this kind of heterogeneity increases. Moreover, resin is considered aggregate of polymer chains with different protection ratio and molecule weight, and thus having different dissolution speed. It is considered it is one of the factors to worsen LER.

In this paper, an additive was examined as acid generator

distribution improving agent in resist film. We also addressed the effect of molecular weight distribution on LER.

Resist compositions for improvement of LER is described in Table 1.

Table 1. Resist sample composition for improvement of LER

Resist	Mw/Mn of resin	Quencher loading	Additive
A	1.5	×3 times	Unused
B	1.5	×1 time	Unused
C	1.5	×2 times	Unused
D	1.5	×2 times	Used
E	1.1	×2 times	Unused

4.1.2. Small LER Resist

The additive is a low molecule weight organic molecule which has both hydrophilic and hydrophobic units. Compared with resist C which does not contain the additive and has sensitivity of $8.0 \mu\text{C}$ and LER of 9.7nm , resist D which contains the additive has a sensitivity of $8.0 \mu\text{C}$, a LER of 8.7nm . LER improvement effect has been recognized in this case. As to the effect of resin molecular weight distribution on LER, we found resist C (resin, Mw/Mn=1.5) has sensitivity of $8.0 \mu\text{C}$ and LER of 9.7nm , but resist E (resin, Mw/Mn=1.1) has sensitivity of $8.0 \mu\text{C}$ and LER 7.5nm . The improvement effect was recognized by applying narrow molecular weight distribution resin.

The top-down SEM of each resist is shown in Figure 2. Figure 3 shows the sensitivity and LER balance of each resist. Resist D and F are superior to resist A, B, C which have less quencher loadings.

4.2. Resolution

4.2.1. The image of Resolution aggravation

For high-temperature-baking type resist using protection group with high activation energy, acid diffusion control in PEB process at which deprotection progress occurs is important. Through diffusion, acid can be uniformly distributed in resin matrix. In this case, LER would be excellent, but resolution would get worse since acid also diffuses to the non-exposed area. Furthermore, in the high sensitivity resist with few amounts of Dose, since there are few amounts of acid, it is thought that the development of resist which has high sensitivity and excellent resolution is very difficult.

Base on this idea, we examined the acid generator with short diffusion length type. Resist compositions for improvement of resolution is described in Table 2.

Figure 2; Top-down pictures of Resist A, B, C, D and E. 300nm film thickness, 150nm L/S and exposed by 50kV DWEB (HL800D).

Figure 3; Sensitivity and LER balance of Resist A, B, C, D and E. 300nm film thickness, 150nm L/S and exposed by 50kV DWEB (HL800D).

Table 2. Resist sample composition for improvement of resolution

Resist	Diffusion length of acid	Strength of acid
F	Long	Strong
G	Short	Strong
H	Short	Weak

4.2.2. Excellent Resolution Resist

Resist F which contains an acid generator generating strong acid with long diffusion distance showed a sensitivity of $6.4 \mu\text{C}$ and a resolution of 90nm by DWEB (50kV). Compared with it, the resist G which applied acid generator generating strong acid with short diffusion length showed a sensitivity of $5.8 \mu\text{C}$ and a resolution of 80nm by DWEB (50kV). On the other hand resist H

which consists of an acid generator generating weak acid with short diffusion length failed in resolving 100nm size pattern by $7\mu\text{C}$. This result is shown in Figure 4. The effectiveness of controlling the strength and the diffusion length of acid generated from the acid generator on resolution has been proved by this examination.

Exposure by EPL is also performed for resist G, and the result is shown in Figure 5, 6. Consequently, a very good result; a sensitivity of $8\mu\text{C}$, are excellent resolution of 60nm, small LER, and wide DOF was obtained.

Figure 4; Cross section pictures of Resist F and G. 500nm film thickness, 1:2=C/H and exposed by 50kV DWEB (HL700D)

Figure 5; Cross section pictures of Resist G. 500nm film thickness, 1:1=C/H, $8\mu\text{C}/\text{cm}^2$ and exposed by Nikon's 100kV EPL experimental column.

5. Conclusion

Chemical amplified positive resist resists were investigated in this paper for EPL. In this examination, the control of resin molecular weight distribution or the addition of an additive which has specific structure maintained the sensitivity which has influence on a throughput, and having been effective in improvement of LER was recognized. Moreover, it was recognized that acid generator generating strong acid with short diffusion length was effective in improvement of resolution. It was proved by EPL exposure that resist which applied above acid generator is promising for 65nm node application in sensitivity, resolution, LER and DOF.

If EPL application is considered as next generation lithography, the further high sensitivity is the subject of

Figure 6; Focus series of 100-70nm contact. Resist G is 350nm film thickness. Defocus value of $0\mu\text{m}$ is around the best focus and the opposite defocus side is out of exposed defocus range.

resist and it is necessary to accelerate development of resist towards it.

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