

Polymer Communication

Acid diffusion control in chemically amplified resists

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Abstract

A new chemically amplified resist containing a basic monomer, 3-(*t*-butoxycarbonyl)-1-vinylcaprolactam, in the matrix polymer was prepared for post-exposure delay stability. Poly(3-(*t*-butoxycarbonyl)-1-vinylcaprolactam-co-*t*-butyl methacrylate) was synthesized and evaluated as a new matrix resin. The diffusion lengths of photogenerated acid in the resist films were studied for various fractions of the basic monomer in the copolymers. The results show the copolymer with a basic monomer can control the acid diffusion without a severe decrease in sensitivity. This new resist system enables us to form fine patterns and attain 2 h post-exposure delay stability without any additional treatment. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Chemically amplified resists (CARs) with KrF excimer laser lithography are the most promising technologies for sub-micrometer patterns because of their high transparency and sensitivity [1,2]. However, while the resolution of CAR has advanced to better than 0.5 μm , there still remain some problems. One of the most serious problems is the deterioration of CAR performance due to airborne contamination. The basic contaminants such as ammonia and 1-methyl-2-pyrrolidinone in the air can neutralize the surface acid in the exposed area of the photoresist during post-exposure delay (PED) between the exposure and the post-exposure bake (PEB) steps, and cause T-shaped profiles and enlarged critical dimensions. Another PED effect is acid diffusion into the unexposed area which can cause resist line width and profile changes. Special methods, such as overcoats [3], chemical filters [4] and stabilizing additives [5], have been used in order to reduce the PED effects. However, the best way to solve the problem would be to prepare a new resist system that is resistant to these effects.

We propose a new CAR system including a basic monomer in the matrix polymer. This paper describes the synthesis of basic matrix polymers and their effects on PED stability.

2. Experimental

2.1. Materials

t-Butyl methacrylate (TBMA) was purchased from Aldrich chemical company and distilled prior to use. 1,4-Dioxane, purchased from Lancaster chemical company, was refluxed for 2 days over sodium metal and distilled prior to use. The photoacid generator (PAG), triphenylsulfonium trifluoromethanesulfonate (TPSTFMS), was synthesized according to the literature [6]. 3-(*t*-Butoxycarbonyl)-1-vinylcaprolactam (BCVC) was prepared as described in our previous publications [7,8].

2.2. Copolymerization of TBMA with BCVC

The copolymers were synthesized with various monomer feed ratios using 1 mol% 2,2'-azobisisobutyronitrile (AIBN) as an initiator in 1,4-dioxane at 60°C under vacuum in a sealed ampoule for 12 h. The copolymers were precipitated into a large amount of petroleum ether or pure water. The precipitate was filtered and dried under reduced pressure.

2.3. Measurement of the acid diffusion length [9,10]

The copolymer solution in cyclohexanone without the PAG was spin-coated onto silicon wafers and baked on a

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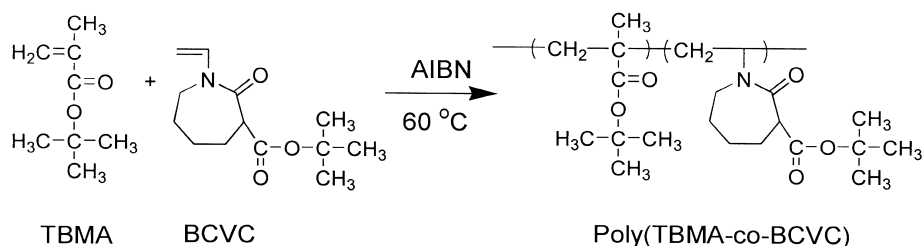


Fig. 1. Polymerization scheme.

hot-plate at 100°C for 2 min. Then a mixture solution of poly(vinyl alcohol) and TPSTFMS in water was spin-coated on top of the copolymer films and baked again at 100°C for 2 min. To generate acid in the poly(vinyl alcohol) top layer, the films were exposed to deep-UV light at a dose of 100 mJ cm⁻². The films were stored in the air for various lengths of time. During this delay, the acid diffused into the bottom copolymer layer. The top layer was removed by washing with pure water. Then, the remaining copolymer bottom layer was baked at 120°C for 2 min. The copolymer film was developed in 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution for 2 min. The depth difference between exposed and unexposed areas in the copolymer film was measured with an Alpha-step 500 surface profiler (Tencor Instrument).

2.4. Lithographic evaluation

A resist solution consists of the copolymer, TPSTFMS and cyclohexanone. This solution was filtered through a 0.2 μm filter and spin-coated onto silicon wafers at 2000–3000 rpm to obtain about 1 μm thickness films. The wafers were then cut into small pieces and subsequently exposed to obtain sensitivity curves. Exposures were taken using a Nikon NSR 2005 KrF excimer laser stepper whose numerical aperture value was 0.55. For the PED stability test, the exposed wafer was stored for 2 h before the PEB in a cluster with a chemical filter in which the ammonia concentration was 5 ppb. The exposed films were baked at 120°C for 2 min and developed in 2.38 wt% TMAH aqueous solution.

3. Results and discussion

3.1. Polymerization

Copolymerizations of TBMA with BCVC were carried out with various molar feed ratios using 1 mol% AIBN as a radical initiator (Fig. 1). The results are summarized in Table 1. The polymer composition was determined by using the Fox equation from the glass transition temperature T_g of the copolymer.

3.2. Sensitivity curves

The sensitivity curves of the resists with various mole fractions of BCVC are shown in Fig. 2. It is clear that the higher the BCVC fraction is, the lower the sensitivity becomes. These resists show good sensitivities (10–20 mJ cm⁻²) in spite of the high content of the basic moiety because BCVC has a low basicity compared with the organic base additives (e.g. 1-methyl-2-pyrrolidinone) which have been used in the dispersed system [5,7].

3.3. Diffusion length of photogenerated acid

The acid generated from the PAG diffuses in the resists during the PEB and encounters and deprotects t-BOC protecting groups as a catalyst. After the acid takes part in the reaction, it diffuses again in the resists. The photogenerated acid can diffuse into the unexposed area during the PED and cause line width variation. The diffusion length of the acid in the resist film during PED was measured to investigate the behaviour of the acid in the

Table 1. Radical polymerizations of TBMA with BCVC

Polymer	Monomer feed ratio (TBMA/BCVC)	Polymer composition ^a (TBMA/BCVC)	Yield (%)	Inherent Viscosity ^b (dl g ⁻¹)	T_g ^c (°C)
A	0/100	0/100	88	0.42	181
B	50/50	54/46	82	0.57	153
C	60/40	65/35	83	0.61	146
D	70/30	74/26	87	0.63	139
E	100/0	100/0	95	0.53	118

^a Compositions were determined by using Fox equation from T_g values.

^b Inherent viscosity η_{inh} was measured at a concentration of 0.5 g dl⁻¹ in cyclohexanone at 25°C.

^c T_g was measured with a Perkin-Elmer TA 7 system at a heating rate 10°C min⁻¹.

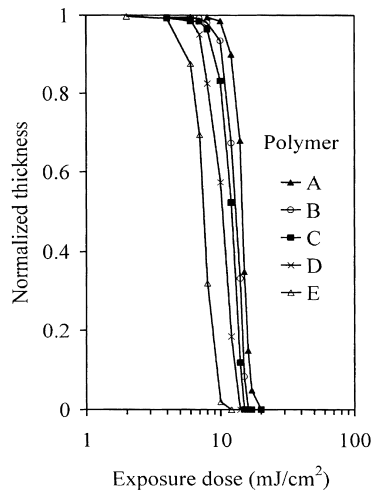


Fig. 2. Plot of the normalized thickness versus exposure dose: poly(TBMA-co-BCVC)/TPSTFMS (93/7 wt ratio); PEB conditions, 120°C for 2 min.

presence of a basic matrix polymer. The regions penetrated by the acid become soluble in the developer; thus, the diffusion length could be determined from the depth difference between exposed and unexposed regions. The depth difference was plotted as a function of PED time for a baking temperature of 120°C, as shown in Fig. 3. The diffusion length in poly(TBMA) (polymer E) sharply increased with PED time. In contrast, the diffusion lengths in the copolymers which contain basic BCVC slightly increased with PED time and became almost constant for PED times longer than 1 h. Comparing the diffusion lengths, BCVC exhibited a diffusion suppression effect. In addition, it is clear that the greater the BCVC fraction is, the shorter the diffusion length becomes. These results show incorporation of the basic BCVC in the matrix polymer can trap acid and control the acid diffusion.

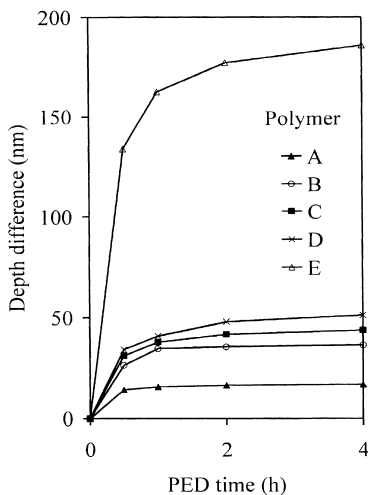


Fig. 3. Relationship between PED time and the diffusion length of acid.

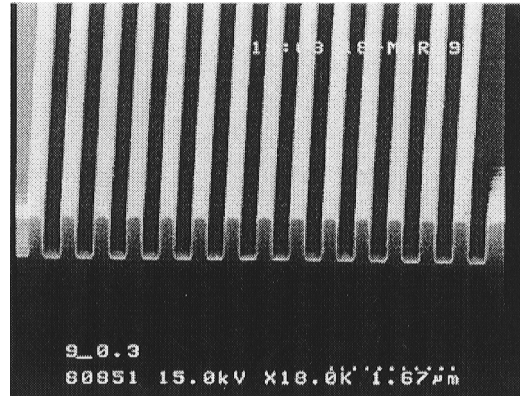


Fig. 4. Scanning electron micrograph of 0.30 μm L/S positive images of poly(TBMA-co-BCVC)(B) resist at 25 mJ cm^{-2} (PED time: 2 h).

3.4. Patterning

The scanning electron micrograph of patterns after 2 h delay time is shown in Fig. 4. The pattern profile is not deteriorated and T-top is not observed. The basic groups in the matrix polymer deactivate the photogenerated acid uniformly throughout the exposed region. Therefore T-top formation due to local deactivation of the acid in the top portion of the exposed region by airborne basic contaminants can be suppressed.

4. Conclusions

Copolymers of TBMA and BCVC with various molar feed ratios were synthesized as matrix polymers in CARs to improve the PED stability. These copolymers which contain basic monomer units reduced the diffusion length of acid dramatically and prevented T-top formation. Thus we have established a new simple method to control the diffusion length of acid during PED and to reduce T-top formation which have been the most serious problems in CARs.

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