LITHOGRAPHIC CHARACTERISTICS OF ALICYCLIC POLYMER BASED ArF SINGLE LAYER RESISTS

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A new positive-tone ArF single layer resist based on chemical amplification is described. High transparency at 193 nm and dry-etch resistance required for ArF single layer resist can be achieved by introducing compounds containing alicyclic groups, such as adamantyl derivatives, in the resins. The dry-etch resistance of the resist is comparable to that of novolac resists, and high transparency ensures pattern imaging at 193 nm. This resist is capable of resolving 0.2 μm features with an ArF exposure system, and is suitable for ArF single layer resist.

1. Introduction

Increasing device integration demands improved resolution from lithographic technology. One of the most promising techniques is excimer laser lithography. Recent developments in KrF lithography combined with chemically amplified resists are remarkable. Only a few reports have been made, however, for ArF lithography [1-9], since the lack of suitable resists prevents its use in ULSI production. Because most deep UV or KrF excimer resists contain aromatic rings to provide dry-etch resistance, they cannot be used for ArF lithography due to the high absorbance of their aromatic rings at 193 nm. Therefore, early application of 193 nm lithography has been limited to surface-imaging or bilayer resist systems [1-3]. Recently, chemically amplified resists composed of acrylate polymers have been shown to serve as ArF single layer resists [6-8]. However, since the etch resistance of such resists is relatively poor, they are not suitable for practical use. Therefore, for ArF lithography to be successful, a new resist with both high transparency and high dry-etch

resistance is required.

For that purpose, we proposed a new chemically amplified resist which contained alicyclic hydrocarbons such as adamantyl or norbornyl groups [9]. The alicyclic group is highly transparent, even at 193 nm, and has a high dry-etch resistance comparable to that of the aromatic group. We suggested the possibility of applying it to ArF lithography, but our experimental results were limited to KrF lithography.

When applied to ArF lithography, sensitivity of the resist is another problem. Since the photoacid generator (PAG) used in this experiment contains aromatic rings, its concentration must be lowered. Therefore, higher sensitivity is required for the resist. Most chemically amplified resists based on acrylate polymer contain a t-butyl group as the acid-catalyzed deprotecting group, but the deprotecting abilities of the t-butyl group are not high. Hence, the contrast between exposed and unexposed areas is not sufficient with very low PAG concentrations. In order to enhance the alkali dissolution rate in the exposed area, we designed a new deprotecting group, 3-oxocyclohexyl group. The 3-oxocyclohexyl group has α -protons which are more acidic, so that its deprotection abilities are higher than those of the t-butyl group. Furthermore, using mixtures of isopropyl alcohol with aqueous base as the developer increases the dissolution rate of the exposed area. Consequently, the resist system becomes highly sensitive even with reduced amounts of PAG, thus achieving the high transparency required for ArF single layer resist.

This paper will report on our first application of alicyclic polymer to ArF lithography. The experimental results show that the new chemically amplified resist has a dry-etch resistance high enough for practical use and can resolve 0.2- μm features.

2. Experiment

Materials

Figure 1 shows the structure of the resist system we used in this experiment. The 3-oxocyclohexyl methacrylate and adamantyl methacrylate copolymers (OCMA-AdMA) were synthesized by NARD Institute Ltd.. Triphenylsulfonium hexafluoroantimonate (Ph_3SSbF_6) used as PAG was purchased from Midori Kagaku Co..

We confirmed the structures of the copolymers by FT-IR spectroscopy. We determined their composition and molecular weight by ^1H -NMR and GPC. The VUV spectra were recorded on a JASCO VUV-200 system using 1- μm -thick films spin-coated on quartz substrates. We investigated the dry-etch resistance of the copolymer with CF_4 and Ar etching gases.

Figure 1. Resist structures: (a) 3-oxocyclohexyl methacrylate and adamantyl methacrylate copolymer (OCMA-AdMA), and (b) triphenylsulfonium hexafluoroantimonate (Ph_3SSbF_6).

Lithographic evaluation

We prepared the resist solutions by dissolving the copolymer and PAG in cyclohexanone and filtering the solutions through 0.2- μm filters. We spin-coated the resists on cured novolac resin on silicon wafers, and prebaked them on a hotplate for 100 seconds at 100 °C. We set the film thickness to 0.4 μm . We exposed the resist films with an ArF exposure system (NIKON: NA=0.55), followed by a post exposure bake (PEB) for 60 seconds at 150 °C. We developed the exposed and baked films in dip mode for 60 seconds with 2.38% tetramethylammonium hydroxide (TMAH) solutions or with mixtures of isopropyl alcohol (IPA) and TMAH. We then rinsed the samples for 15 seconds with distilled water.

3. Results and Discussions

Dry-etch resistance

In our previous work [9], we reported the etch rates of various alicyclic polymers and showed that the dry-etch resistance of copolymers containing more than 50 mol% of the adamantyl group is comparable to that of novolac resist. Therefore, the OCMA-AdMA copolymer is also expected to have high dry-etch resistance.

The etch rates of the OCMA₄₀-AdMA₆₀ copolymer for CF_4 and Ar etching gases are summarized in Table 1, along with those of polymethyl methacrylate (PMMA) for comparison.

These values are normalized to those of novolac resin. As seen in the table, the OCMA-AdMA copolymer has a high dry-etch resistance in spite of the lack of aromatic rings. This copolymer is comparable to that of novolac resist, as we would expect. Consequently, we believe that the copolymer is practical for ULSI production.

	CF ₄	Ar
Novolac resin	1.0	1.0
OCMA-AdMA copolymer	0.9	1.1
PMMA	1.4	2.0

Table 1. Dry-etch resistance of the OCMA-AdMA copolymer. All values are normalized to those of novolac resin. The etching conditions are 0.02 torr, 200 W, 5 min, and 100 sccm.

Transparency

Figure 2 shows the VUV spectra of the OCMA-AdMA copolymer, and formulated resists with 1 and 2 wt% of PAG. The transmittance of the copolymer at 193 nm in a 1 μ m-thick film is 54%. High transparency is achieved by excluding the aromatic ring from the polymer. On the other hand, Ph₃SSbF₆, which is used as PAG, contains aromatic rings, so the transmittance of the resist depends strongly on the concentration of PAG. It must be lowered to meet the requirements of high transparency for single layer processing. By including 1 and 2 wt% of PAG in the resist, the transmittance decreases to 40% and 29%. The results of KrF lithography show that the pattern profiles of the resist become worse when its transmittance is less than 25%. We believe this is also true for ArF lithography. Therefore, from the standpoint of the transparency, the maximum concentration of PAG is limited to 2 wt%.

Figure 2. VUV spectra of OCMA-AdMA copolymer: (a) without PAG, (b) with 1 wt% of PAG, and (c) with 2 wt% of PAG. Films were 1- μ m thick.

Lithographic evaluation

Figure 3 shows the results of our preliminary experiment using a KrF excimer stepper. Since the adamantyl group is a strong dissolution inhibitor, the dissolution rate of the copolymers containing the adamantyl group in an aqueous base is relatively low. When a 2.38% TMAH solution is used solely as the developer, the resist system does not achieve a sufficient dissolution rate with only a 1 or 2 wt% of PAG. In such case, the resist cannot be developed, even at 300 mJ/cm² (Figure 3(a)). To enhance the dissolution rate of the exposed area, we used a mixture of isopropyl alcohol (IPA) with TMAH as the developer. IPA is known to enhance the dissolution rate of the resists based on acrylate polymers [10]. Figure 3(b) shows the contrast curve developed in the mixture. The composition of the mixture is optimized to 1:1. Although the sensitivity increases with increasing IPA content, the excess IPA causes cracks in the resist films. As can be seen from the figure, the dissolution rate is greatly enhanced by the addition of IPA.

According to the results of KrF lithography, we used a 1:1 mixture of IPA and TMAH in ArF lithography. Figure 4 shows a contrast curve of the resist exposed by an ArF exposure system. The resist is composed of OCMA₅₀-AdMA₅₀ (Mw=14000, Mw/Mn=1.44) and 1 wt% of PAG.

The encouraging results show a rather high contrast and the sufficient sensitivity to be used as ArF single layer resist.

Figure 3. Contrast curves for the OCMA₅₀-AdMA₅₀ copolymer with 1 wt% of Ph₃SSbF₆, exposed by a KrF excimer stepper. The resist was developed in (a) 2.38% TMAH solution, and (b) in a 1:1 mixture of IPA and TMAH.

Figure 4. Contrast curve for the OCMA₅₀-AdMA₅₀ copolymer with 1 wt% of Ph₃SSbF₆, exposed by an ArF exposure system and developed in the 1:1 mixture of IPA and TMAH.

(a)

(b)

(c)

Figure 5. Resist patterns of (a) 0.2 μm , (b) 0.25 μm , and (c) 0.3 μm lines and spaces printed by an ArF exposure system (NA=0.55). The resist consists of OCMA₅₀-AdMA₅₀ copolymer and 1 wt% of Ph₃SSbF₆. The film thickness is 0.4 μm . The exposure dose is 24 mJ/cm² and 1:1 mixture of IPA and TMAH is used as the developer.

Resist patterns printed using the ArF exposure system are shown in Figure 5. The concentration of PAG is also 1 wt% and the thickness of the film is 0.4 μm . We developed these patterns in the 1:1 mixture of IPA and TMAH. 0.2 μm line/space patterns are obtained at a dose of 24 mJ/cm². These features exhibit tailings at the bottom of the pattern to some extent. We believe that the tailings are not attributed to the deficiency of light intensity due to the low transmittance and that the substrates used in pattern profile evaluation are responsible for the tailings. Since the adhesion of the alicyclic polymer is relatively poor, hard-baked novolac resin coated on Si wafer is used as the substrate. When these substrates are used in the patterning experiment, the features exhibit appreciable tailings. The tailings may be due to contamination at the surface of the substrate. In KrF lithography, we confirmed the influence of the substrate on the resist pattern profile. When the silicon substrate treated with hexamethyldisilazane (HMDS) vapor is used instead of the novolac resin, there are no tailings in the pattern profiles and vertical profiles are obtained. Therefore, in ArF lithography, the pattern profile will be improved by using HMDS treated Si substrates. We believe that 0.2 μm or smaller features will be obtained easily by improving the pattern profile and that our new resist system based on alicyclic polymer will be suitable for the ArF single layer resist.

4. Conclusion

The results of the first application of alicyclic polymer to ArF lithography was described. The new chemically amplified resist consists of the 3-oxocyclohexyl methacrylate and adamantyl methacrylate copolymer. The adamantyl group provides high dry-etch resistance compared to novolac resin, providing acceptable resist for practical ULSI production. The transmittance of the copolymer at 193 nm is very high, and it enables the resist system to work as an ArF single layer resist. The results of the lithography show that the resist has the capability of resolving 0.2- μm features. Experiments are now under way to improve the pattern profiles and increase the resolution below 0.2 μm . Our new resist system is very promising for ArF single layer resist.

5. References

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