Synthesis and polymerization of 3-(*t*-butoxycarbonyl)-1-vinyl-caprolactam and application as deep UV resists

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Summary

Poly(3-(t-butoxycarbonyl)-1-vinylcaprolactam) (PBCVC) was synthesized and evaluated as a potential deep UV photoresist. The synthesized polymer has excellent transmittance at 248 nm (absorbance = 0.018 μm⁻¹). In addition, PBCVC possesses good thermal stability up to 220 °C and a high glass transition temperature (174~190 °C). The thermal deprotection of side chain ester groups of PBCVC occurs at 220 °C, whereas in the presence of acid the cleavage of the t-butyl ester groups of PBCVC begins at about 80 °C, and followed by evolution of carbon dioxide at about 150 °C. Deprotection of PBCVC gave the corresponding polymer, poly(1-vinylcaprolactam-3-carboxylic acid). The contrast of the PBCVC resist system was not deteriorated with the post-exposure delay (PED) time.

Introduction

Chemical amplification resists (CAR's), operating in the deep UV region at 248 nm, are accepted today by microelectronics device manufacturers for the production of 256 Mbit and 1 Gbit DRAMs, because of their high transparency and sensitivity (1-6). However, due to the catalytic nature of the imaging mechanisms, CAR's are easily affected by contaminants in the air and on the substrates (7). A number of approaches have been taken to solve this problem (8-9). These approaches have been attempted to prevent the resist from suffering from the deactivation of acid during the period between exposure and post-exposure bake (PEB), since the main causes are basic contaminations such as amines. Some studies have suggested that basic additives can solve this problem effectively (10).

Basic additives 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 line width variations. In spite of these benefits, as an undesired side effect, the resist sensitivity is usually reduced to impractical values thus lowering the throughput, the advantageous character for chemically amplified resists. Furthermore, it is a serious problem that the basic additives migrate to the surface of the resist film during a high temperature process (11).

In order to solve the migration problem of basic additive dispersed systems, we design a new chemical amplification resist based on poly(1-vinylcaprolactam) which incorporates an organic base into a polymer. It has a high transmittance in deep UV region and a high glass transition temperature and exhibits good adhesion. Herein, we prepare a deep UV photoresist material, PBCVC, which has a basic moiety in the matrix polymer. We describe

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the design concept of the new system and the results of our evaluation of PBCVC including improvment of the post-exposure delay (PED) stability.

Experimental

Materials: Caprolactam, n-butyllithium, di-tert-butyldicarbonate and 2,2'-azobisisobutyro-nitrile (AIBN) were purchased from Aldrich chemical company and used without further purification. The onium salt photoinitiator, triphenylsulfonium hexafluoroantimonate was prepared as described in several publications (12-14). Diisopropylamine, tetrahydrofuran and diethyl ether purchased from Junsei chemical company were refluxed for two days over sodium metal and distilled prior to use.

Measurements: Proton NMR spectra were recorded in deuterated chloroform using a Varian model 2000 spectrometer equipped with a Fourier transform accessory. Infrared spectra were obtained on a Bio-Rad FTS-165 spectrometer. UV spectra were recorded on a Shimadzu UV-240 spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data were obtained on a Dupont 2950 thermal analysis system. TGA and DSC measurements were made at a heating rate of 20 °C/min in nitrogen. Lithographic evaluations were made with a Nicon NSR 2005 KrF excimer laser stepper (0.55 NA).

Preparation of 1-vinylcaprolactam (VC): Into 1.8 liter stainless steal autoclave was charged 350 g (3.1 mol) of ε-carprolactam and 5.17 g (0.046 mol) 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 0.5 mmHg. The product was obtained at 71~73 °C. (120 g, 27.9 %) : IR (cm-1) 2932 (cyclic CH), 1671 (C=O of amide), 1626 (vinyl)

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-butyl dicarbonate (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 etheral 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, CH$_2$=), 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).

Free radical polymerization of BCVC: A solution of BCVC in benzene or dioxane that contained AIBN was heated at 65 ℃ under vacuum in a sealed ampoule. The polymer was precipitated in fresh petroleum ether and dried under reduced pressure.

Lithographic evaluation: A resist solution was made by dissolving 2 g of the polymer and 0.14 g of the acid precursor in 10 g of propylene glycol methyl ether acetate (PGMEA). Triphenylsulfonium hexafluoroantimonate as a photoacid generator was synthesized according to the literature (12-14). This solution was filtered through a 0.2 μm filter and spin-coated onto silicon wafers at 2500~3000 rpm to obtain about 1 μm-thick films. The films for the determination of the deep UV absorption spectrum were spun to quartz discs with 0.9 μm thickness from PGMEA solution and baked at 120 ℃ for 2.5 min to remove residual solvent. The wafers were then cut into small pieces and subsequently exposed to obtain sensitivity curves. The exposure system consisted of a high-pressure mercury lamp with a narrow-band 250 nm interference filter. The exposed films were post-exposure baked at 125 ℃ for 2.5 min and developed in 2.38 wt% tetramethylammonium hydroxide (TMAH) solution.

Results and discussion

For introduction of the t-butoxycarbonyl (t-BOC) group to the 3-position of 1-vinylcaprolactam, a 1-vinylcaprolactam enolate intermediate was generated by using lithium diisopropylamide (LDA) and then was reacted with DtBDC. BCVC was obtained as a white powder and was sufficiently pure without recrystallization. Scheme 1 illustrates the preparation of BCVC and its free radical polymerization.

< Scheme 1 >
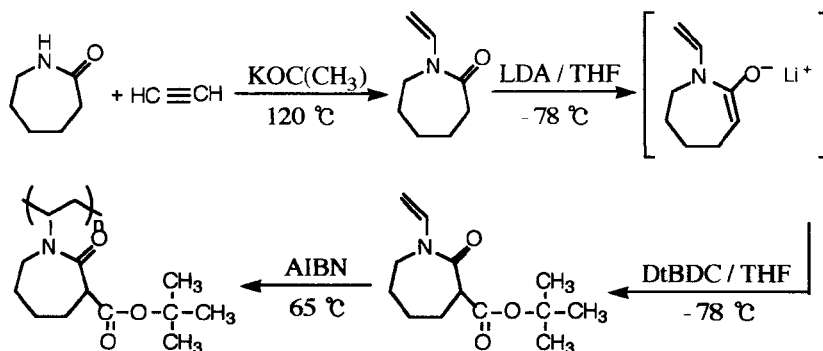
The polymerization results are shown in Table 1. The t-BOC protected monomer was easily polymerized under radical polymerization condition. The FT-IR spectrum of the monomer showed a vinyl absorption at 1635 cm^{-1} which after polymerization disappeared completely. Solvents seemed to have a strong effect on the polymerization. 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.

Table 1. Radical polymerizations of BCVC

Solvent	AIBN[a] (mol%)	M/S[b] (g/ml)	Time (h)	Conversion (%)	Inherent viscosity[c] (dl/g)	Tg (°C)
Bulk	1	–	12	–	*	–
Benzene	1	1	12	88	0.32	179
Benzene	1	1.3	12	88	0.75	183
Benzene	1	2	12	90	1.27	190
Dioxane	1	1	12	91	0.30	174
Dioxane	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 (η) were measured at a concentration of 0.5 g/dl in cyclohexanone at 25 °C.

* Partial gel formation.

Before imaging tests were carried out, the acid catalyzed cleavage of the protected polymer was studied using TGA and FT-IR. The TGA curve of PBCVC shown in Figure 1a indicates that PBCVC possesses good thermal stability up to 220 °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. The PBCVC was converted to poly(1-vinylcaprolactam) (PVC) as shown in Scheme 2.

In the presence of a photogenerated acid stepwise deprotection of t-BOC groups occurred as indicated in Figure 1b. The cleavage of the t-butyl groups of PBCVC is found to begin around 80 °C [I], and then the carbon dioxide was evolved at about 150 °C subsequently [II].

< Scheme 2 >
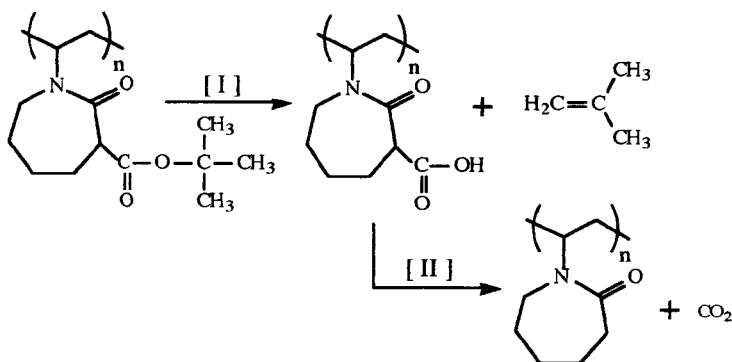
By comparing curves (a) and (b) in Figure 1, the thermal deprotection of the t-BOC groups of PBCVC resulted in almost the same weight loss of 42 wt% with or without acid, which corresponds to the theoretically calculated weight loss due to the evolution of carbon dioxide and isobutylene from the polymer.
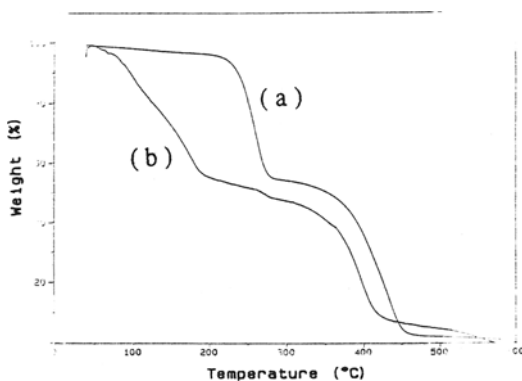
Figure 1. Comparison of TGA thermograms of PBCVC containing 7 wt% of triphenylsulfonium hexafluoroantimonate before (a) and after (b) UV exposure.

Figure 2b shows that the cleavage reaction resulted in disappearance of the t-butyl group and formation of the carboxylic acid functionality on the polymer. The C-H bending band of the t-butyl group at 1368 cm^{-1} disappeared after cleavage with formation of a new broad band corresponding to the carboxylic O-H stretching band at about 3400 cm^{-1}. In addition, the absorption band of the amide carbonyl group is split into two. The amide carbonyl band of the poly(1-vinylcaprolactam-3-carboxylic acid) is shown at 1590 cm^{-1} and the other band at 1632 cm^{-1} is characteristic of amide carbonyl of poly(1-vinylcaprolactam). Then, Figuire 2c shows that cleavage of t-butyl groups and decarboxylation occurred completely and PBCVC was converted to poly(1-vinylcaprolactam).

The photoacid-catalyzed cleavage of pendant t-butyl groups in the exposed area resulted in a large change of polarity

In a typical experiment for solid-state photolysis studies, a solution of PBCVC containing 7 wt% of a photoacid generator, triphenylsulfonium hexafluoroantimonate, was spun on a NaCl pellet. A FT-IR spectrum of the film was recorded as shown in Figure 2a. The film was exposed for 25 sec using a 450 W high-pressure mercury lamp with a narrow-band 250 nm interference filter to deep UV radiation (25 mJ/cm^2) and baked at 125 ℃ (Fig. 2b), 160 ℃ (Fig. 2c) for 3 min respectively. In Figure 2a, the absorption bands at 1733 cm^{-1}, 1642 cm^{-1} and 1368 cm^{-1} correspond to ester carbonyl, amide carbonyl, t-butyl groups, respectively.
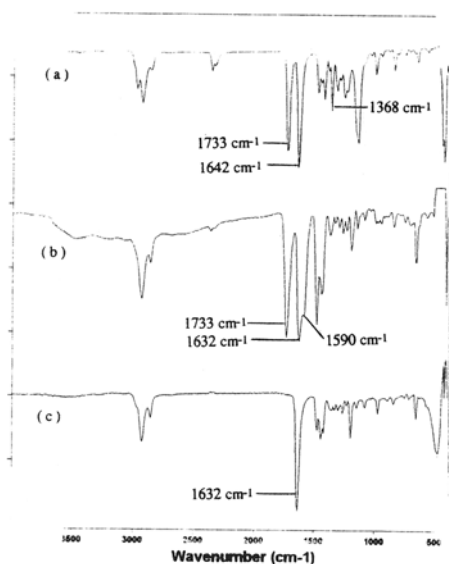

Figure 2. Infrared spectral change of PBCVC before (a) and after (b), (c) acidolysis. (b: PEB at 125 ℃ for 3 min , c: PEB at 160 ℃ for 3 min)

of the polymer from aqueous base insoluble PBCVC to soluble poly(1-vinylcaprolactam-3-carboxylic acid) or poly(1-vinylcaprolactam). The UV spectrum shows that PBCVC film displays excellent transparency at 248 nm (Fig. 3a). The major contributor to the absorption of the photoresist at this wavelength is the onium salt photoacid generator (Fig. 3b). On irradiation and subsequent post-exposure baking (PEB), the absorption coefficient was lowered slightly at 248 nm (Fig. 3c). The absorption coefficient for this polymer at 248 nm

in the solid state was determined to be 0.018 μm^{-1}. This is much lower than the absorption of poly(vinyl phenol)-based resist polymers (15). The protected polymer used in this resist has a high resistance toward development, the thickness of the unexposed film is unaltered by 2.38 wt% TMAH solution.

However once exposed to deep UV and baked at a sufficient temperature, the development in a TMAH solution is fast. The sensitivity of the investigated resist system slightly depends on the molecular weight of polymers. Figure 4 shows typical sensitivity curves obtained using deep UV (250 nm) exposure of a 1 μm thick film of a resist. Using a PEB of 125 ℃ for 2.5 min, the sensitivities of the resists were about 8 ~ 17 mJ/cm^2 according to molecular weight of the protected polymer. This resist shows a high sensitivity in spite of high concentration of the basic moiety because PBCVC has a low basicity as compared with organic base additives (e.g. 1-methyl-2-pyrrolidinone) which have been used in the dispersed system.
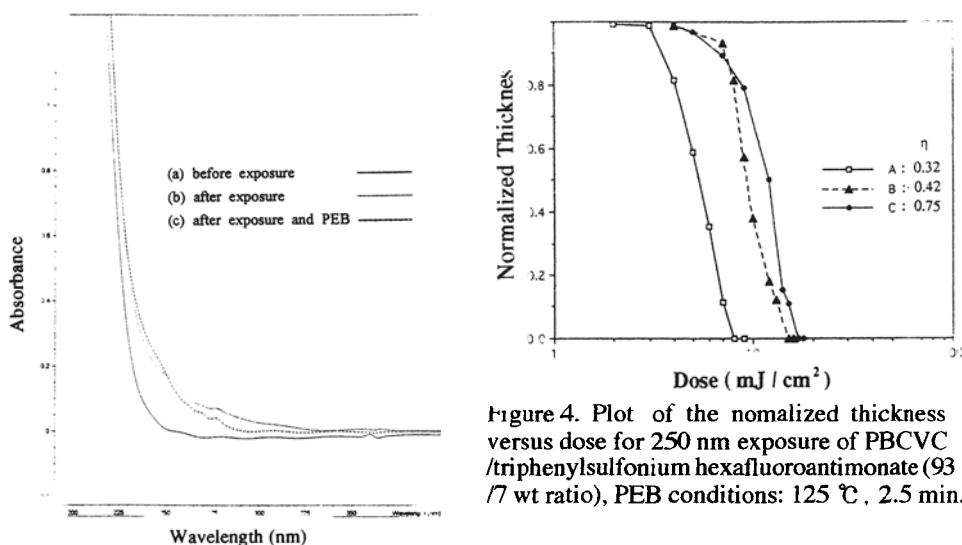

Figure 3. UV absorption spectra of a 0.9 μm thick film of PBCVC without (a), with (b) 7 wt% triphenylsulfonium hexafluoroantimonate and after exposure and PEB (c)

Figure 4. Plot of the nomalized thickness versus dose for 250 nm exposure of PBCVC /triphenylsulfonium hexafluoroantimonate (93 /7 wt ratio), PEB conditions: 125 ℃, 2.5 min.

In combination with 7 wt% triphenylsulfonium hexafluoroantimonate, this polymer gave a resist with high transmittance and high sensitivity.

These photoresists have good contrast values according to molecular weight of the protected polymer (γ: 4.1~6.2). This suggests that once a certain threshold concentration of the photogenerated acid is reached, extensive catalytic deprotection of the tert-butyl ester groups occurs along the polymer backbone. We examined PED stability on the PBCVC resist system. In this experiment, resist films were left in air without any treatment. Exposure characteristic curves with different PED times are shown in Fig. 5. The contrast of this resist was not deteriorated with the PED time. The scanning electron microscope (SEM) photograph of patterns after 2 h delay time are shown in Fig. 6. The system based on PBCVC shows several advantages over conventional chemically amplified photoresists. By using PBCVC as a backbone, a higher transparency could be attained in the deep UV region
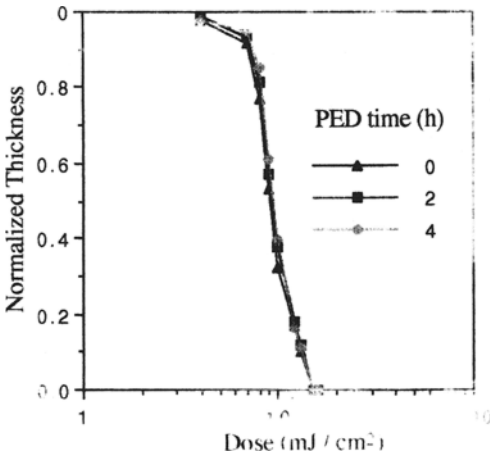
Figure 5. PED effect on exposure characteristic curves of PBCVC resist. PEB: 125 ℃/2 min.

Figure 6. SEM photograph of 0.6 μm L/S positive images formed of PBCVC resist at 22 mJ/cm^2 (PED time : 2 h).

relative to poly(vinyl phenol) which has been most widely used as a polymer backbone.

Additionally, this new PBCVC resist system was found to possess desirable properties such as PED stability, high glass transition temperature and facile deprotection for application as thermally stable, sensitive deep UV resist materials for imaging of < 0.5 μm patterns based on the chemical amplification concept. A detailed lithographic evaluation of the PBCVC resist which has a proper molecular weight and copolymerizations with selected comonomers are in progress, and a full account of the results will be published.

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