CHEMICAL AMPLIFICATION RESISTS FOR FUTURE LITHOGRAPHY

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The technologies for future lithography have been proposed, such as i-line phase-shifting lithography, deep-UV lithography and electron beam lithography. We have proposed several types of chemical amplification resist systems for future lithography. These are based on the change in dissolution rate by acid catalyzed reaction for aqueous development: dissolution inhibitor to dissolution promoter for positive resists and the reverse for negative resist. Deprotection reaction of tetrahydropyranyl protected poly(hydroxystyrene) is used for positive resists. Silanol condensation reaction by acid catalyzed reaction was applied to negative resists. Pinacol rearrangement, etherification and intramolecular dehydration of carbinols can also be used for negative resists.

1. Introduction

The design requirements of successive generation of VSLI circuits have led to a reduction in lithographic critical dimensions. The trend of lithography and resists is shown in Fig. 1. It can be recognized from Fig. 1 that the second turning point will come soon. The first turning point was the change from a negative resist composed of cyclized rubber and a bisazide to a positive resist composed of a diazonaphthoquinone (DNQ) and novolak resin. This was induced by the change of exposure system from a contact printer to a g-line reduction projection step-and-repeat system, so called a stepper. The cyclized rubber system had the problem of resolution capability due to the swelling during the development. The positive resist shows high resolution using alkali development.

Performance of a g-line stepper was improved by increasing numerical aperture (NA). Although shorter wavelength i-line (365nm) lithography was introduced, the DNQ-novolak resist is still used for i-line lithography. Of course, much effort has been made to improve the resolution capability as well as depth-of-focus latitude. [1] Effect of chemical structure of novolak resin and DNQ on dissolution inhibition capability has been investigated to get high dissolution contrast: difference in dissolution rate between exposed and unexposed region. The progress of this type resist is remarkable to achieve the resolution below the exposure wavelength of i-line (0.365µm). It is generally accepted for 0.35µm processes that a high NA i-line stepper in conjunction with a DNQ-novolak resist will be used.
The second turning point will come when the conventional lithography using an i-line stepper combined with a positive resist faces the resolution limitation. Several competing lithographic technologies have been proposed as future lithography: wavefront engineering of i-line, deep-UV lithography and electron beam lithography.\cite{2} The wavefront engineering includes off-axis illumination (OAI), pupil filtering and phase-shifting lithography. In the following sections we will consider the resists for future lithography.

2. Resists for Future Lithography

2.1 Wavefront Engineering

A positive resist composed of DNQ and novolak resin can be used for OAI and pupil filtering technologies, though high-contrast resists are required to make good use of low contrast aerial image for extending resolution limitation. Phase shifting lithography requires negative resists with high resolution.\cite{3} When a positive resist is used for phase-shifting lithography, bridging of patterns occurs at the end of the line-and-space arrays. High coherence illumination in phase-shifting lithography is effective for high contrast imaging, which results in low intensity at the wafer plane. Therefore, high sensitive resists are necessary for phase-shifting lithography.

Fig. 1 Development trend of lithography and resists
2.2 Deep-UV Lithography

Deep-UV lithography has the problem of low emitting intensity from a high pressure Hg lamp below 300nm. The exposure system using the Hg lamp as a light source was proposed by Perkin-Elmer (the present company: SVGL): a reflective type reduction projection step-and-repeat system (Micrascan). This system requires the resist sensitivity of 10mJ/cm² due to its low light intensity at deep-UV region. Another choice for deep-UV source is KrF excimer laser. Since the transmittance in deep-UV region limits the optical materials for exposure systems to calcium fluoride or quartz, the spectral narrowed KrF excimer laser (∆λ~pm) should be used for a stepper to avoid the color aberration. Although this laser itself gives high intensity, intensity at the wafer plane of the stepper is lower than that of g-line and i-line steppers. The required resist sensitivity is 20~50 mJ/cm².

2.3 Electron Beam (EB) Lithography

One of the advantage of EB lithography is pattern forming capability, since focused electron beams can be rapidly deflected either electromagnetically or electrostatistically. This technology is widely used for photomask fabrication. Electron beam direct writing technology is also useful for ASIC device production. One of the problems for EB lithography is low throughput. Recently cell projection[4] has been proposed to improve the throughput. The concept of this technology is based on exposing an array of memory cell in one shot by electron projection lithography.

![Fig.2 Relation between EB sensitivity and UV sensitivity](image-url)
However, the azide-novolak resist suffers from low sensitivity and severe standing wave effect due to high transmittance, when it is used as a single layer resist on Si wafer.

### 3.2 Chemical Amplification Resists

One approach to improving the sensitivity and standing wave effect is the use of chemical amplification concept. Acid catalyzed silanol condensation reaction was applied to an i-line negative resist.[9] The concept of this resist system is based on the change from alkali dissolution promoter to dissolution inhibitor. It was shown that silanol compounds accelerate dissolution in novolak resin for alkali aqueous development.[10] Silanol condensation products, siloxanes, are expected to render dissolution inhibition effect. 2-naphthoylmethyltetramethylenesulfonium salt was selected as an acid generator for i-line. It was confirmed that diphenylsilanediol acts as a dissolution promoter, since dissolution rate increases with the increase of Ph2Si(OH)2 concentration. On the contrary, dissolution rate after post-exposure-baking (PEB) decreases with the increase of exposure dose. This decrease can be ascribed to the formation of siloxane oligomers by acid catalyzed reaction. The formation of siloxane oligomers was confirmed by IR spectroscopy and GPC measurement. The large change in dissolution rate gives high resolution capability as shown in Fig.3a. Space patterns of 0.3µm were resolved using an i-line stepper in conjunction with a phase-shifting mask. Since severe standing wave effect is not observed on Si substrate even for high transmittance (80% for 1 µm film thickness), acid diffusion during PEB may relax the standing wave effect. However, it is pointed out that there might be a residue problem during oxygen plasma removal processes.

Without a residue problem, the same concept as silanol condensation can be realized when intramolecular dehydration reaction of carbinol is used (Scheme 1). The resist is composed of novolak, bis(α-hydroxypropyl)benzene and naphthoylmethyltetramethylenesulfonium salt.[11] The dissolution rate characteristic showed the similar behavior as described for silanol condensation. Line-and-space patterns of 0.275µm can be obtained using an i-line stepper and a phase-shifting mask as shown in Fig.3b.

### 4. Deep-UV Resists

#### 4.1 Positive Deep-UV Resists

A lot of resists systems have been reported for deep-UV lithography.[12] Ito and Willson[13] proposed the chemical amplification resist using acid catalyzed reaction for deep-UV lithography. The requirement of high sensitivity for deep-UV lithography is caused by low intensity from a high pressure Hg lamp for reflective 1:1 exposure system. The resist was composed of t-butoxycarbonyl (t-BOC) protected poly(hydroxystyrene) (PHS) and an onium salt acid generator. Photogenerated acid causes deprotection reaction to yield PHS. This reaction induces the polarity change of the polymer from nonpolar to polar polymer. Therefore, the exposed area can be dissolved away with a
To improve the throughput, the sensitivity of electron beam resists is also a critical issue. Fig. 2 shows the relation between electron beam sensitivity and UV sensitivity. The UV sensitivity was estimated from the absorbed electron energy in resist film on the basis of Bethe's equation. Only several percent of electron energy is absorbed in the resist film for 30kV electron beam. This kind of rough estimation indicates that 1µC/cm² corresponds to 1mJ/cm², while a DNQ-novolak positive resist shows 100-200mJ/cm². This figure indicates that EB resist should have two order higher sensitivity than a conventional positive photoresist. When the higher acceleration voltage, 50kV, is used to improve the energy deposited profile in the resist film, the deposited energy in the resist film become further lower. The further improvement in resist sensitivity is necessary.

3. i-line Negative Resists
3.1 Azide Systems
Iwayanagi et al. reported an i-line negative resist composed of an azide compound and phenol resin as a non-swelling type resist using alkali-aqueous development. This resist, however, suffers from high absorbance at i-line, which results in high gradient of light intensity along the film thickness. In the course of the survey of azide compounds, we have found that 3,3'-dimethoxy-4,4'-diazidobiphenyl shows high transmittance at i-line. Line-and-space patterns of 0.3µm were achieved using i-line phase-shifting lithography. Systematic evaluation of bisazides of biphenyl derivatives shows a correlation between sensitivity and φ, where ε is the molar extinction coefficient of an azide compound and φ is quantum yield of photodissociation of an azide compound.

Fig. 3 (a) Space patterns of 0.3µm of the resist using silanol condensation and (b) line-and-space patterns of 0.275µm using intramolecular dehydration of a carbinol. Exposure was carried out with an i-line stepper in conjunction with a phase-shifting mask.
polar solvent to obtain positive image. Another advantage of chemical amplification resist gives high transmittance of protected PHS compared to novolak resin at around 250nm. Conventional DNQ-novolak positive resists show low transmittance in the deep-UV region.

We have proposed tetrahydropyranyl (THP) group as a protecting group. Expected deprotection reaction by photogenerated acid is shown in Fig.4a. Since 100% THP-protected PHS shows poor developability with an alkali-aqueous developer, we have proposed partially protected polymer as alkali developable resists. The relation between THP protection degree and dissolution rate of protected PHS is shown in Fig.4b. When 2.38% tetramethylammonium hydroxide (TMAH) is used, the dissolution rate is negligible above 30% protection degree. Since an onium salt shows dissolution inhibition effect, the polymer of 20% THP-protection degree is used for formulating the resist. It was also found that partially protected THP-M can reduce the surface inhibition effect.

A three component resist system composed of novolak, THP-PHS and Tris(methanesulfonyl)oxybenzene (MeSB) was also evaluated as an alkali developable resist. In the course of this study, it was shown that alkylsulfonates can act as an acid generator in deep-UV region and the acid generating reaction is based on the sensitization by novolak resin.

Fig.4 (a): Acid catalyzed deprotection reaction of tetrahydropyranyl protected poly (hydroxystyrene). (b): Relation between dissolution rate and THP protection degree for various developers.
4.2 Negative Deep-UV Resists

Acid catalyzed silanol condensation reaction can also be used for a deep-UV negative resist.[19] This resist shows high resolution capability and high sensitivity. Again, there is a possibility of residue problem during oxygen removal process. Uchino et al. have proposed several types of interesting acid catalyzed reaction, such as Pinacol rearrangement[20] and etherification[21] of carbinols. These acid catalyzed reactions are shown in scheme 1. The basic concept for application to resist system is the same as that using silanol condensation: a carbinol act as a dissolution promoter in novolak resin while acid-catalyzed reaction products act as a dissolution inhibitor.

5. Electron Beam Resists

5.1 Positive EB Resists

To achieve high sensitivity, chemical amplification resists are indispensable to EB resists. A three component resist composed of novolak resin, a dissolution inhibitor, and an acid generator was formulated to get alkali-developable resists. From the viewpoint of sensitivity, dissolution inhibition capability and acid generating capability of various compounds and polymers were

Scheme 1. Acid catalyzed reactions for negative chemical amplification systems
evaluated. As a dissolution inhibitor, a polymer inhibitor of THP-protected PHS shows high dissolution inhibition capability. As an acid generator, tris(methanesulfonyloxy)benzene (MeSB) shows high sensitivity as well as high thermal stability. In addition, MeSB shows less negative tone behavior compared to onium salts for high EB dose. We have also investigated the acid-catalyzed reaction in the polymer matrix and the effect of novolak matrix on resist performance. 0.3 µm L/S patterns can be obtained with 2 µC/cm² and 0.3 µm contact holes with 3.5 µC/cm² for 50kV electron beam exposure.

5.2 Negative EB Resists

Acid hardening type resist, SAL of Shipley, shows high sensitivity and high resolution capability. Since this resist is alkali-developable, it has been evaluated by a lot of researchers, which stimulated the research and development of chemical amplification resists. Basically the change from dissolution promoter to dissolution inhibitor by acid catalyzed reaction can be applied to negative EB resists. Shiraishi et al. first applied silanol condensation reaction to electron beam resists. The same concept described in deep-UV resists (4.2) can also be applied to EB negative resists.

6. Conclusion

The resolution limitation of i-line lithography using an i-line stepper combined with a DNQ-novolak positive resist has stimulated the research and development of several technologies for future lithography, such as wavefront engineering of i-line, deep-UV lithography and electron beam lithography. Here chemical amplification resists proposed by our group have been discussed as the resists for future lithography. Chemical amplification resists show high sensitivity as well as high resolution capability, which indicates that chemical amplification resists are promising for future lithography. However, several problems associated with this type of resists have been pointed out, such as time delay problems, effect of acid diffusion on resolution, and influence of substrates on resist profiles. Since the chemical amplification resists are sensitive to the process conditions and the environment, co-operation with process group is necessary for actual use of chemical amplification resists.

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