Silicon Containing Photoresists

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This work describes several novel Si-containing polymers with low optical densities at 193nm and acid labile protecting groups. These materials are evaluated at 193nm lithography as one of the top surface imaging techniques to enhance lithography performance. Additionally, norbornene/maleic anhydride copolymers containing silicon side chains are synthesized. Experimental results indicate that the unexposed and exposed regions differ in terms of silicon content to the extent that patterns are formed using oxygen reactive ion etching. Moreover, a polymer with at least 3.5% wt of Si content can provide effective etch resistance in this study. 0.11 μm line/space patterns are also obtained using conventional developer with an ArF excimer laser stepper.

Keywords: ArF, silicon containing, bilayer resist, 193nm

1. Introduction

Photoresists play a crucial role in the lithography process. With the increasing demand for IC memory associated with a high density, chemically amplified resists, which involve 248nm as well as 193nm photoresists, have replaced conventional i-line and g-line resists. Sensitivity, contrast, etch resistance and purity are features of all resists. Most i-line, g-line and DUV resists are based on hydroxy aromatic polymers such as novolac and poly-hydroxystyrene. These materials have an excellent resistance to plasma etching and excellent aqueous base solubility for image development. However, the opacity of conventional UV and DUV organic resins, photoresists and components at 193nm have necessitated a shift in resist materials design. The leading resist technology candidates for 193nm lithography are top surface imaging (TSI)[1-5], bilayer[6-10] and single layer resists. Each approach has its merits and limitations. Lithographic aspect ratios and other issues must have thinner resist film (about 0.5–0.6 μm) for sub-0.18 μm devices, thus, requiring either a modified etch process, or enhanced etch resistance for the resist, or both. Therefore, excellent plasma etch resistance is a critical feature for ArF resist formulation. Our previous work[11], investigated

the performance of silicon containing resists of acrylate/norbornene copolymers. Herein, we synthesize the novel derivatives of Si-containing norbornene/maleic anhydride copolymers, which exhibit a low absorption and enhanced etching resistance. Moreover, these polymers are successfully employed to formulate 193nm bilayer photoresists.

2. Experimental

2.1 Preparation of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid 2-trimethylsilyl-ethyl ester (TSENB)

To a net acryloyl chloride (9.05 g, 100 mmol) was cooled at ice bath, freshly cracked cyclopentadiene (7.92 g, 120 mmol) was added dropwise and, then, the mixture was warmed up. After stirring for 2 hr, the crude bicyclo[2.2.1]-hept-5-ene-2-carbonyl chloride product was diluted with dry THF (150 ml), 2-(trimethyl silyl) ethanol (11.8 g, 100 mmol) was added and cooled in an ice bath. Dry Et_3N (11.1g, 110 mmol) and 4-DMAP (0.61 g, 5 mmol) in THF (50 ml) were slowly added and, then, the mixture was warmed up to RT, and stirred at RT for 3 hr. The resulting mixture was quenched with an aqueous NH_4Cl solution, the aqueous phase was extracted with ether (twice) and the combined ethereal solution was washed

with water (twice). The organic layer was dried over MgSO_4 and concentrated in *vacuo*. Purifying the residue by flash column chromatography yielded TSENB (19.0 g, 80%) as a colorless liquid.

The other Si-containing monomers were synthesized in our laboratory using proprietary methods.

2.2 Polymerization

To a solution of silicon containing monomer, *t*-butyl norbornene carboxylate (TBNB) and maleic anhydride (MA) in THF was added a solution of radical initiator (V601) in THF under reflux. When the addition was complete, the reaction mixture was stirred at 70°C for an additional 10 hr. After cooling to room temperature, the reaction mixture was slowly added with stirring to 2L of de-ionized water. The resulting precipitate was isolated by filtration and re-precipitated from 2L of hexane. Finally, the precipitate was dried in vacuum oven to yield a white powder (Table 1).

2.3 Preparation of photoresist solution

Si-containing polymer, triphenyl sulfonium nonaflate and killer base were dissolved in PGMEA, and the solutions were filtered through 0.45 μm membrane filter.

2.4 Resist Processing

The wafers were coated with resist on tract and baked at 130°C for 60 sec. The spin speed was 1800~5000 rpm to produce a normal resist thickness of 0.20~0.22 μm . The resist thickness was measured by Nanospec. Imaging experiments were carried out with ISI ArF exposure tool (NA=0.6). After exposure, PEB was performed at 130~140°C for 60 sec. The wafers were developed with 60 sec. of puddle developing with 2.38% TMAH. Finally, the line widths were measured on Hitachi 4200SEM.

3. Results and Discussions

3.1 Preparation of matrix polymers

Table 1 summarizes the polymerization results of Si-containing monomer, MA, and TBNB. The polymers were prepared in a satisfactory yield by free radical polymerization method, and the molecular weights ranged from 2200~2800. The polymers were sufficiently transparent at 193nm. For example, Figure 1 displays the UV spectrum of polymer D. The optimum feed ratio was determined by evaluating

the resists based on the polymers in Table 1.

Table1. Radical polymerization* of Si-monomer/MA

Polymer	Mw	PD	Yield (%)
A	2298	1.9	87
B	2066	2.4	99
C	2714	2.0	91
D	2550	2.1	99
E	1835	1.8	72
F	2409	1.9	70

*The polymers were prepared by varying the monomer ratios in feeding.

Figure 1. UV spectrum of polymers D

3.2 Polymer considerations

The design of our new silicon containing polymers is based on the building block approach. The possibility to combine specific monomers provides an effective means of synthesizing polymers with widely tunable physical properties. Syntheses of imaging polymers using these compounds under free radical conditions were quite straightforward. Polymers A~F were prepared by combining TBNB, MA, and Si-containing monomers. Figure 2 illustrates the general chemical structures of the polymers.

Figure 2. General structure of the polymers A~F

Silicon side chain provides not only etch resistance, but also induces cleavage through β -effect[12]. Higher silicon contents might also decrease thermal flow stability. Figure 3 shows the TGA curves of polymers D, revealing that this polymer has a significantly higher deblocking temperature than that of norbornene/maleic anhydride alternating copolymer.

Figure 3. TGA thermogram of polymers D

3.3 Etch resistance

In a bilayer system, the imaging polymer is applied on top of a thicker underlayer coating. The developed image in the upper layer is anisotropically transferred through the underlayer with an oxygen plasma etching, and the imaging layer must act as an effective etch mask during this process.

In order to introduce a sufficient plasma etch selectivity between the imaging layer and the underlayer, polymers with silicon contents between 3~10 wt% were targeted.

As mentioned earlier, silicon containing monomers can be incorporated into the system to modify the performance characteristics. Figure 4 plots the etch selectivity (O_2 RIE) between a novolac underlayer and silicon containing polymers, indicating polymer D with a 5.6%wt of Si content the etch selectivity is 8.2

Figure 4. Etch Selectivity for polymers A~F

3.4 Lithographic performance

A resist film was prepared by spin coating the silicon containing photoresist on a underlayer (PFI-38A9, Simitomo), and soft bake at 130°C for 90 seconds. Exposure was carried out on ArF exposure tool. The silicon in the imageable layer caused the film to etch more slowly than the underlayer during etch process. The high resolution feature that can be delineated with the imageable layer can be successfully transferred through the underlayer using RIE. Figure 5 shows 0.11 μm to 0.15 μm L/S patterns before and after being transferred through the underlayer. Isolated lines can be transferred by the same etch process. The optimum PEB temperature was slightly higher than that of norbornene/maleic anhydride alternating copolymer.

Figure 5. SEM images of patterned resist based on polymer D prior to oxygen plasma etching before (left) and after (right) a 130°C/60s bake.

With PSM technology, preliminary results with our silicon containing bilayer resists are highly promising candidates for 193nm lithography: Figure 6 shows the exposure latitude of polymer D for 0.12 μm and the focus latitude is 0.5 μm . at 3.3 mJ/cm². However, the feature size

could not be reduced lower than 0.11 μm and subsequently, the pattern collapsed after development and RIE processes.

4. Conclusion

This study has presented a novel platform of bilayer resist system, which is based on novel norbornene/maleic anhydride copolymer bearing acid labile and silicon containing groups. Prepared by free radical polymerization method, these polymers showed a good etch resistance and achieved good transparency at 193nm. Owing to a unique combination of the monomeric building block, polymers with a moderate silicon concentration shows promising oxygen plasma etch resistance. Using PSM, 110nm L/S patterns were resolved at 193nm. Further studies are underway.

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Figure 6. Lithography performance of 0.12 μm L/S at 3.3 exposure dose.

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