Chemically Amplified Resists Containing Vinylactam Derivatives

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A new environmentally stable positive tone deep UV resist has been designed by incorporating basic units into a matrix polymer for stabilization toward airborne contaminants. Poly(3-(*t*-butoxycarbonyl)-1-vinylcaprolactam) (poly(BCVC)), and poly(3-(*t*-butoxycarbonyl)-1-vinylcaprolactam-co-*t*-butyl acrylate-co-hydroxystyrene) (poly(BCVC-co-TBA-co-HOST)) were prepared and evaluated as potential deep UV photoresists. 0.2 μ m line/space patterns were obtained for these resist systems using a KrF excimer stepper (NA 0.55) with a dose of 25 mJ/cm². And these resists did not change pattern profile after 2 hours post exposure delay (PED) time in which ammonia concentration was 5 ppb. 3-(*t*-Butoxycarbonyl)-1-vinyl-2-caprolactam (BCVC) unit as a basic moiety can not only solve the amine contamination problem effectively, but also improve the resolution of the resists. BCVC unit reduces the diffusion of acid and it results in sharp contrast at the interface between the exposed and unexposed areas. Therefore, adding BCVC unit in matrix polymer leads to the stabilization of the pattern profile and higher resolution.

Keywords: vinylactam, chemically amplified resist, environmental stability

1. Introduction

Continued advances in microelectronics and photolithography have accelerated the demand for photoresists with ever higher photosensitivity and resolution capabilities. The current goal of the microelectronic industry is to develop integrated circuits with minimum features of less than 0.25 μ m. It is well recognized that to accomplish this goal, exposure tools which operate in the deep UV region (190 ~ 300 nm) of the spectrum will have to be used. Today, the best irradiation source which has been developed for use in this region is the KrF excimer laser emitting at 248 nm. Accordingly, most recent developmental photoresist efforts are being directed specifically to respond to this exposure tool. To develop photoresists responsive to the 248 nm region,

several major problems must be overcome. The first of these is the problem of achieving adequate sensitivity in this region of the electromagnetic spectrum. Therefore, there has been an increased interest in "chemical amplification" photoresist systems for deep UV photolithography. The basic idea utilizes the initial photogeneration of proton, followed by a subsequent (catalytic) chemical reaction to induce a change in solubility of the exposed area. [1,2] While the combination of high throughput and high resolution offered by chemically amplified resist (CAR) is attractive, the drawback of this technology is the environmental and substrate dependency of these materials. Most CARs suffer from T-topping and/or footing. They are easily affected by contaminations existing in the air and on the

substrates, since resists of this type use a strong acid as a catalyst and become unstable to the environmental conditions. The contamination problem has been alleviated to some extents by purifying the enclosing atmosphere, [3] applying protective topcoat, [4] annealing the resists [5] and incorporating additives in resist formulation. [6,7] However, there still exists a serious need for designing a chemical amplification resist which is insensitive to airborne contamination. Of those methods, we had an interest in the basic additives, typically amines, which do not only improve the delay time stability considerably but also act as acid scavengers especially for long range diffusion of acid molecules to increase contrast between exposed and unexposed areas. However, it remained a serious problem that the basic additives migrate to the surface of the resist film during a high temperature process.[8]

Here, we propose new resist systems composed of chemical amplification positive resists incorporating a basic unit in the matrix polymer chain. We describe the design concept of the new systems and prove that the new resist systems improve the post exposure delay (PED) stability.

2. Experimental

2.1. Materials

2.1.1. Preparation of 1-Vinylcaprolactam (VC)

Into 1.8 liter stainless steel autoclave was charged 350 g (3.1 mole) of ϵ -caprolactam and 5.17 g (0.046 mole) of potassium *t*-butoxide. The autoclave was purged three times with nitrogen at room temperature and then heated 120~130 °C. Acetylene (partial pressure 65 psi) was added and the solution was agitated at a speed of 500 rpm. After 19 h of vinylation, the solution was fractionally distilled under 10 mmHg. The product was obtained at 71~73 °C /10 mmHg (120 g, 34.2 %): IR (cm⁻¹) 2932 (cyclic CH), 1671 (C=O of amide), 1626 (vinyl)

2.1.2. Preparation of 3-(*t*-Butoxycarbonyl)-1-vinylcaprolactam (BCVC)

A 2.5 M solution of *n*-butyllithium (40 ml, 0.1 mol) in hexane was added dropwise to a solution of diisopropylamine (14 ml, 0.1 mol) in 40 ml of anhydrous tetrahydrofuran (THF) at -

78 °C with stirring under nitrogen atmosphere. After the addition was completed, the reaction was allowed to warm up to room temperature. The solution was cooled again to -78 °C, followed by dropwise addition of 30 ml of an anhydrous THF solution of VC (13.9 g, 0.1 mol) and the resulting pale yellow solution was maintained at -78 °C for 30 min. Di-*tert*-butyldicarbonate (DtBDC) (24 g, 0.11 mol) in THF was added dropwise to the solution at -78 °C. The reaction mixture was stirred for 2 h at -78 °C and then poured into diethyl ether.

The ethereal layer was washed with water. The organic solution was dried and concentrated to give a pale yellowish syrup, which was purified by column chromatography on silica gel with ethyl acetate/hexane (1/3) as eluent. The desired fractions were combined, concentrated and dried in a vacuum oven. White powdery BCVC was obtained in a yield of 76% as sufficiently pure material without recrystallization: m.p. 55 °C; ¹H-NMR (CDCl₃) δ 7.0 (1H, q, =CH-), 4.5 (2H, m, CH₂=), 3.6 (1H, m, C3H), 3.4 (2H, m, C5H), 1.4~2.1 (15H, m); IR (cm⁻¹) 2936 (cyclic CH), 1740 (C=O of ester), 1665 (C=O of amide), 1626 (vinyl), 1368 (*t*-butyl).

2.2. Polymerization

2.2.1. Preparation of Poly(BCVC)

A solution of BCVC in benzene or dioxane that contained AIBN was heated at 65 °C under vacuum in a sealed ampoule respectively. The polymer was precipitated in fresh petroleum ether and dried under vacuum.

2.2.2. Preparation of Poly(ACOST-co-TBA-co-BCVC)

A solution of ACOST, TBA and BCVC in toluene that contained AIBN was heated at 65 °C under vacuum in a sealed ampoule. The terpolymer was precipitated in fresh petroleum ether and dried under vacuum: ¹H-NMR (CDCl₃) δ 6.7~6.2 (br. ArH), 4.7 and 3.5 and 3.3 (COCHCO and N-CH and N-CH₂ of BCVC), 2.23 (s, OCH₃), 1.9~1.0 (br, -C(CH₃)₃, CH₂, and CH).

2.2.3. Preparation of Poly(HOST-co-TBA-co-BCVC)

15 ml of 28% ammonia water was added to a solution of poly(ACOST-co-TBA-co-BCVC) (10

g) in methanol. The reaction mixture was neutralized with acetic acid and poly(HOST-co-TBA-co-BCVC) thus obtained was purified by precipitation in water, isolated by filtration, and dried in a vacuum oven at 50 °C (9.4 g, 92% yield): $^1\text{H-NMR}$ (CD_3OD) δ 6.5~6.2 (br, ArH), 1.9~1.0 (br, $\text{C}(\text{CH}_3)_3$, CH_2 , and CH), 1.4~0.9 (br, $-\text{C}(\text{CH}_3)_3$, CH_2 , and CH).

2.3. Thin Film Casting

The resist solutions were prepared by dissolving matrix polymers (11~14 wt% for solution) in propylene glycol methyl ether acetate. Triphenylsulfonium hexafluoroantimonate (TPSHFA) (5~7 wt% for matrix polymers) as a photoacid generator, which was synthesized according to the literature,[9, 10] was mixed with the solutions. These solutions were filtered through a 0.45 and/or 0.2 μm filter. From the solutions, 0.8~1 μm films were obtained by spin-coating with 2500~3000 rpm, 30 seconds on NaCl plates for IR spectroscopy, on quartz cells for UV spectroscopy and on silicon wafers for lithographic evaluation.

2.4. Lithographic Evaluation

For the lithographic evaluation, the resist solutions were spin-coated at 2600 rpm and the films on silicon wafers were pre-baked at 120~140 °C for 2 min to remove residual solvent. Exposures were carried out on KrF excimer stepper (0.55NA). For PED stability test, the exposed wafer was stored for 2 hours before PEB process in a cluster with chemical filter in which ammonia concentration is 5 ppb. The exposed films were post-exposure baked at 120~145 °C for 3 min and developed in 2.38 wt% TMAH aqueous solution.

3. Results and Discussion

3.1. Preparation of Monomers and Polymers

3.1.1. Synthesis and Polymerization of BCVC

Preparation of VC is generally carried out in two-stages where potassium t-butoxide is reacted with the ϵ -caprolactam to produce the corresponding ϵ -caprolactam salt and followed by vinylation of ϵ -caprolactam with acetylene. The FT-IR spectrum of VC showed a vinyl absorption peak at 1626 cm^{-1} . For introduction

of the t-butoxycarbonyl (t-BOC) group to the 3-position of VC, 1-vinylcaprolactam enolate intermediate was generated by using lithium diisopropylamide (LDA) and then was reacted with di-t-butyl dicarbonate (DtBDC). The BCVC was obtained as a white powder and was sufficiently pure without recrystallization. Scheme 1 illustrates the preparation of VC and BCVC.

< Scheme 1 >

The polymerization results are shown in Table 1. The t-BOC protected monomer was easily polymerized under radical polymerization condition. The FT-IR spectrum of the monomer showed a vinyl absorption at 1635 cm^{-1} which after polymerization disappeared completely. Bulk polymerization resulted in partial gel formation, but solution polymerization resulted in proper molecular weight for a resist. As shown in Table 1, the proper molecular weight was obtained when benzene or dioxane was used as a solvent. Molecular weight of the poly(BCVC) was controlled by the amount of the initiator and solvent used in the polymerization.

Table 1. Radical Polymerization of BCVC

Solvent	AIBN ^a (mol%)	M/S ^b (g/ml)	Time (h)	Conver- sion (%)	Inherent viscosity ^c (dl/g)	T _g (°C)
Bulk(2a)	1	-	12	-	*	-
Benzene(2b)	1	1	12	88	0.32	179
Benzene(2c)	1	1.3	12	88	0.75	183
Benzene(2d)	1	2	12	90	1.20	190
Dioxane(2e)	1	1	12	91	0.30	174
Dioxane(2f)	0.5	2	12	90	0.42	181

Polymerizations were carried out at 65 °C.

^a Mol% of the initiator AIBN to the total amount of monomer.

^b M/S is the ratio of the total weight of monomer to the volume of solvent.

^c Inherent viscosities were measured at a concentration of 0.5 g/dl in cyclohexanone at 25 °C.

* Partial gel formation.

3.1.2. Preparation of Poly(HOST-co-TBA) and Poly(HOST-co-TBA-co-BCVC)

In the case of terpolymerization, the composition of the BCVC in terpolymer was very small compared with the fraction of the BCVC monomer which had been fed to the reaction (Table 2). In the IR spectra of the copolymer and terpolymers, the carbonyl bands in acetoxy group of ACOST and in t-butyl ester group of TBA were shown at 1765.6 cm⁻¹ and 1725.5 cm⁻¹. The amide carbonyl band of BCVC appeared at 1647.9 cm⁻¹ with very low intensity and the absorption band of t-butyl ester carbonyl group was overlapped with those of ACOST and TBA.

The hydrolysis step using ammonium hydroxide was extremely selective. The t-butyl ester group of TBA and BCVC survived the basic reaction condition. From the IR spectrum of poly(HOST-co-TBA) the complete removal of the acetoxy group was confirmed. The photochemically-induced acid-catalyzed conversion of the ester to the carboxylic acid in the resist film can be monitored by following shrinkage of the absorptions at 1368 cm⁻¹ and 1149 cm⁻¹.

Table 2. Radical Polymerization of Poly(ACOST-co-TBA) and Poly(ACOST-co-TBA-co-BCVC)

Sample #	Molar feed ratio ^a (l : m : n)	AIBN ^b (mol%)	M/S ^c (g/mol)	Time (hr)	Conversion (%)	Inherent viscosity ^d	Composition of polymer ^e (l : m : n)
4a	10 : 7 : 0	0.2	2.5	20	82	0.53	62.0 : 38.0 : 0.0
4b	10 : 6 : 0.5	0.2	2.5	20	80	0.51	64.3 : 35.0 : 0.7
4c	10 : 6 : 1	0.2	2.5	20	81	0.49	63.6 : 35.0 : 1.4
4d	10 : 7 : 3	0.2	2.5	20	72	0.46	58.1 : 59.3 : 2.6

^a Polymerization was carried out at 65 °C (l : ACOST; m : TBA; n : BCVC).

^b Mol% of the initiator AIBN to the total amounts of monomer.

^c M/S is the ratio of the total weight of monomer to the weight of toluene.

^d Inherent viscosities were measured at a concentration of 0.5 g/dl in DMF at 25 °C.

^e The composition of polymer is the mole ratio of monomers in polymer.

The compositions of the copolymer and terpolymers can be calculated from the $^1\text{H-NMR}$ spectrum and TGA plots. According to the $^1\text{H-NMR}$ spectra of poly(HOST-co-TBA) and poly(HOST-co-TBA-co-BCVC), the complete removal of acetoxy group can be confirmed again by the fact that the single peak of three protons of acetoxy group at 2.23 ppm disappeared.

3.2. Physical Properties of the Resist Polymers

3.2.1. Thermal Analysis of Poly(BCVC)

Before imaging tests were carried out, the acid catalyzed cleavage of the protected polymer was studied using TGA and FT-IR. The TGA thermogram of poly(BCVC) shown in Figure 1a indicates that poly(BCVC) possesses good thermal stability up to 200 °C. At that temperature, a rapid weight loss took place due to evolution of isobutylene and carbon dioxide resulting from spontaneous thermolysis of the t-BOC groups. Poly(BCVC) were converted to poly(N-vinylcaprolactam) by thermal deprotection of the t-BOC groups as shown in Scheme 2.

< Scheme 2 >

In the absence of acid, the deprotection of the t-BOC groups of poly(BCVC) occurred above 220 °C whereas, in the presence of a generated acid, the cleavage of the t-butyl groups of poly(BCVC) was found to begin around 60 °C as shown in Figure 1b and completed at about 120 °C, and then the carbon dioxide was evolved subsequently.

The thermal deprotection of the t-BOC groups of poly(BCVP) resulted in almost the same weight loss of 42 wt% with or without a generated acid, which corresponds to the theoretically calculated weight loss due to the evolution of carbon dioxide and isobutylene from the polymer.

Figure 1. Comparison of TGA thermograms of poly(BCVC) containing 7 wt% of TPSHFA before (a) and after (b) UV exposure

3.2.2. Thermal Analysis of Poly(HOST-co-TBA) and Poly(HOST-co-TBA-co-BCVC)

Thermal properties of the copolymer and terpolymers are shown in Table 3. The glass transition temperature of Poly(HOST-co-TBA) or Poly(HOST-co-TBA-co-BCVC) was about 165 °C.

The onset temperature of the thermal deprotection of the polymers was ca. 180 °C and the deprotection completed at about 250 °C. But the shape of two step cleavage of the BCVC units in the TGA thermogram was not so clear.

3.2.3. Acid-Catalyzed Deprotection Studies by FT-IR spectrophotometer

In a typical experiment for solid-state photolysis, solutions of poly(BCVC) containing 7 wt% of a photoacid generator, triphenylsulfonium hexafluoroantimonate, was spun on a NaCl pellet. FT-IR spectra were recorded as shown in figure 2a. The film was exposed for 20 sec using a 450 W high-pressure mercury lamp with a narrow-band 250 nm interference filter (20 mJ/cm²) and baked at 125 °C (figure 2b) and 160 °C (figure 2c)

Table 3. Thermal properties of Poly(HOST-co-TBA) and Poly(HOST-co-TBA-co-BCVC)

Composition of polymer (l:m:n) ^a	T _g ^b (°C)	T _{dp} ^c (°C)	T' _{dp} ^d (°C)	Mass loss ^e (%)
62.0 : 38.0 : 0.0	165.1	184	135	16.5
64.3 : 35.0 : 0.7	164.7	181	131	15.6
63.6 : 35.0 : 1.4	165.2	182	136	16.1
58.1 : 59.3 : 2.6	165.5	187	136	16.9

^a l : HOST, m : TBA, n : BCVC^b T_g of polymers measure by DSC in the second run at a heating rate of 10 °C / min.^c T_{dp} : onset deprotection temperature of copolymer and terpolymers measured by TGA^d T'_{dp} : onset deprotection temperature of copolymer and terpolymers after exposure measured by TGA^e Measured in wt % by TGA

In a FT-IR spectrum (Figure 2a), the absorption peaks of 1733 cm⁻¹, 1642 cm⁻¹, 1368 cm⁻¹ corresponded to esteric carbonyl, amide carbonyl and t-butyl group, respectively.

Figure 2. Infrared spectral change of poly(BCVC) before (a) and after (b), (c) exposure (b: PEB at 125 °C for 3 min, c: PEB at 160 °C for 3 min)

Figure 2b showed that the cleavage reaction resulted in disappearance of the t-butyl group and formation of the carboxylic acid on the polymer. The C-H symmetric bending band of t-butyl group at about 1368 cm⁻¹ disappeared after

cleavage while formation of new broad band corresponded to the carboxylic O-H stretching at about 3500 cm⁻¹.

In addition, the absorption bands of amide carbonyl groups were split into two. Amide carbonyl peak of the poly(1-vinyl-2-caprolactam carboxylic acid) was shown at about 1590 cm⁻¹ and the other peak (1632 cm⁻¹) was amide carbonyl peak of the poly(1-vinyl-2-caprolactam). Then, Figure 2c showed that the carbon dioxide was evolved and poly(BCVC) was converted to poly(1-vinyl-2-caprolactam). The photoacid-catalyzed cleavage of pendant t-butyl groups in the exposed area resulted in a large change of polarity of the polymer.

In case of the other BCVC containing polymers, it showed the same result as poly(BCVC).

3.2.4. Transmittance

Table 4 shows the UV absorbance of the polymers. From the UV spectra, poly(BCVC) resist film displayed excellent transparency in the 220 ~ 300 nm region. The major contributor to the absorption at these wavelengths is the onium salt photoacid generator. Upon irradiation and subsequent post exposure baking (PEB), the absorption band shifted to slightly longer wavelengths. The absorption coefficients for poly(BCVC) at 248 nm in the solid state were determined to be 0.045 μm⁻¹ (T=90%). Moreover the other polymers that contained BCVC have excellent transparency at 248 nm (Table 4).

Table 4. UV Absorbance of resist polymers at 248nm

Polymers	Absorbance of 1 μm thickness resist film	Absorbance of 1 μm thickness resist film with 5 wt% TPSHFA	
		Before exposure	After exposure ^c and PEB ^d
poly(BCVC)	0.045	0.211	0.233
poly(HOST-co-TBA) ^a	0.119	0.315	0.325
poly(HOST-co-TBA-co-BCVC) ^b	0.107	0.309	0.312

^a Composition of polymer : HOST/TBA = 62.0/38.0^b Composition of polymer : HOST/TBA/BCVC = 58.1/59.3/2.6^c Resist film was exposed to deep UV (250nm) irradiation with 20 mJ/cm²^d Exposed resist film was baked at 145 °C, 2 min

3.3. Lithographic Evaluation

In chemically amplified resist systems, holding time between exposure and post-exposure baking often affects the sensitivity and the resolution. We examined PED stability on the poly(BCVC) resist system. In this experiment, resist films were left in air without any treatment. Exposure characteristic curves with different PED times are shown in Figure 3. The contrast of this resist was not deteriorated with the PED time. The scanning electron microscope photographs of patterns after 2 h delay time are shown in Figure 4.

Figure 3. PED effect on exposure characteristic curves of poly(BCVC) resist (PEB : 125 °C, 3min)

Figure 4. SEM photograph of 0.6 μm L/S positive images formed of poly(BCVC) resist at 22 mJ/cm² (PED time : 2h)

In the case of poly(HOST-co-TBA-co-BCVC) resist system, figure 5 and 6 show the SEM photographs of patterns of poly(HOST-co-TBA) and poly(HOST-co-TBA-co-BCVC) for immediate PEB and PEB after 30 min, 2 h delay time. Conventional photoresist, poly(HOST-co-TBA) resist system shows T-top and do not develop in TMAH solution after 30 min PED time. However, the pattern profile of poly(HOST-co-TBA-co-BCVC) resist system is not deteriorated and T-top is not observed.

The new resist systems containing vinyl lactam derivatives were found to possess desirable properties such as PED stability, thermally stability and high resolution.

Figure 5. SEM photographs of positive images formed of poly(HOST-co-TBA) (4a) resist at 15 mJ/cm² (a : no PED time, b : 30 min PED time)

4. Conclusion

New resist systems were proposed in order to improve the environmental stability. We prepared new deep UV photoresist materials which have basic moiety in the matrix polymer. Poly(3-(*t*-butoxycarbonyl)-1-vinylcaprolactam) and poly(3-(*t*-butoxycarbonyl)-1-vinylcaprolactam-co-*t*-butylacrylate-co-hydroxystyrene) were synthesized and evaluated as potential deep UV photoresists. The synthesized polymers have excellent transmittance at 248 nm (absorbance=0.018~0.041 μm^{-1}). In addition, the synthesized polymers possess good thermal stability up to 200 °C and high glass transition temperatures (140~195 °C). And we examine post-exposure delay (PED) stability on the synthesized polymer resist systems. As a result of exposure characteristic curves with different PED times, the contrast of this resist was not deteriorated with the PED time.

Figure 6. SEM photographs of positive images formed of poly(HOST-co-TBA-co-BCVC) (4d) resist at 24 mJ/cm² (PED time : 2h)

We obtained 0.2 μm line/space patterns. The pattern profile is not deteriorated and T-top is not observed with 2 h PED time. By introducing basic units into a matrix polymer, this new resist system can prevent basic additives from migrating to the surface.

We knew that the new resist systems have desirable properties such as high transparency in deep UV region, facile deprotection, and proper sensitivity. And we confirmed improvement of environmental stability by introducing basic unit. The basic additives were employed to play dual roles: 1) improvement of environmental stability and 2) reduction of the diffusion of photogenerated acid to unexposed area. The quantitative study of the diffusion of acid in the presence of basic unit will be carried out to determine the proper basic unit composition in the resist polymer, which satisfies the requirements of suitable sensitivity,

improvement of PED stability, and reduction of diffusion of acid for fine pattern.

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