Development of SSQ Based 157nm Photoresist

Raymond J. Hung, Takashi Chiba*, Haruo Iwasawa*, Akihiro Hayashi*, Noboru Yamahara* and Tsutomu Shimokawa*

JSR Micro
1280 N. Mathilda Ave. Sunnyvale, CA 94089

* JSR Corporation
100 Kawajiri-cho, Yokkaichi, Mie, JAPAN 510-8552
rhung@jsrusa.com

Lowering absorbance of functional SSQ resists at 157nm continues to be a challenging task. In the previous report, we showed the absorbance data and lithographic performance of several different SSQ platforms developed at JSR [1]. Two new SSQ platforms (σ and π) which showed improved absorbance value were reported in this article. New σ type and π type resist showed 157nm absorbance value of $1.76 \mu\text{m}^{-1}$ and $1.62 \mu\text{m}^{-1}$ respectively. The absorbance value of π type polymer was as low as $1.19 \mu\text{m}^{-1}$. These improved resists also showed great lithographic properties. σ type resist is capable of resolving 55nm 1:1 L/S with square profile using 0.85NA tool. Integration aspects of this bilayer system were also presented.

Keywords: 157 nm lithography, silsesquioxane, siloxane, resists.

1. Introduction

Among many next generation lithography (NGL) technologies, 157 nm optical lithography is the leading candidate for the 70 nm technology node. Fluorocarbon polymers and siloxane/silsesquioxane (SSQ) polymers have been identified to be the most transparent polymers at 157 nm [2]. Improvement in the transparency of the existing fluorocarbon based polymer and silsesquioxane at 157nm posted a challenging task to resist chemists. Limited polymerization route and availability of transparent monomers are the main obstacles in getting the absorbance value down to satisfactory values.

New fluorocarbon polymers which were polymerized by cyclic polymerization of novel monomers designed by Asahi glass and Selete [3] showed great improvement in reducing absorbance at 157nm. The absorbance value as low as $0.40 \mu\text{m}^{-1}$ for a functional Asahi-Selete's polymer was

achieved. Daikin industries and Selete also showed its improved version of TFE-based polymers [4] which had absorbance value as low as $0.46 \mu\text{m}^{-1}$.

In the last report, we showed our progress in developing SSQ polymers for 157nm resist [1]. Several SSQ resist platforms were developed and the resist absorbance values were reduced from initially $\sim 6.0 \mu\text{m}^{-1}$ to $\sim 1.9 \mu\text{m}^{-1}$ (λ type). Here, we report two novel SSQ platforms aimed at reducing the absorbance at 157nm. Their lithographic imaging performances and integration aspects of this bilayer system are also presented.

2. Methods

2.1 Monomers

The designed functions of each monomer which was used in the experiments are summarized in Table 1. These monomers were synthesized by general hydrosilylation procedure

Table 1. Function of each monomer

Monomer	Function	F content
A	Solubility switch	low
B	Hydrophilicity	middle
C	Transparency enhancement	high
D	Transparency enhancement	high
E	Hydrophilicity and Transparency enhancement	high

2.2 Polymers

SSQ polymers were synthesized by a typical condensation reaction. The α type polymer was synthesized as described elsewhere[1]. The composition, molecular weight, and yield of the other synthesized polymers were summarized in Table 2.

Table 2. Summary of synthesized polymers

Polymer	Composition	Mw	Yield
ϵ	A / B	2100	97%
λ	A / B / C	2800	98%
σ	A / B / D	2600	99%
π	A / E / C	2600	90%

2.3 Lithographic Evaluation

The formulated resist consisted of 9 wt% of SSQ polymers, 0.3 wt% photoacid generator (PAG), and quenchers in Methyl n-Amyl Ketone (MAK). Formulated resist solution was coated on either given substrate or JSR spin-on carbon layer (NFC B200) and baked (SB) at 140 °C for 90 sec to give either a 1000 or 1200 Å film thickness.

F₂ exposure was carried out with 0.6 NA 157 nm Exitech ministepper at International Sematech (ISMT) RTC or with 0.6 NA F₂ Ultratech microstepper or a 0.85 NA Exitech microstepper at Semiconductor Leading Edge Technologies (Selete) using an alternating phase shift mask (alt-PSM). For imaging work done at ISMT, wafer processing was done on FSI polaris 2000. This track is not connected with the stepper. For imaging work done at Selete, wafer processing was done on a integrated track with the stepper, Tokyo Electron Act 8. Exposed resist film was baked (PEB) at 90 °C or 110 °C for 60 sec and developed in a 2.38 wt% tetramethyl- ammonium hydroxide (TMAH) for 20 sec.

2.4 VUV Absorbance Measurement

VUV absorbance at 157 nm was measured either by VUV-VASE (J. A. Woolam Co., Inc) or VU201 vacuum UV spectrometer (Bunkoh-Keiki Co, Ltd.). Formulated resist solution was coated on a silicon wafer (for VUV-VASE) or on a magnesium fluoride substrate (for VU201), baked at 140 °C for 90 sec, and applied for the measurement.

3. Results and discussion

3.1 JSR SSQ Design Strategy

The basic design of JSR SSQ polymers consists of three sub modules (Fig. 1). The acid-labile module is for polymer's solubility switch and chemical amplification (CA). This can be either t-butyl ester or protected HFA (hexafluoroalcohol) functional group.

Fig. 1 The design concept of JSR SSQ based polymers

The hydrophilic module is for better adhesion and wettability. It can be a free non-acidic alcohol or a slightly acidic polar group such as HFA. The third module is a highly transparent unit to provide higher transparency to the polymer. In our past study, we have developed our SSQ resist system without using highly transparent unit to make our system simple to avoid difficulty in adhesion or wettability of developer. Taking this strategy, we have successfully built several platforms; α to ϵ types. Our effort in improvement of the transparency resulted in reducing the absorbance of early platform, α type resist ($3.4 \mu\text{m}^{-1}$), down to $2.5 \mu\text{m}^{-1}$ at ϵ type resist.

Imaging results of the ϵ type resist using 0.6 NA tool are shown in Figure 2. In order to

reduce the absorbance further, we took two approaches: a) to introduce highly transparent nonfunctional monomer (high fluorine content) and b) to replace hydrophilic unit with more transparent one.

Fig. 2. SEM cross section of ϵ type resist (0.6 NA)

3.2 Strategy to improve absorbance

3.2.1 Introduction of Highly Transparent Module

We synthesized a monomer C which has very high content of fluorine and introduced the unit to a ϵ type polymer to give a λ type polymer (A/B/C). The polymer was formulated (Abs. = $1.91 \mu\text{m}^{-1}$) and printed on various substrates; NFC B200 (JSR Corporation), Sematech SiON, and Sematech SiN. Lines and spaces (1:1) features were well resolved down to 90 nm using 0.6 NA tool with square profiles as shown in Fig. 3. The results indicate that SSQ resist can be used as a single layer resist.

Higher transparency should be obtained with a higher loading of the new monomer C. However, we encountered with a serious coating problem when the loading of the C unit became higher (>10%). The problem occurred presumably due to very high content of fluorine in the polymer.

Fig. 3. SEM cross section of λ type resist on various substrate (0.6 NA)

To avoid the potential coating problem, we searched for a different type of monomer that has high fluorine content and minimum lipophobicity at the same time. As fluorinated compounds generally show hydrophobic and lipophobic nature, the challenge was to possess these two incompatible natures in one monomer. We designed a new monomer D. The coating property of a polymer having the D unit was good even at high loading level of the monomer D (>10%). Preliminary imaging polymer, a σ type polymer, was synthesized with a composition of A, B, and D (~10%) monomers.

Fig. 4. SEM cross section of σ type resist (0.85 NA)

A resist was formulated with the σ polymer and the absorbance was $1.85 \mu\text{m}^{-1}$. Imaging experiments of the resist were carried out at Selete using 0.85 NA tool. The results were shown in Fig. 4[5].

The σ type resist clearly resolved 55 nm L/S with good profile. By increasing the amount of the D unit to 15%, we were able to reduce the absorbance to $1.76 \mu\text{m}^{-1}$. The lithographic performance study is in progress.

3.2.2 Replacement of Hydrophilic Unit

Another route to reduce the polymer absorbance is to replace the hydrophilic unit to a more transparent one. We modified the monomer B to have more fluorine in it and thus synthesized the

monomer E. Preliminary polymer, π polymer, was prepared (~60% E units) and a resist was formulated. The absorbance of the polymer itself was $1.19 \mu\text{m}^{-1}$ and that of the resist was $1.59 \mu\text{m}^{-1}$. However, the imaging quality was not as good as λ or σ type system at this moment probably because the polymer composition was not optimized well yet.

3.3 Etching properties of our SSQ based resists

One of the most important properties of our SSQ resist is the high etch performance; pattern transfer ability to underlying carbon hardmask being an etch-resist to substrate. Figure 5 illustrates the whole etch process starting from lithography to substrate etching at contact hole application. The stack information for this experiment was 120nm SSQ / 300nm B200 / 400nm SiO₂ substrate. The pattern transfer from SSQ to B200 was done with N₂/O₂ gas mixtures and the contact transfer from B200 to SiO₂ was done by using fluorocarbon based gases. Successful pattern transfer was demonstrated on silicon dioxide substrate.

Fig. 5. Demonstration of C/H pattern etch with σ type resist/NFC B200/SiO₂ (0.85 NA)

4. Conclusion

We have developed SSQ based 157nm photoresist materials and the preliminary imaging experiments have shown very promising results. The absorbance of our transparent ϵ type resist ($2.5 \mu\text{m}^{-1}$) was improved and λ type resist ($1.91 \mu\text{m}^{-1}$) and σ type resist ($1.85 \mu\text{m}^{-1}$) were developed. The λ type resist shows good profile and high resolution on various substrates. This implies that the resist has a potential as a single layer resist.

The σ type resist resolved 55 nm L/S with a square profile with 1200Å thickness on a spin-on carbon substrate, NFC B200 using 0.85 NA exposure tool. Pattern transfer experiment of contact holes shows our SSQ is quite promising as bilayer resists as well. Newly synthesized π type resist shows the absorbance value of $1.59 \mu\text{m}^{-1}$. Although the imaging quality of the polymer is not as good as other platforms, the resists are still quite promising because the transparency is high. Overall, we improved SSQ resists in both the absorbance and the lithographic performance.

Acknowledgements:

Authors would like to acknowledge Selete and International Sematech for providing access to their 157nm exposure tools. Karen Turnquest, Yung-Tin Chen, and Shashikant Patel are appreciated for their assistance at International Sematech. We also would like to thank Dr. Seiro Miyoshi and Takamitsu Furukawa for their imaging work and Dr. Toshiro Itani for his kind assistance at Selete. This paper is written and submitted by JSR Corporation's request.

References

1. R. J. Hung, M. Yamachika, T. Chiba, H. Iwasawa, A. Hayashi, N. Yamahara, T. Shimokawa, J. Photopolym. Sci. Technol., **15** (2002) 693.
2. R. R. Kunz, T. M. Bloomstein, D. E. Hardy, R. B. Goodman, D. K. Downs, and J. E. Curtin, Proc. SPIE, **3678**, 13, 1999.
3. S. Kodama, I. Kaneko, Y. Takebe, S. Okada, Y. Kawauchi, N. Shida, S. Ishikawa, M. Toriumi, and T. Itani, Proc. SPIE, **4690**, 76, 2002.
4. M. Toriumi, M. Koh, T. Ishikawa, T. Kodani, T. Araki, H. Aoyama, T. Yamashita, T. Yamazaki, T. Furukawa, and T. Itani, Proc. SPIE, **5039-09**, 2003.
5. S. Miyoshi, T. Furukawa, E. Kawaguchi, T. Itani, Proc. SPIE, **5039-50**, 2003.