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Maleic anhydride type ArF photoresist

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ArF excimer laser (λ = 193 nm) lithography is a potentially applicable technology for the sub-0.18 μm design rule. However, in practical use of ArF technology, many problems must be solved for the properties of photoresist. To solve these problems, we synthesized ArF polymer resin, poly (2-hydroxyethyl acrylate/2-(*t*-butoxycarbonyl)-5-norbornene/5-norbornene-2-carboxylic acid/maleic anhydride). 2-hydroxyethyl acrylate is very suitable adhesion promoter to the silicon wafer substrate. Using this resist, 0.14 μm L/S pattern was obtained with 12 mJ cm^{-2} exposure by ArF stepper on the conventional develop condition, 2.38 wt% tetramethyl ammonium hydroxide aqueous solution. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: ArF photoresist; 2-hydroxyethyl acrylate; maleic anhydride)

Introduction

ArF excimer laser (λ = 193 nm) lithography is a potentially applicable technology for the sub-0.18 μm design rule. However, in the practical use of ArF technology, many problems must be solved for the properties of photoresist such as light transparency for 193 nm, dry etching resistance, adhesion, sensitivity and use of 2.38 wt% tetramethyl ammonium hydroxide (TMAH) aqueous solution as a develop solution. As novolac and poly(4-hydroxystyrene) polymers cannot be used owing to their absorption to 193 nm, acrylate type is a candidate polymer for ArF photoresist. However, compared to novolac resin, the etch rate of acrylate type polymer was so fast that it could not be used as a mask for the etch step in chip production. Also, the optical lens of the exposure tool is damaged by 193 nm strong radiation, so patterning must be enabled by low exposure energy about 10 mJ cm^{-2}. This requires highly sensitive photoresist. As the pattern size becomes smaller, the capillary force between the lines increases, but the contact area of line and substrate decreases. As a result the pattern is collapsed. To overcome this pattern collapse, the adhesion of photoresist to the wafer substrate must be strong. Another required property of ArF photoresist is the use of 2.38 wt% TMAH aqueous solution as a developer. In chip production, the ArF process and the *i*-line (365 nm) process will be used simultaneously. The develop solution of *i*-line is 2.38 wt% TMAH aqueous solution. In cost reduction and process stabilization, the develop solution of ArF photoresist must be the same as that of *i*-line photoresist. However, it is not easy to satisfy this develop property. In novolac or poly(4-hydroxystyrene) resin, phenol group appears from the decomposition of blocking unit that is attached to this phenol group by strong acid generated by photo acid generator. In ArF photoresist, as aromatic compounds cannot be used as matrix resins, carboxylic acid is used instead of phenol. The develop rate of carboxylic acid is so much faster than phenol in 2.38 wt% TMAH alkali solution that it is not easy to use 2.38 wt% TMAH solution as a developer in ArF photoresist. Therefore, much research has been focused on solving these problems. To increase the dry etch resistance the alicyclic unit was introduced as a pendant group[1–8]. Recently it has been reported that an alternating copolymer of norbornene and maleic anhydride is a new matrix resin for ArF resist polymers[9]. In spite of this research, there is no photoresist that satisfies all these properties yet. In this study, we synthesized ArF polymer resin, poly(2-hydroxyethyl acrylate(HEA)/2-(*t*-butoxycarbonyl)-5-norbornene(BNOR)/5-norbornene-2-carboxylic acid(NORA)/Maleic anhydride(MA)) and its lithographic performance results will be shown.

Experimental

Preparation of monomer. HEA was purchased from Aldrich and purified by vacuum distillation. MA was purchased from Aldrich and used without further purification. BNOR was prepared by Diels–Alder reaction between cyclopentadiene and *t*-butylacrylate[10–13]. The reaction product was purified by vacuum distillation. NORA was prepared by Diels–Alder reaction between cyclopentadiene and acrylic acid. The reaction product was purified by vacuum distillation. The onium salt photoinitiator, triphenylsulfonium triflate was prepared by the method in several publications[14,15].

Polymerization. All of the polymers were synthesized easily by radical polymerization. Monomers (HEA/BNOR/NORA/MA = 0.07/0.85/0.05/1.00 in mole feed ratio) were dissolved in tetrahydrofuran (THF) solution and *N,N'*-azobis(isobutyronitrile) was added to this mixture solution as a radical initiator. Polymerization was performed at 60°C for 10 h under a N_2 atmosphere. After the reaction, the reaction mixture was diluted by the addition of THF. Then the resulting polymer solution was precipitated by pouring the reaction mixture into excess ethyl ether and purified. The synthetic scheme is showed in *Figure 1*.

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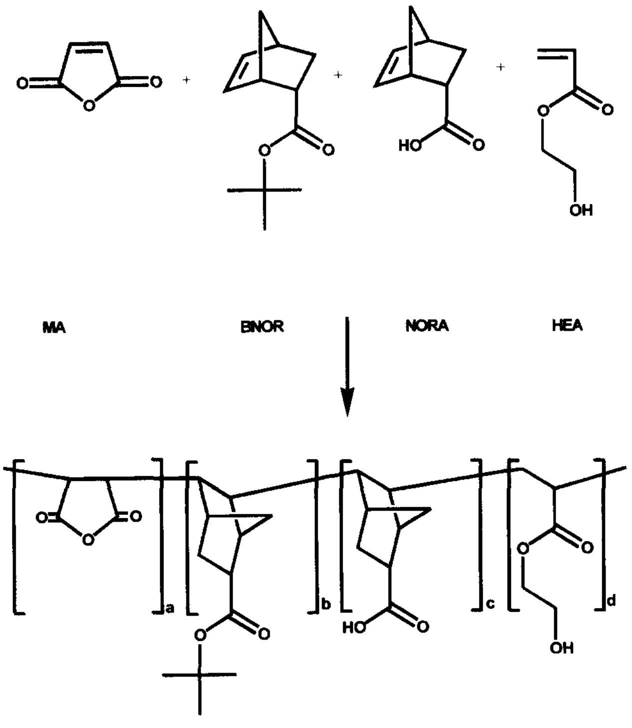

Figure 1 Synthetic scheme of poly(BNOR/NORA/HEA/MA)

Figure 2 SEM of 0.14 μm L/S pattern of ArF photoresist

Preparation of photoresist solution Poly(HEA/BNOR/NORA/MA) (5 g) and triphenylsulfonium triflate (0.075 g) were dissolved in 20 g methyl 3-methoxypropionate solvent. The solution was filtered through 0.2 μm membrane filter and used as a photoresist solution.

Measurements. The molecular weight of polymer was determined by gel permeation chromatography (g.p.c.) in THF using a TOSOH HLC-8020. Imaging experiments wre conducted using a ISI ArF exposure tool.

Results and discussion

Polymer characterization. At first we synthesized poly(BNOR/NORA/MA) as a matrix resin for photoresist but its lithographic performance was not good. Owing to the poor adhesion to the wafer substrate, 0.40 μm L/S could not be defined. So we introduced HEA into the polymer to increase adhesion of photoresist to the wafer substrate. The molecular weight of this synthesized polymer is 5700 and its dispersity is 1.33. The BNOR unit was introduced as a dissolution inhibitor and HEA as a adhesion promoter, and NORA was introduced to increase sensitivity.

Lithographic performance. A resist film was prepared by spin coating of photoresist solution on a hexamethyldisilazane treated silicon wafer substrate and soft baked at 110°C for 90 s. Exposure was carried out using an ArF exposure tool and baked again at 110°C for 90 s. After being baked, the wafer was developed in 2.38 wt% TMAH aqueous solution for 40 s. The scanning electron micrograph (SEM) of the L/S pattern for the ArF photoresist of poly(BNOR/NORA/HEA/MA) is shown in *Figure 2*. As can be seen, the 0.14 μm L/S pattern is well defined with 12 mJ cm^{-2} doses. With addition of the HEA unit, the adhesion of photoresist increases enormously and a good pattern can be obtained. With the addition of NORA, the sensitivity of photoresist increases enormously.

Conclusion

We have synthesized ArF resist polymers composed of alicyclic main chains. We also obtained very sensitive resist. Using this resist, 0.14 μm L/S pattern was obtained with 12 mJ cm^{-2} exposure by ArF exposure tool on the conventional develop condition, 2.38 wt% TMAH solution.

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