Positive and Negative Chemically Amplified Resists for Excimer Laser Lithography

Nobuaki HAYASHI*, Takumi UENO, Hiroshi SHIRAISHI, Leo SCHLEGEL and Takao IWAYANAGI

Received July 29, 1991; Accepted September 12, 1991

Alkaline-developable three-component positive and negative chemical amplification resist systems were investigated. These resist systems were composed of the acid generator and an acid-labile dissolution controlling material in a novolak matrix resin. The dissolution controlling materials achieve sufficient differential solubility between the exposed and unexposed areas of a resist film. In the case of positive resist systems, we found that tetrahydropyranyl protected polyhydroxystyrene can act as an efficient dissolution inhibitor. In the case of negative resist systems, silanol compounds show a catalytic condensation reaction by acid from a photo-acid-generator, and the condensation products act as a dissolution inhibitor after exposure and post-exposure baking. These resist systems show high sensitivity (<10 mJ/cm²) and high resolution using a KrF excimer laser stepper.

1 INTRODUCTION

The design requirements of successive generations of VLSI circuits have led to reduction in the lithographic critical dimensions. Among the several competing strategies utilizing shorter wavelength radiation than g-line or i-line light from mercury lamp in the conventional photolithography is the deep UV lithography with a KrF excimer laser.

Recently, there has been increased interest in “chemical amplification” resist systems for deep UV lithography since the pioneering work by Ito and Willson, and Frechet et al[1]. In the chemical amplification resist, a photosensitive acid generator is decomposed to produce acid during the exposure. The following acid-catalyzed thermal reaction renders the exposed area of the resist soluble in the case of positive resists, or insoluble in negative resists.

We have focused on alkaline-developable resist systems composed of an azide compound and a phenolic resin for UV[2], deep UV[3] and electron beam[4] lithography. In this paper, we will report alkaline developable chemically amplified resists developed in our laboratory[5,6]. These are three-component systems composed of an acid generator, an acid-labile dissolution controlling material and a novolak resin.

2 EXPERIMENT

The syntheses of tri(methanesulfonyloxy)benzene (MeSB) and onium salt have been described in previous publications[7,8]. The inhibitor compound THP-M (polyhydroxystyrene protected with tetrahydropyranyl group) was synthesized as described in the literature[9]. Diphenylsilanediol and triphenylsilanol were obtained from Shin-etsu Chemical Co. The binder polymer was a conventional m/p-cresol novolak obtained from Hitachi Chemical Co.
Resist films spin-coated from solutions onto silicon wafers and prebaked at 120°C on a hot-plate were exposed to 250 nm radiation from a Xe-Hg lamp through an interference filter to generate an acid. After a post-exposure-baking (PEB) at 80°C on a hot plate, the films were tank-developed in an aqueous alkylammonium solution (NMD-3; tetramethylammonium hydroxide obtained from Tokyo Ohka Kogyo Co.). Film thickness measurements were made with an Alphastep profilometer. Lithographic evaluation were made with a KrF excimer laser stepper (Nikon, NA = 0.42).

UV absorption spectra were measured with a Hitachi U-3410 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1720 FT-IR spectrometer.

3 RESULTS AND DISCUSSION

The preferable relationship of dissolution rate between before exposure and after post-exposure-baking is shown in Fig. 1. The positive resist film composed of photo-acid generator, dissolution inhibitor and base resin shows slower dissolution rate than that of base polymer. During post-exposure-baking, the dissolution inhibitor converts to the dissolution promoter with modified polarity and solubility. In the case of negative resist, acid-catalyzed reaction changes the dissolution promoter to the dissolution inhibitor.

3.1 Positive resist systems

3.1.1 Resist formulation In a previous paper\(^8\), we reported a two-component resist system composed of polyhydroxystyrene protected with tetrahydropropyl group (THP-M) and an onium salt. This resist system, however, has a problem on development in aqueous alkaline solution. THP-M shows strong dissolution inhibition effect in novolak resin\(^9\), as can be seen in Fig. 2 where the dissolution rate of mixture from THP-M with novolak is plotted as a function of THP-M content. It can be seen that the dissolution inhibition capability of THP-M in a novolak resin is stronger than that of a typical inhibitor compound NQD (triester of naphthoquinonediazide sulfonic acid with trihydroxy benzophenone). It is expected that THP-M can be used as a dissolution inhibitor for these three component positive resist systems.

MeSB was selected as the acid generator, since this compound showed some distinct advantages compared to the widely used onium salts\(^5\)\(^7\). We evaluated the resist system composed of MeSB, THP-M and novolak resin as a positive chemical amplification system. The reaction mechanism of this resist system is shown in scheme 1.

![Fig. 1](image1.png)  
Fig. 1  The preferable relationship of dissolution rate between before exposure and after post-exposure baking.

![Fig. 2](image2.png)  
Fig. 2  Effect of THP-M concentration on dissolution rate.
An exposure characteristic curve of this resist system is shown in Fig. 3. The sensitivity curve of the resist system with an onium salt as a acid generator is also shown for comparison. It is noted that the sensitivity with MeSB is higher than that obtained with the onium salt. Moreover, the negative tone behavior was observed at higher exposure dose for the onium salt. Increase in onium salt concentration made this situation worse. This effect was not observed for MeSB up to at least 100mJ/cm² exposure dose.

Then, we have examined the effects of MeSB concentration on the exposure characteristics. The sensitivity shows the strong dependence on the MeSB concentration up to 6%.

Due to the relatively high absorbance of the novolak resin, the optical density of this resist film at 248 nm is 0.5 μm⁻¹.

3.1.2 Imaging The resist described above was examined by KrF excimer laser stepper exposure for various process conditions. The composition of the resist was chosen to MeSB/THP-M/novolak = 4/10.5/85.5%. SEM photographs of fine line patterns of 0.35 μm are shown in Fig. 4. Fine patterns were obtained with the exposure dose of only 4.5mJ/cm².

3.2 Negative resist systems 3.2.1 Resist formulation We found that silanol compounds act as a dissolution promoter in novolak resin for aqueous alkaline development. It is known that an acid catalyzes the condensation reaction of silanol compounds which results in polysiloxane as shown in scheme 2.

While silanols are dissolution promoters, polysiloxanes are hydrophobic, aqueous base insoluble resin that may act as dissolution inhibitors. Based on this acid catalyzed reaction, a three-component negative chemical amplification resist system is formulated: an acid generator, a silanol compound and novolak resin.

Exposure characteristic curves for various silanol compounds are shown in Fig. 5.
Triphenylsulfonium triflate (Ph₃S⁺OTf) is used as the acid generator. Every silanol compound investigated here gives a negative resist system. It is considered from these results that the acid produced by exposure induces the silanol condensation during the post-exposure-baking step and this condensation product acts as a dissolution inhibitor. This is confirmed by measurement of the difference IR spectrum, as shown in Fig. 6. The absorption of Si-O-Si bond increases after PEB, while the strong absorption of OH decreases.

The influence of diphenylsilanediol (Ph₂Si(OH)₂) concentration on the dissolution characteristics is shown in Fig. 7. It is noted from Fig. 7 that the dissolution rate increases with Ph₂Si(OH)₂ concentration and the rate decreases drastically with increasing exposure dose for higher Ph₂Si(OH)₂ concentration.

3.2.2 Imaging The resist described above was evaluated with the KrF excimer laser stepper. The resist composition was Ph₃S⁺ OTf/Ph₂Si(OH)₂/novolak = 2/20/78%. High resolution of 0.30μm line and space patterns was obtained as shown in Fig. 8, when the resist film was exposed with 3mJ/cm² of 248 nm radiation by KrF excimer laser stepper and post-baked at 80°C for 10 min.
CONCLUSION

Alkaline-developable three-component positive and negative chemical amplification resist systems were investigated. These resist systems were composed of the acid generator and an acid-labile dissolution controlling material in a novolak matrix resin. The dissolution controlling materials achieve sufficient differential solubility between the exposed and unexposed areas of a resist film.

In the case of positive resist systems, we found that tetrahydropyranyl protected polyhydroxystyrene can act as an efficient dissolution inhibitor. With optimize prebaking and post-exposure baking conditions, 0.35μm features with good line profile could be obtained by excimer laser stepper exposure with 4.5mJ/cm² dose.

In the case of negative resist systems, silanol compounds show a catalytic condensation reaction by acid from a photo-acid-generator, and the condensation products act as a dissolution inhibitor after exposure and post-exposure baking. This resist system resolves 0.30μm line and space patterns using a KrF excimer laser stepper with 3mJ/cm² dose.

We are grateful to Nikon Co. for the access to the KrF excimer laser stepper. We also thank Dr. S. Nonogaki, Dr. S. Okazaki, Mr. S.M.A. Hesp, Ms. K. Tadano, Mr. S. Uchino and Mr. H. Fukuda for their helpful discussions.

REFERENCES