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Amine gradient process for DUV lithography

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Abstract

Poly(acrylic acid-*co*-methyl acrylate) was synthesized as a base resin for over-coating materials. By adding l-proline as an amine source to the over-coating material, amine gradient could be useful for lithography. Using this amine gradient process, vertical pattern of 140 nm line/space could be obtained even though the light transmission of photoresist to 193 nm wavelength was not good enough. The amine gradient process might be one of solutions for light absorption problem of photoresist for the next generation lithography. © 2000 Published by Elsevier Science Ltd.

Keywords: Poly(acrylic acid-*co*-methyl acrylate); Photoresist; Amine gradient process

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1. Introduction

After a lot of research and development efforts, KrF DUV ($\lambda = 248$ nm) lithography has been successfully introduced into high volume semiconductor manufacturing for 180 nm applications and is being pushed to its limit down to sub-150 nm regime [1–5]. To accomplish a minimizing feature size to sub 150 nm, new light sources for photolithography are emerging now, such as ArF($\lambda = 193$ nm), F_2($\lambda = 157$ nm) and EUV(Extremely Ultraviolet, $\lambda = 13$ nm) [6]. However, there is a strong need for new photoresists, which are transparent to these light sources. For an ArF photoresist, aromatic polymers used as a base resin for I-line (365 nm) and KrF (248 nm) photoresist could not be used owing to their strong absorption to 193 nm. For this reason, instead of aromatic polymers, cycloaliphatic polymers or acrylate polymers that have cycloaliphatic pendant groups have been used as a base resin owing to their transparency to 193 nm and etch resistance [7–24].

In this study we will propose a new process "amine gradient process (AGP)" for photolithography. The basic idea is that amine gradient induced by the over-coating material can overcome the problem induced by light absorption of photoresist. For this purpose, we synthesized ArF photoresist and over-coating materials. Using these materials, the lithographic performance has been evaluated.

2. Experimental

2.1. Materials

2.1.1. Preparation of monomer

2.1.1.1. t-Butyl bicyclo[2,2,1]hept-5-ene-2-carboxylate (BBC). BBC was prepared by the Diels–Alder reaction between cyclopentadiene and *t*-butylacrylate. A small amount (1.0 mol) of cold cyclopentadiene (−30°C) and 300 g of tetrahydrofuran (−30°C) were charged in 2 l round flask and the temperature of the reaction vessel was adjusted below −30° and then 1.2 mol of *t*-butyl acrylate was slowly added using a dropping funnel. After the dropping was complete, it was reacted under 23°C for 24 h. After the reaction was complete, tetrahydrofuran and residual *t*-butylacrylate were eliminated by rotary evaporator and finally BBC was purified by vacuum distillation (10^{-2} torr) at a temperature of 80°C. NMR (in $CDCl_3$): vinyl 2H at 6.20–5.84 ppm [6.20–6.12(m, 0.75), 6.12–6.02 (s, 0.5), 5.94–5.84 (m, 0.75), from this, *endo*/*exo* = 75:25], 1H of next to carbonyl at 3.17–2.94 ppm [3.17–3.15 (s, 0.75), 2.99–2.94(s, 0.25), 2H of bridge head at 2.9–2.78 ppm (m, 2), other 13H at 2.17–1.11 ppm. Yield = 78%.

2.1.1.2. 2-Hydroxyethyl bicyclo[2,2,1]hept-5-ene-2-carboxylate (HBC). HBC was prepared by the same method as mentioned in synthesis of BBC. Instead of 1.0 mol of *t*-butyl acrylate, 2-hydroxyethyl acrylate was used. Finally, HBC was purified by vacuum distillation

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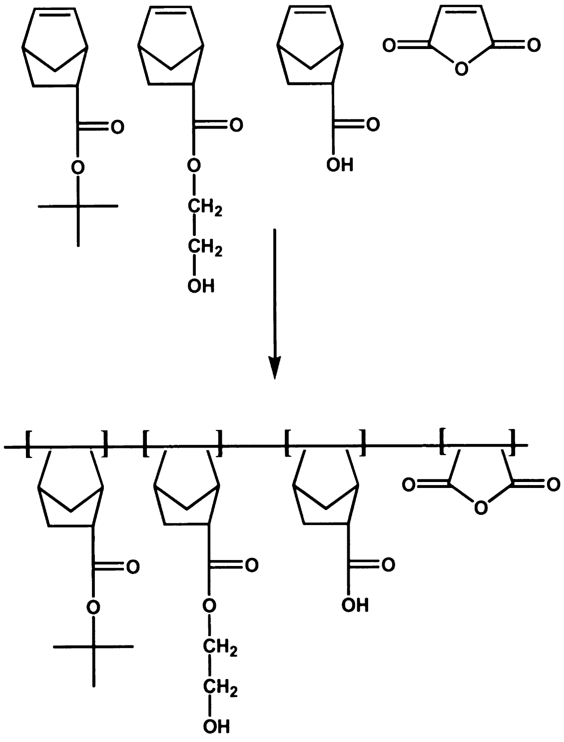

Scheme 1.

(10^{-2} torr) at the temperature of 120°C. NMR(in $CDCl_3$): vinyl 2H at 6.20–5.84 ppm [6.20–6.12 (m, 0.78), 6.12–6.02 (m, 0.44), 5.94–5.84 (m, 0.78) from this, *endo*/*exo* = 78:22], methylene 4H of 2-hydroxy ethyl 4.36–3.59 ppm [4.36–3.96 (m, 2), 3.87–3.59 (m, 2), 1H of next to carbonyl at 3.17–2.94 ppm [3.17–3.15 (s, 0.78), 2.99–2.94(s, 0.22)], 2H of bridge head at 2.94–2.71 ppm (m, 2), 1H of hydroxyl group at 2.48–2.27 ppm (s, 1), other 4H at 2.27–1.06 ppm. Yield = 87%.

2.1.1.3. Bicyclo[2,2,1]hept-5-ene-2-carboxylic acid (BC)

BC was prepared by the same method as mentioned in synthesis of BBC. Instead of 1.0 mol of *t*-butyl acrylate, acrylic acid was used. Finally, BC was purified by vacuum distillation (10^{-2} torr) at a temperature of 110°C. NMR (in $CDCl_3$): 1H of acid at 12.3–9.5 ppm, vinyl 2H at 6.28–5.92 ppm [6.28–6.15 (m, 0.8), 6.15–6.05 (m, 0.4), 6.04–5.92 (m, 0.8)from this, *endo*/*exo* = 80:20], 1H of next to carbonyl at 3.30–3.05 ppm [3.30–3.15 (s, 0.80), 3.12–3.05 (s, 0.20)], 2H of bridge head at 3.05–2.84 ppm (m, 2), other 4H at 2.27–1.10 ppm. Yield = 89%.

2.1.2. Synthesis of photoresist resin (poly(BBC/HBC/BC/MA))

The polymers were synthesized by radical polymerization as shown in Scheme 1. Monomers 18.46 g of BBC, 2.26 g of HBC, 0.86 g of BC and 10.96 g of maleic anhydride (MA) were dissolved in 24 g of tetrahydrofuran (THF) solution and 0.715 g of *N*,*N*′-azobis(isobutyronitrile) (AIBN) was added to this mixture solution as a radical initiator and then sealed with rubber setrum. After several times of degassing, the mixture solution was polymerized at 65°C for 10 h under vacuum condition. After the reaction was completed the polymer solution was precipitated in ethyl ether and purified. ($M_w = 6700$, polydispersity = 1.3, yield = 33%). The composition of poly(BBC/HBC/BC/MA) was confirmed by ^{1}H NMR and elemental analysis. From the ^{1}H NMR we could obtain that the ratio of methylene of HBC (4H of 2-hydroxy ethyl, at 4.36–3.59 ppm) to other protons of the polymer except the acid proton of BC (3.5–0.8 ppm) is 1:17.3. From elemental analyzer we could obtain that the mass ratio of total protons to total carbon is 1:9.91. As the cyclo-olefin and maleic anhydride make alternative polymers, we can get the polymer composition by combining ^{1}H NMR and elemental analysis. The composition of polymer is poly(BBC/HBC/BC/MA = 0.68:0.25:0.07:1.00).

2.1.3. Synthesis of over-coating material (poly(acrylic acid-co-methyl acrylate))

The polymer was synthesized by radical polymerization. In 500 ml three neck round flask where condenser was established, 9 g of acrylic acid, 1 g of methyl acrylate, 45 g of isobutylmethylketone, 45 g of propylene glycol methyl ether acetate and 0.3 g of AIBN were charged. Sustaining N_2 bubbling, the mixture solution was polymerized at 65°C. During the polymerization, a white polymer was precipitated in the mixture solution. After 3 h of reaction, this polymer was purified by filtering and washing with ethyl ether ($M_w = 7200$, polydispersity = 1.8, yield = 54%).

2.1.4. Other reagents

All solvents, maleic anhydride, AIBN, *t*-butyl acrylate, acrylic acid, 2-hydroxyethyl acrylate, methyl acrylate, l-proline were purchased from Aldrich and used without further purification. Cyclopentadiene was collected under −30°C by cracking of Aldrich cicyclopentadiene at 165°C. Photo Acid Generator (PAG), triphenylsufonium triflate was supplied by Korea Kumho Petrochemical Ind. Ltd.

2.1.5. Preparation of photoresist solution

A small amount (10 g) of Poly(BBC/HBC/BC/MA), 0.12 g of triphenylsufonium triflate and 0.0156 g of tetramethylammonium hydroxide pentahydrate were dissolved in 80 g of propylene glycol methyl ether acetate. The photoresist solution was used after filtering by using 0.20 μm disk filter.

2.1.6. Preparation of over-coating material

A small amount (5 g) of poly(acrylic acid-*co*-methyl acrylate) was dissolved in 200 g of DI water and 0.16 g of l-proline was added to this solution. The over-coating solution was used after filtering by using 0.20 μm disk filter. L-proline was used as an amine source for the amine

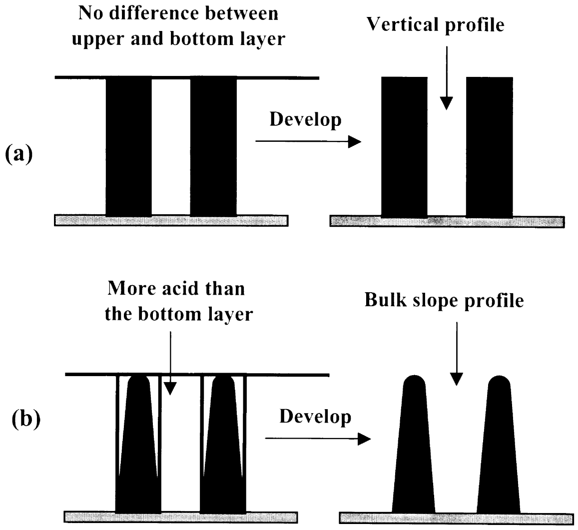

Fig. 1. (a) Expected fine pattern shape, in the case when a very transparent photoresist to the light source is used. (b) Expected deformed pattern shape, in the case where an opaque photoresist to the light source is used.

gradient process. The thickness of the over-coating material was 80 nm.

2.2. Equipment

The molecular weight of the base polymer of photoresist was determined by gel permeation chromatography (GPC) in tetrahydrofuran for poly(BBC/HBC/BC/MA) and DI water for poly(acrylic acid-*co*-methyl acrylate) using a TOSOH HLC-8020. For NMR, Bruker DPX300 was used. Elemental analysis was carried out on a CHNSO analyzer, EA1110 (CE Instrument Co., Ltd.). Imaging experiments were performed on an ISI ArF ($\lambda = 193$ nm) exposure tool (0.6 NA).

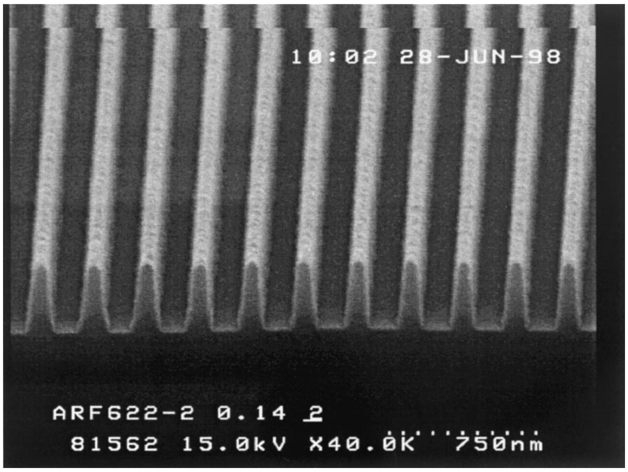

Fig. 2. SEM micrograph of 140 nm L/S pattern obtained under <1 ppb amine concentration using conventional illumination with ArF ISI stepper ($\lambda = 193$ nm, NA = 0.6).

2.3. Method

2.3.1. Process conditions

2.3.1.1. Without over-coating. A resist film was prepared by spin coating of the photoresist solution on a hexamethyldisilazane (HMDS) treated bare silicon wafer substrate and soft baked at 150°C for 90 s. Exposure was carried out on an ArF exposure tool and baked again at 140°C for 90 s. After baking, wafer was developed in 2.38 wt% TMAH aqueous solution for 40 s.

2.3.1.2. With over-coating. A resist film was prepared by spin coating of the photoresist solution on a hexamethyldisilazane (HMDS) treated bare silicon wafer substrate and soft baked at 110°C for 90 s. On this resist coated wafer, over coating materials was coated by spin coating and baked again at 90°C for 60 s. Exposure was carried out on an ArF exposure tool and baked again at 110°C for 90 s. After baking, the wafer was developed in 2.38 wt% TMAH aqueous solution for 40 s.

2.3.1.3. Amine environment adjustment. We have monitored amine concentration (NH_3) of our process environments daily. The NH_3 gas was collected by impinger method and the concentration of NH_3 was analyzed by ion chromatography. After exposure, the exposed wafers were stayed in four different environments for 90 s before developing. The NH_3 concentration of four different environments were lower than 1 ppb in ISI stepper, 5 ppb in KrF stepper, 20 ppb in process bay 1 and 40 ppb in process bay 2.

3. Results and discussion

If the light transmission of a resist is poor, the upper layer of the photoresist will be more irradiated than the bottom layer and more acid is generated in the upper layer. In a chemically amplified type photoresist, this difference makes a bulk slope after developing as shown in Fig. 1(b). To obtain a vertical fine pattern, the photoresist must be transparent to the irradiating light as shown in Fig. 1(a).

When the resist made by poly(BBC/HBC/BC/MA) was coated with 1 μm thickness on a quartz wafer, 193 nm transmission was 30%. Owing to this high absorption to 193 nm, we can anticipate that the profile of the resist will have a bulk slope. When the amine concentration of environment was lower than 1 ppb, we only obtained a bulk slope profile as shown in Figs. 1(b) and 2. However, when the amine concentration of environment was 5 and 40 ppb, we could obtain vertical fine patterns and t-top profile, respectively, as shown in Figs. 3 and 4. Under a highly amine contaminated environment, amine penetrates into the resist and neutralizes acid that was generated by photo reaction of triphenylsulfonium triflate [25,26]. If the amine diffusion in resist is well matched and compensates for the acid gradient caused

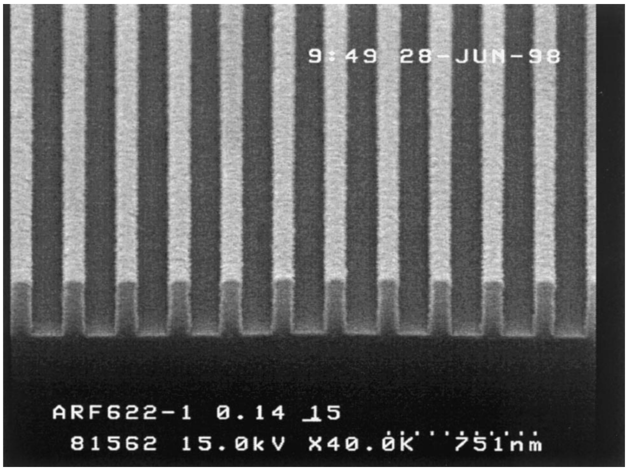

Fig. 3. SEM micrograph of 140 nm L/S pattern obtained under 5 ppb amine concentration, using conventional illumination with ISI stepper.

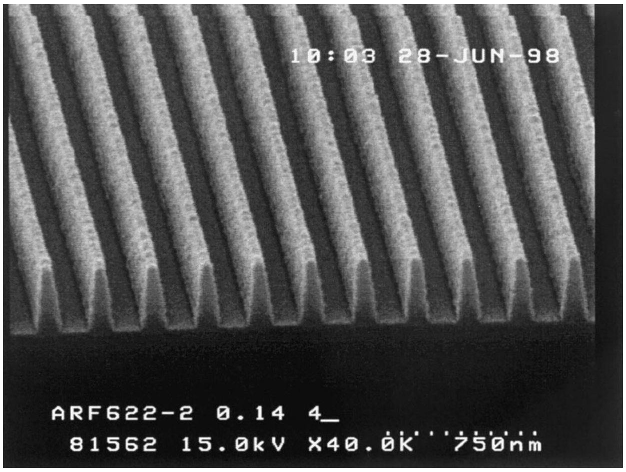

Fig. 5. SEM micrograph of 140 nm L/S pattern obtained under 20 ppb amine concentration, using conventional illumination with ISI stepper. Over-coating without l-proline was performed at the top of the photoresist.

by light absorption of resist, a vertical fine pattern can be obtained (See Fig. 3). Under 40 ppb amine concentrated environment, amine diffusion exceeds the acid gradient and the results show t-top profile pattern as shown in Fig. 4. This amine dependent phenomenon of resist profile makes it difficult to use in a real device process where amine fluctuation occurs.

One solution for this amine fluctuation is the use of over-coating method that blocks the amine penetration [27,28]. The over-coating material must be water soluble because it should not mix with photoresist which is insoluble in water. Using over-coating materials that was made by poly(acrylic acid-*co*-methyl acrylate), we could only obtain a bulk slope profile as shown in Fig. 5 under 20 ppb amine contaminated environment. As the over-coating material prevents amine penetration, the acid gradient caused by light absorption of the resist cannot be compensated. As a result, like Fig. 1(b), we could only obtain a bulk slope pattern.

In order to obtain the vertical pattern, the amine source should compensate the acid gradient. For this purpose, we introduce l-proline as an amine source in the over-coating material. When this l-proline containing over-coating material was coated on the photoresist coated wafer, l-proline diffused into the photoresist region and compensated for the acid gradient and a vertical fine pattern could be obtained as shown in Fig. 6. The more acid on the upper part is generated because the upper part is more irradiated by 193 nm owing to light absorption of the photoresist. On the other hand, in the upper layer of the photoresist, there is more l-proline than the bottom layer of the photoresist because more l-proline diffuses into the upper layer than the bottom of the photoresist. As a result, there is more neutralization reaction in the upper region than the bottom region and a vertical fine pattern can be obtained. In other words, the amine gradient made by the over-coating material

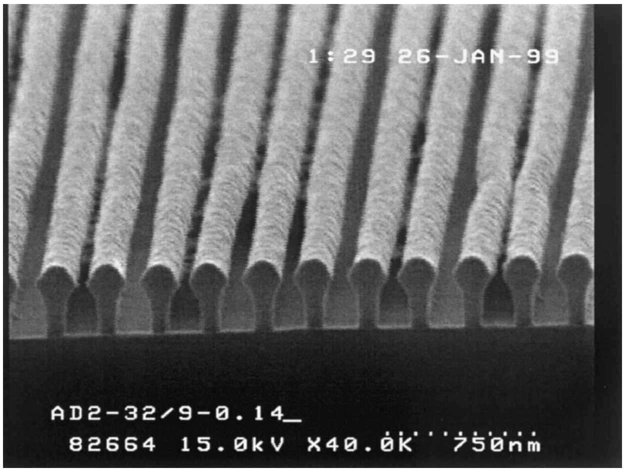

Fig. 4. SEM micrograph of 140 nm L/S pattern obtained under 40 ppb amine concentration, using conventional illumination with ISI stepper.

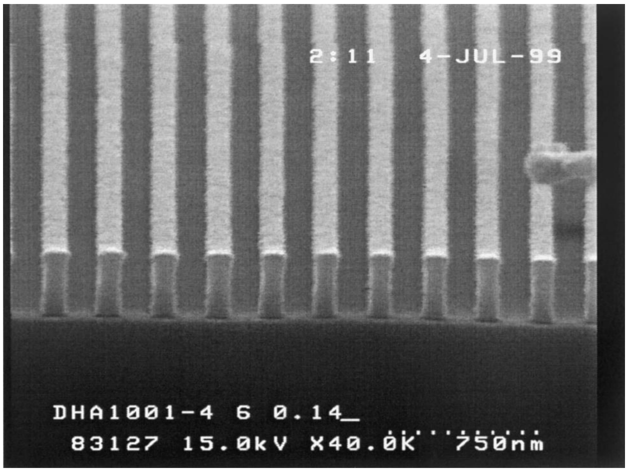

Fig. 6. SEM micrograph of 140 nm L/S pattern obtained under 20 ppb amine concentration, using conventional illumination with ISI stepper. Over-coating containing l-proline was performed at the top of the photoresist.

overcomes the acid gradient made by light absorption of the photoresist.

4. Conclusions

We proposed an amine gradient process using amine containing a over-coating material and could obtain a vertical fine pattern even though the light absorption of the photoresist was serious. As the wavelength of light source is shrinked to minimize device feature size, it is more difficult to develop new materials that are transparent to this short wavelength. Amine gradient method can be a solution to cope with light absorption problem of base polymer.

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