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A NOVEL WATER DEVELOPABLE PHOTORESIST FOR DEEP UV LITHOGRAPHY

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Abstract—Poly(3-(*t*-butoxycarbonyl)-1-vinyl-2-pyrrolidinone) (PBCVP) was synthesized and evaluated as a potential deep UV photoresist. The synthesized polymer has excellent transmittance at 248 nm (absorbance = 0.041 μm^{-1}). In addition, PBCVP possesses good thermal stability up to 200°C and a high glass transition temperature (140–155°C). The thermal deprotection of side-chain ester groups of PBCVP occurs at 200°C, whereas in the presence of acid the cleavage of the *t*-butyl ester groups of PBCVP begins at about 60°C and completes at about 100°C, followed by evolution of carbon dioxide at ~ 150°C. The deprotected polymer poly(1-vinyl-2-pyrrolidinone-3-carboxylic acid) is soluble in pure water. This resist has a high sensitivity (~ 1 mJ/cm^2). © 1997 Elsevier Science Ltd

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 0.5 μm. It is well recognized that to accomplish this goal, exposure tools which operate in the deep UV region (190–300 nm) will 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 [1–3]. 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 [4–9].

To achieve its inherent high sensitivity, all the components of the photoresist except a photoacid generator must be as transparent as possible in the deep UV region. Therefore, aliphatic polymers such as poly (*tert*-butyl methacrylate) or poly (di-*tert*-butyl fumarate), etc. have been investigated for deep UV resists [10–11]. They are highly transparent in the deep UV region, but their dry-etch resistance is poor. Recently, Kaimoto *et al.* have demonstrated a substantial increase in dry-etch resistance of methacrylate polymers through introduction of aliphatic cyclic structures [12].

Here, we propose a new water developable chemical amplification resist based on poly(1-vinyl-2-pyrrolidinone) (PVP). PVP has a cyclic aliphatic structure and is water soluble. Also, it has a high transmittance in deep UV region and a high glass transition temperature and exhibits good adhesion. Herein, we design a deep UV photoresist material which has a *t*-butoxycarbonyl (BOC-t) group at the 3-position of the PVP and describe the results of our evaluation of PBCVP as a novel deep UV photoresist.

EXPERIMENTAL PROCEDURES

Materials and measurements

1-Vinyl-2-pyrrolidinone, *n*-butyllithium, di-*tert*-butyldicarbonate, 2,2′-azobisisobutyronitrile (AIBN) were purchased from Aldrich chemical Co. and used without further purification. The onium salt photoinitiator, triphenylsulfonium hexafluoroantimonate was prepared as described in several publications [13–15]. Diisopropylamine, tetrahydrofuran and diethylether purchased from Junsei chemical Co. were refluxed for 2 days over sodium metal and distilled prior to use.

Proton NMR spectra were recorded in deuterated chloroform using a Varian model 2000 spectrometer equipped with a Fourier transform accessory. IR 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, DSC measurement were made at a heating rate of 20°C/min in nitrogen.

Preparation of 3-(t-butoxycarbonyl)-1-vinyl-2-pyrrolidinone (BCVP)

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

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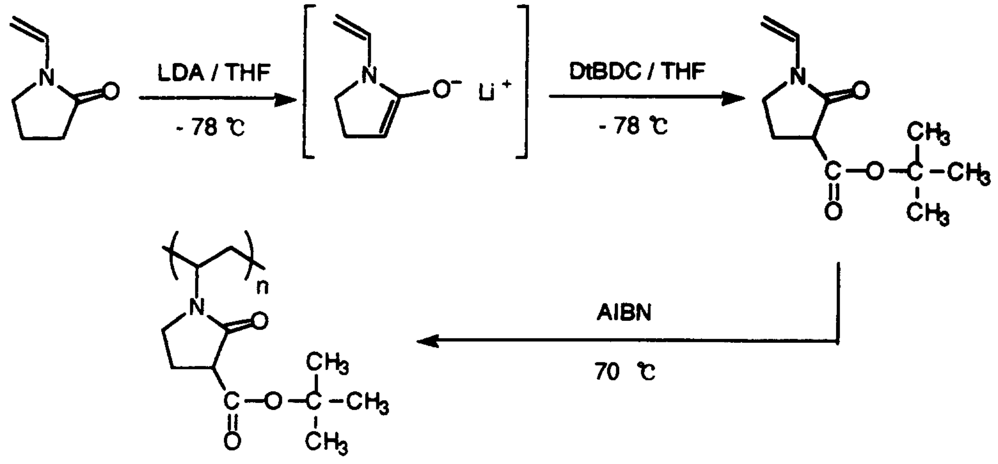


Scheme 1.

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 1-vinyl-2-pyrrolidinone (11.1 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 hr at −78°C and then poured into diethyl ether. The ethereal layer was washed successively with water until the unreacted 1-vinyl-2-pyrrolidinone was completely removed. 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 vacuo* to yield 15 g (71%) of BCVP. ^{1}H NMR ($CDCl_3$: δ 7.0 (1H, q), 4.5 (2H, m), 3.6 (1H, m, C3 H), 3.4 (2H, m, C5 H), 2.3 (2H, m, C4 H), 1.4 (9H, s, Bu-t); IR (KBr, cm^{-1}): 2981 (cyclic CH), 1733 (ester carbonyl), 1707 (amide carbonyl), 1635 (vinyl), 1370 (Bu-t).

Free radical polymerization of BCVP

A solution of 2.1 g of BCVP in 2.1 g of a solvent that contained AIBN was heated at 70°C under vacuum in a sealed ampoule. The polymer was precipitated in fresh petroleum ether and dried under vacuum.

Lithographic evaluation

A resist solution was made by dissolving 2 g of the polymer and 0.2 g of the acid precursor in 10 g of cyclohexanone. Triphenylsulfonium hexafluoroantimonate as a photoacid generator was synthesized according to the literature [13–15]. This solution was filtered through a 0.45 μm filter and spin-coated onto silicon wafers at 2300-3000 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 1.7 μm thickness from cyclohexanone solution and baked at 120°C for 3 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 120°C for 3 min and developed in water.

RESULTS AND DISCUSSION

For introduction of the BOC-t group to the 3-position of 1-vinyl-2-pyrrolidinone, a 1-vinyl-2-pyrrolidinone enolate intermediate was generated by using lithium diisopropylamide (LDA) and then was reacted with di-*tert*-butyl dicarbonate. The unreacted 1-vinyl-2-pyrrolidinone was easily removed from the reaction mixture by washing with water. Scheme 1 illustrates the preparation of BCVP and its free radical polymerization.

The polymerization results are shown in Table 1. The BOC-t 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

Table 1. Radical polymerizations of BCVP

Solvent	AIBN[a] (mol %)	M/S[b] (g/mL)	Time (hr)	Conversion (%)	Inherent viscosity[c] (dL/g)	T_g (°C)
Bulk	1	—	12	89	[d]	–
Benzene	1	1	12	89	[d]	–
Dioxane	1	1	12	91	0.77	155
Dioxane	0	1	12	91	0.81	158
Bz/MEK[e]	0.5	1	12	90	0.41	151

Polymerizations were carried out in pure or mixed solvent at 70°C.

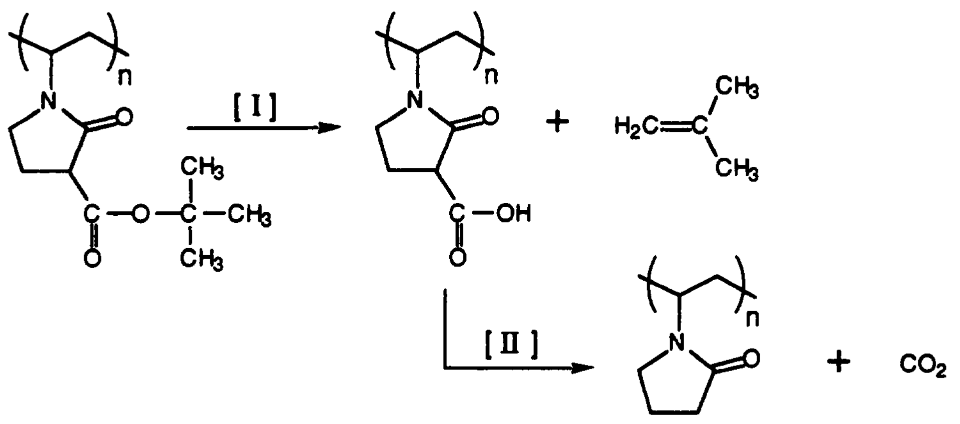
[a] MOL% of the initiator AIBN to the total amount of monomer.

[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.

[d] Gel formation.

[e] Bz/MEK: benzene/methyl ethyl ketone (9/1).



Scheme 2.

strong effect on the polymerization. Bulk polymerization resulted in partial gel formation, but solution polymerization resulted in proper molecular weight for a resist. It was interesting that the polymerization of BCVP in benzene gave rise to gel formation. This problem could be overcome by using a mixed solvent (benzene:methyl ethyl ketone = 9:1). This is probably due to a chain-transfer effect of the methyl ethyl ketone. As shown in Table 1, the proper molecular weight was obtained when dioxane was used as a solvent.

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 PBCVP shown in Fig. 1(a) indicates that PBCVP possesses good thermal stability up to 200°C. At that temperature, a rapid wieght loss took place due to evolution of isobutylene and carbon dioxide resulting from spontaneous thermolysis of the BOC-t groups. The PBCVP was converted to PVP as shown in Scheme 2.

In the presence of photogenerated acid stepwise deprotection of BOC-t groups occurred as indicated in Fig. 1(b). The cleavage of the *t*-butyl groups of PBCVP is found to begin around 60°C and completed at 100°C [I], and then the carbon dioxide was evolved at about 150°C subsequently [II].

By comparing curves (a) and (b) in Fig. 1, the thermal deprotection of the BOC-t groups of PBCVP resulted in almost the same weight loss of 48 wt% with or without acid, which corresponds to the theoretically calculated weight loss due to the

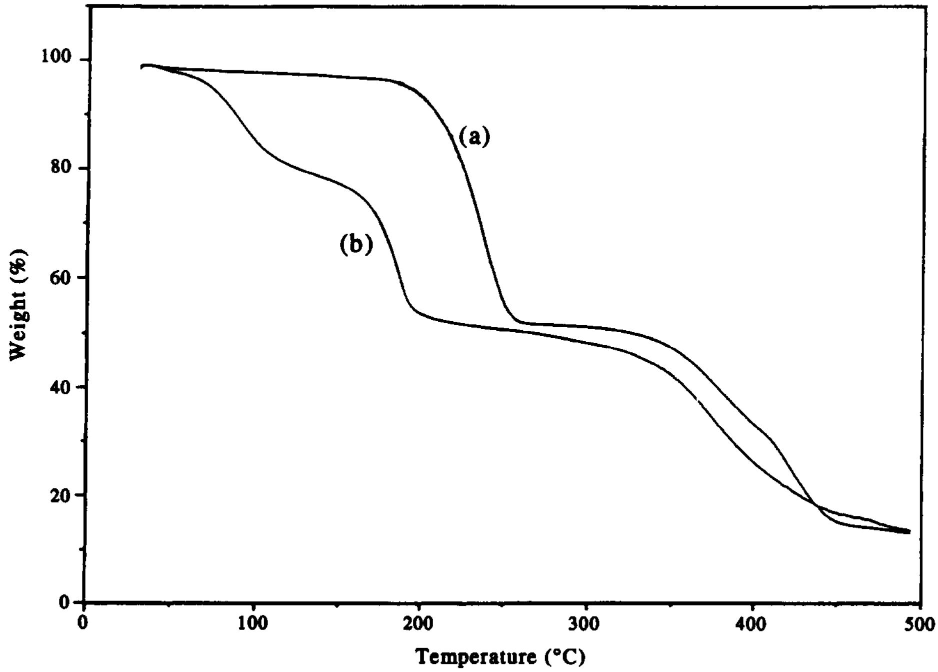


Fig. 1. Comparison of TGA thermograms of PBCVP containing 7 wt% of triphenylsulfonium hexafluoroantimonate before (a) and after (b) UV exposure.

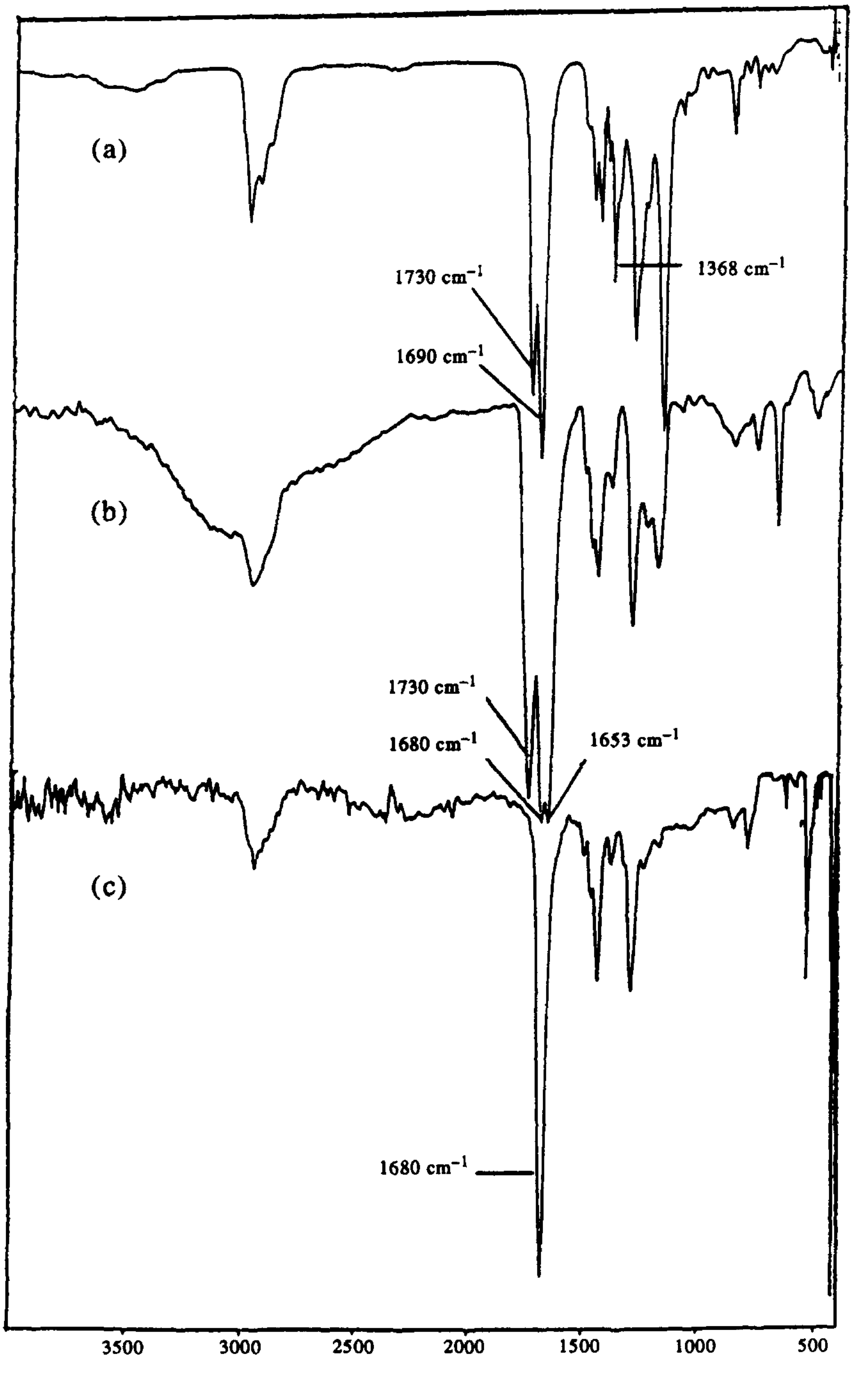


Fig. 2. IR spectral change of PBCVP before (a) and after (b), (c) acidolysis. [(b): PEB at 120°C for 3 min, (c): PEB at 160°C for 3 min.]

evolution of carbon dioxide and isobutylene from the polymer.

In a typical experiment for solid-state photolysis studies, a solution of PBCVP 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 Fig. 2(a). The film was exposed for 20 sec using a 450 W high-pressure mercury lamp with a narrow-band 250 nm interference filter to deep UV radiation (20 mJ/cm^2) and baked at 120°C [Fig. 2(b)] and 160°C [Fig. 2(c)] for 3 min, respectively. In Fig. 2(a) the absorption bands at 1730, 1690 and 1368 cm^{-1} correspond to ester carbonyl, amide carbonyl, *t*-butyl groups, respectively. Figure 2(b) shows that the cleavage reaction resulted in the disappearance of the *t*-butyl group and the formation of the carboxylic acid functionality on the polymer. The C—H stretching 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 carbonyl band of the poly(1-vinyl-2-pyrrolidinone-3-carboxylic acid) is shown at 1653 cm^{-1} and the other band at 1680 cm^{-1} is characteristic of amide carbonyl of PVP. Then, Fig. 2(c) shows that cleavage of *t*-butyl groups and decarboxylation occurred completely and PBCVP was converted to PVP. The photoacid-catalyzed cleavage of pendant *t*-butyl groups in the exposed area resulted in a large change of polarity of the polymer: from water insoluble PBCVP to water soluble poly(1-vinyl-2-pyrrolidinone-3-carboxylic acid) or PVP.

The UV spectrum shows that PBCVP film displays excellent transparency at 248 nm [Fig. 3(a)]. The major contributor to the absorption of the photoresist at this wavelength is the onium salt photoacid generator [Fig. 3(b)]. On irradiation and subsequent post exposure baking (PEB), the absorption band shifted to slightly longer wavelengths [Fig. 3(c)]. The absorption coefficient for this polymer at 248 nm in the solid state was determined to be 0.041 μm^{-1}. This is lower than the absorption of poly(vinyl phenol)-based resist polymers [4].

Figure 4 shows a typical sensitivity curve obtained using deep UV (250 nm) exposure of a 1 μm thick film of a resist. Using a PEB of 120°C for 3 min, the sensitivity of the PBCVP was about 1 mJ/cm^2. In combination with 9 wt% triphenylsulfonium hexafluoroantimonate, this polymer gave a resist with high transmittance and high sensitivity. The contrast value of this photoresist is 6.3. This suggests that once a certain threshold of the photogenerated acid is reached, extensive catalytic deprotection of the *tert*-butyl ester groups occurs along the polymer backbone.

The system based on PBCVP shows several advantages over conventional chemically amplified photoresists. By using PVP as a backbone, a higher transparency could be attained in the deep UV region relative to poly(vinylphenol) which has been most widely used as a polymer backbone. In addition, the resist can be developed with pure water. This new PBCVP was found to possess desirable properties such as excellent transparency in the deep UV region, 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. The lithographic evaluation of the PBCVP resist is in progress and will be published.

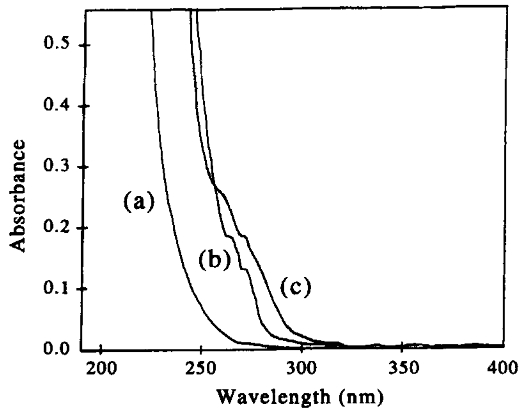


Fig. 3. UV absorption spectra of a 1.7 μm thick film of PBCVP without (a), with (b) 9 wt% triphenylsulfonium hexafluoroantimonate and after exposure and PEB (c).

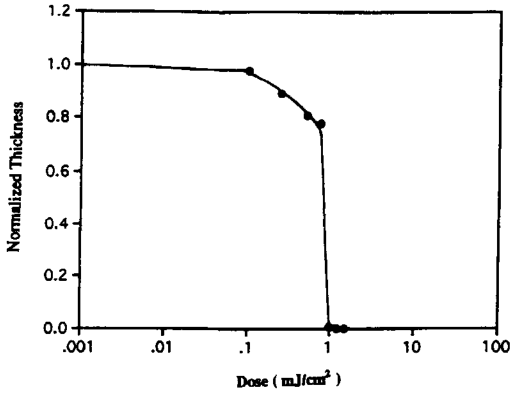


Fig. 4. Plot of the normalized thickness vs dose for 250 nm exposure of PBCVP/triphenylsulfonium hexafluoroantimonate (91/9 wt%), PEB conditions: 120°C, 3 min.

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