JOURNAL OF Materials CHEMISTRY

A positive-working alkaline developable photoresist based on partially *tert*-Boc-protected calix[4]resorcinarene and a photoacid generator

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Received 16th July 2001, Accepted 25th October 2001
First published as an Advance Article on the web 20th November 2001

A positive working low-molecular-weight photoresist based on partially *t*-Boc protected tetra-*C*-methylcalix[4]resorcinarene (***t*-Boc C-4-R**) and a photoacid generator (PAG), diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) has been developed. ***t*-Boc C-4-R**s were prepared by the reaction of **C-4-R** with di-*tert*-butyl dicarbonate in the presence of 4-dimethylaminopyridine (DMAP). A clear film cast from a 20 wt% ***t*-Boc C-4-R** solution in cyclohexanone showed high transparency to UV above 300 nm. The appropriate *t*-Boc protecting ratio was about 60 mol% in view of adhesion, deprotection temperature and dissolution rate. The photoresist consisting of 60 mol% ***t*-Boc C-4-R** (95 wt%) and DIAS (5 wt%) showed a sensitivity of 13 mJ cm^{-2} and a contrast of 12.6 when it was exposed to 365 nm light and postbaked at 105 °C for 90 s, followed by developing with a 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) solution at room temperature. A fine positive image featuring 1.5 μm of minimum line and space patterns was observed on the film of the photoresist exposed to 40 mJ cm^{-2} of UV-light at 365 nm by the contact mode.

Introduction

Amorphous materials are attractive for their excellent processability, flexibility, transparency, inexistence of grain boundaries, and isotropic properties.[1] As amorphous organic materials, many polymers are known and have received attention from both fundamental and practical viewpoints.[2] However, little attention has been paid to low-molecular-weight materials that form stable amorphous glasses above room temperature.

To meet the upcoming demand of next generation lithography, new chemically amplified resist materials should be developed for fabrication of devices whose critical dimensions are close to the size of a molecule. All commercially available resists so far are based on linear polymers in the formation of chemically amplified resist systems. Low-molecular-weight materials, which have a definite structure and no molecular weight distribution, as is inevitable in the case of polymer, have several advantages over linear polymers as patterning features become smaller.[3] The limit of resolution can be expanded to a molecular level since the building block of the image feature shrinks to a small molecular size. When a polymer is used as the building block of patterns, the image size never excels over the size of building block itself and small patterns on the order of a molecule can not be delineated. Furthermore, the non-linear small molecular resist helps to dissolve more uniformly during development. The ability to create an image in a resist using the lithographic process depends on the difference in dissolution rates between the exposed and unexposed regions of the resist. The dissolution rate of polymers depends critically on physical properties such as polydispersity, degree of branching, molecular weights, viscosity, *etc.*[4] However, low-molecular-weight amorphous materials such as star shaped molecules do not exhibit strong intermolecular interactions such as chain entanglement due to the short chain length, the small radius of gyration, and the high density of sterically congested peripheral groups. Resist molecules that are free of intermolecular chain entanglement may have implications in decreasing line edge roughness at very small feature sizes. Also, the small uniform size of molecule can be incorporated in multi-component resist systems where these materials serve as a dissolution inhibitor/promoter with good miscibility. We have been exploiting such small molecular materials in the hope of achieving an improved class of resist materials with the capability of imaging features into molecular scale resolution based on dendrimers and calixarenes as core compounds.[5]

In previous work,[6] we reported a positive working photoresist based on fully *t*-Boc protected tetra-*C*-hexylcalix[4]-resorcinarene which was prepared from resorcinol and hexan-1-al, followed by successive protection with di-*tert*-butyl dicarbonate in the presence of 4-dimethylaminopyridine (DMAP), where a long alkyl chain was introduced to prevent crystallization of the fully *t*-Boc protected tetra-*C*-methylcalix[4]resorcinarene. This resist, however, has an adhesion problem because of high hydrophobicity. In chemically amplified resists, partially *t*-Boc protected poly(hydroxystyrene)s are employed to control the dissolution rate.[7] Thus, to remedy these problems, we decided to prepare partially *t*-Boc protected tetra-*C*-methylcalix[4]resorcinarene (***t*-Boc C-4-R**). This would give a stable amorphous film with good adhesion to silicon wafer because this consists of various molecular weight compounds possessing many hydroxy groups. Herein we report the synthesis of ***t*-Boc C-4-R** as a new matrix and a lithographic evaluation of a two-component photoresist consisting of ***t*-Boc C-4-R** and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) as a photo-acid generator.

DOI: 10.1039/b106278f

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Experimental

Materials

DIAS was synthesized from diphenyliodonium chloride with sodium 9,10-dimethoxyanthracene-2-sulfate obtained by the reduction of sodium anthraquinone-2-sulfonate with zinc in aqueous sodium hydroxide solution followed by methylation with dimethyl sulfate.[8] Solvents were dried and purified in the usual manner. Other reagents were obtained commercially and used as received.

Tetra-*C*-methylcalix[4]resorcinarene (C-4-R)[9]

A solution of 33.0 g (0.3 mol) of resorcinol and 16.8 mL (0.3 mol) of acetaldehyde in 300 mL methanol was heated at 75 °C. To the solution, 75 mL of concentrated hydrochloric acid was added over 0.5 h. The reaction solution was stirred at 75 °C for 1 h and a yellow solid began to precipitate from the homogeneous mixture. After additional refluxing for 2 h, the mixture was cooled with an ice bath. A precipitate was collected with a glass filter and dried under reduced pressure. The product was recrystallized from methanol. Yield: 23.0 g (57%).

^{1}H-NMR (DMSO-d_6): δ (ppm) 1.36 (d, CH_3, 12H), 4.52 (q, CH, 4H), 6.18 (s, ArH, 4H), 6.83 (s, ArH, 4H); ^{13}C-NMR (DMSO-d_6): δ (ppm) 20.3 (CH_3), 28.7 (CH), 103.6 (ArC), 125.2, 126.1, 152.3.

Octa-*O*-*tert*-butyl carbonated *C*-methylcalix[4]resorcinarene (fully *t*-Boc C-4-R)

To a solution of 0.55 g (1.0 mol) of **C-4-R** and 0.012 g (0.1 mmol) of DMAP in 5 mL of acetone, 2.2 mL (9.6 mmol) of di-*tert*-butyl dicarbonate was added dropwise at room temperature. A vigorous bubbling occurred immediately. The reaction mixture was stirred for 20 min at room temperature and the solvent was evaporated. The obtained white solid was recrystallized from propan-2-ol–acetone (90 : 10 in volume ratio). Yield: 1.0 g (75%).

IR: ν 1758 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): δ (ppm) 1.42 (d, CH_3, 12H), 1.46 (s, CH_3, 72H), 4.43 (q, CH, 4H), 6.89 (br, ArH, 8H); ^{13}C-NMR ($CDCl_3$): δ (ppm) 20.5, 27.7 (CH_3) 31.4 (CH), 82.8 (*tert*-C), 116.3 (ArC), 125.7, 134.0, 147.0, 151.5 (C=O). Anal.Calcd. for $C_{72}H_{96}O_{24}$: C, 64.27; H, 7.19. Found: C, 63.56; H, 7.00%.

Average 60 mol% *t*-Boc C-4-R

To a solution of 2.7 g (5.0 mmol) of **C-4-R** and 0.06 g (0.5 mmol) of DMAP in 15 mL of acetone, 8 mL (36.0 mmol) of di-*tert*-butyl dicarbonate was added dropwise at room temperature. A vigorous bubbling occurred immediately. The reaction mixture was stirred for 20 min at room temperature and the solvent was evaporated. Purification was performed by flash column chromatography (hexane–ethyl acetate = 1 : 1 in volume ratio). The product was obtained as a white powder. Yield: 6.3 g (99%). IR: ν 1758 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$); δ (ppm) 1.40–1.42 (m, CH_3, 12H), 1.46–1.62 (m, CH_3, 43.2H), 4.10–4.60 (m, CH, 4H), 6.02–7.42 (m, ArH, 8H).

Dissolution rate

***t*-Boc C-4-R**s with various protecting ratios (95 wt%) and DIAS (5 wt%) were dissolved in cyclohexanone. The solution was spin-coated onto a silicon wafer that was pre-treated with 1,1,1,3,3,3-hexamethyldisilazane (HMDS) and exposed to 365 nm UV-light, followed by heating at 105 °C for 90 s. The sample was developed in a 2.38 wt% aqueous TMAH solution at room temperature, and rinsed with water. The changes in the film thickness against exposure energy were measured by a Dectak[3] system (Vecco Instruments Inc.).

Lithographic evaluation

Average 60 mol% protected ***t*-Boc C-4-R** and DIAS were dissolved at 20 wt% in cyclohexanone at room temperature. Films spin-cast on silicon wafers pre-treated with HMDS were pre-baked at 100 °C for 3 min and exposed through a filtered super-high-pressure mercury lamp (Ushio USH-200DP). The exposed wafer was baked again and developed by dipping in a 2.38 wt% aqueous TMAH solution. Imagewise exposure through a mask was carried out in a contact-printing mode.

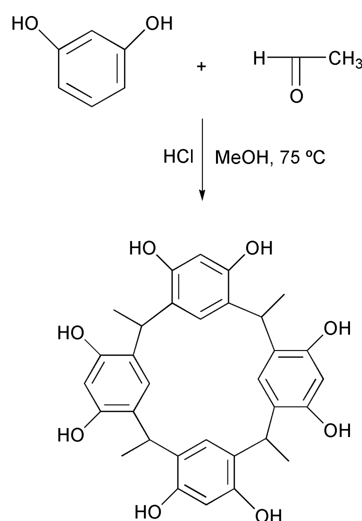
Measurements

FT-IR spectra were measured on a Horiba FT-720 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DPX-300 spectrometer. Thermal analyses were performed on a Seiko SSS 5000 TG-DTA 220 thermal analyzer at a heating rate of 10 °C min^{-1} for thermogravimetry (TG) and 5 °C min^{-1} for differential scanning calorimetry (DSC) under a nitrogen atmosphere, respectively. The temperature on a silicon wafer was measured by Anritsu HFT-40 digital surface thermometer. To examine surface properties of ***t*-Boc C-4-R**s obtained, the contact angles of water and diiodomethane were measured by placing drops of distilled water (H_2O) and diiodomethane (CH_2I_2) on the prepared ***t*-Boc C-4-R** films using a microscope goniometer (Kyowa Interface Science CA-A) at 25 °C. The scanning electron micrograph image was taken by a Hitachi S-800 microscope.

Results and discussion

C-4-R was prepared by condensation of resorcinol and acetaldehyde in aqueous hydrochloric acid at 75 °C and was recrystallized from methanol (Scheme 1). **C-4-R** can in principle exist in the four possible configurations formulated *cis-cis-cis*, *cis-cis-trans*, *cis-trans-trans*, and *trans-cis-trans*. The obtained **C-4-R** was confirmed to have an all-*cis* configuration by a ^{1}H NMR spectrum on the basis of the previous report.[9]

***t*-Boc C-4-R**s with various protecting ratios were synthesized by reaction of **C-4-R** with di-*tert*-butyl dicarbonate in the presence of DMAP in acetone. ***t*-Boc C-4-R**s were characterized by IR and ^{1}H NMR spectroscopies. The IR spectra showed characteristic absorptions at 3450 and 1758 cm^{-1} due to OH and C=O stretchings, respectively. The ^{1}H NMR spectrum for fully ***t*-Boc C-4-R** exhibited a single peak at 1.46 ppm due to characteristic *tert*-butyl protons. On the other hand, complex



Scheme 1

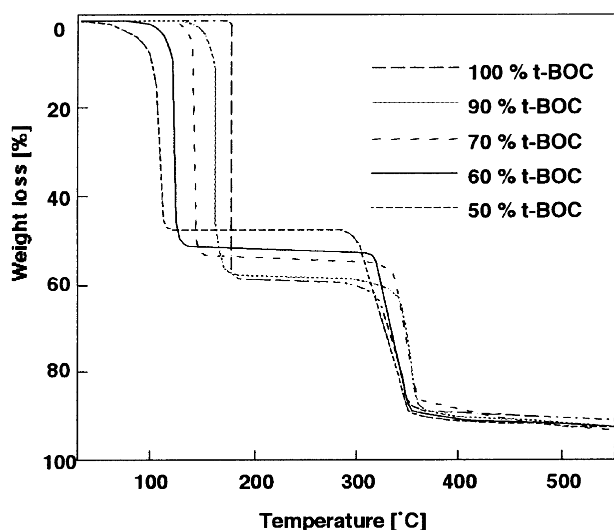


Fig. 1 TG curves of ***t*****-Boc C-4-R** having various protecting ratios.

peaks were observed at 1.46–1.62 ppm for ***t*****-Boc C-4-R**s because of a mixture of several compounds.

The actual protecting ratio of partially ***t*****-Boc C-4-R**s were estimated by TG (Fig. 1). The results are summarized in Table 1. The *tert*-butyl carbonate releases a quantitative amount of carbon monoxide and isobutylene at about 180 °C upon heating at 5 °C min^{-1}. The observed weight-losses are in good agreement with the calculated ones.

t**-Boc C-4-R**s showed good solubility in organic solvents such as propylene glycol methyl ether acetate (PGMEA), ethyl lactate, cyclohexanone, and 2-methoxyethanol at room temperature.

The effects of protecting ratios on the dissolution rate to a 2.38 wt% aqueous TMAH solution and the adhesion to a silicon wafer were investigated (Fig. 2). The dissolution rate was estimated by measuring the film thickness after development, and the adhesion properties of polymers on the silicon substrate were evaluated by calculating work of adhesion (W_{ad}) on the basis of the following eqn. (1) which can be derived from Owens–Wendt's equation.[10]

$$W_{ad}=2\{(\gamma_P{}^d\cdot\gamma_S{}^d)^{1/2}+(\gamma_P{}^h\cdot\gamma_S{}^h)^{1/2}\} \quad (1)$$

(Where γ: surface free energy, P: polymer, S: substrate, d: dispersion force, h: hydrogen bonding force) To solve this equation, the contact angles (θ) were measured with two different liquids of known components (H_2O and CH_2I_2) on the ***t*****-Boc C-4-R** films and HMDS primed silicon wafer and the four components ($\gamma_P{}^d$, $\gamma_P{}^h$, $\gamma_S{}^d$, $\gamma_S{}^h$) were calculated using eqn. (2) derived from Young's equation and Owens–Wendt's equation. Each value of θ for the H_2O and CH_2I_2 is listed in Table 2.

$$\cos\theta\cdot\gamma_L=2\{(\gamma_{PorS}{}^d\cdot\gamma_L{}^d)^{1/2}+(\gamma_{PorS}{}^h\cdot\gamma_L{}^h)^{1/2}\} \quad (2)$$

The calculated values of the work of adhesion for each ***t*****-Boc C-4-R** film are listed in Table 3.

The difference of dissolution rate between the exposed and unexposed areas increased with increasing the ratio of protection since the polarity between exposed and unexposed area changes greatly. On the other hand, the adhesion property decreased with increasing the protecting ratios; clearly, the hydrophilic surface properties of ***t*****-Boc C-4-R**s are governed by the content of phenol units. The 50 mol% protected one can be cast without priming HMDS, but in the cases of 70 mol% and 90 mol% protected ones, the films were peeled off during development.

Table 1 The protecting ratio of partially ***t*****-Boc C-4-R** determined from TG measurement

t-Boc (mol%)		50	60	70	90	100
Weight loss (%)	Calcd.	42.7	47.3	51.1	57.8	59.9
	Found	43	48	51	57	59

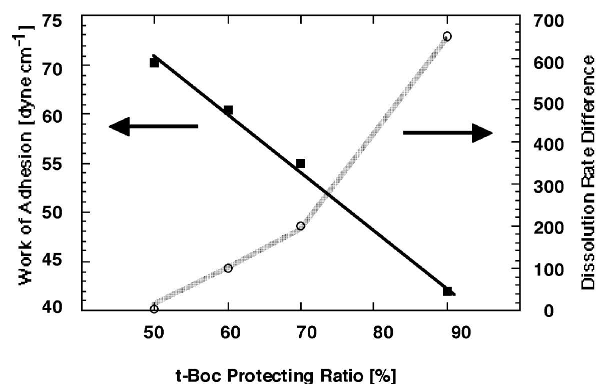


Fig. 2 Effect of protection ratios on the dissolution rate to a 2.38 wt% aqueous TMAH solution and the adhesion to a silicon wafer.

From these data, the appropriate ratio of protection turned out to be an average of 60 mol% in view of adhesion to wafer and dissolution rate contrast.

DSC analysis of 60 mol% protected ***t*****-Boc C-4-R** showed no peak due to the high glass transition temperature (T_g) up to 100 °C, nearly deprotection temperature. This result indicates T_g is above 100 °C and this matrix has a good thermal property as a photoresist.

Lithographic evaluation

Based on these findings, we formulated a resist consisting of ***t*****-Boc C-4-R** and DIAS (5 wt%) as a PAG in cyclohexanone. The UV spectrum of 1.0 µm thick ***t*****-Boc C-4-R** film indicates that it is very transparent around 250 nm and above 300 nm, and this spectrum is very similar to that of poly(hydroxystyrene).

To investigate the dissolution behavior of exposed and unexposed areas, the effects of the post-exposure bake (PEB) temperature and time on the dissolution rate were studied. The results in the case of the resist formulated by mixing average 60 mol% ***t*****-Boc C-4-R** (95 wt%) and DIAS (5 wt%) in cyclohexanone are shown in Fig. 3 and 4, respectively, where the film was exposed to 365 nm UV-light of 30 mJ cm^{-2}

Table 2 Surface free energy of H_2O and CH_2I_2[a]

Liquid	$\gamma_{L/dyne\ cm^{-1}}$	$\gamma_L{}^d$/dyne cm^{-1}	$\gamma_L{}^h$/dyne cm^{-1}
H_2O	72.8	29.1	43.7
CH_2I_2	50.8	46.8	4.0

[a] γ: Surface free energy, γ_d: the part due to the dispersion energy between molecules, γ_h: the part due to the dipole energy, induced dipole moments, and hydrogen bonds. $\gamma=\gamma_d+\gamma_h$.[10]

Table 3 The measurement values of contact angle and calculating data of work of adhesion for various ***t*****-Boc C-4-R** films to silicon wafer

Protecting ratio/mol%	Contact angle/° H_2O	W_{ad}/dyne cm^{-1} CH_2I_2	
50	34.0	50.0	70.3
60	38.0	46.0	65.5
70	92.0	41.0	60.8
90	102.4	31.6	47.0

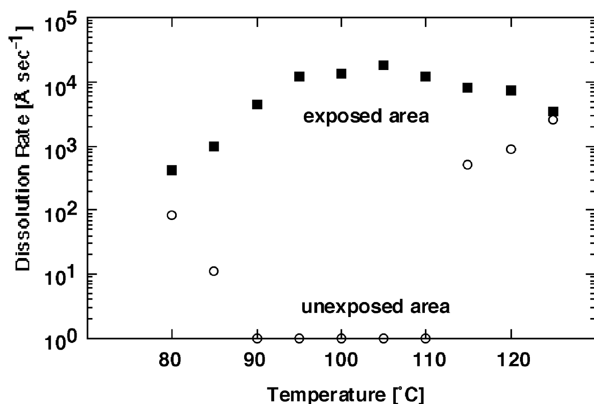


Fig. 3 Effect of PEB temperature on the dissolution rate of average 60 mol% ***t*-Boc C-4-R** film containing DIAS. Exposure 30 mJ cm^{-2} (365 nm); PEB time 3 min; developer 2.38 wt% aqueous TMAH solution.

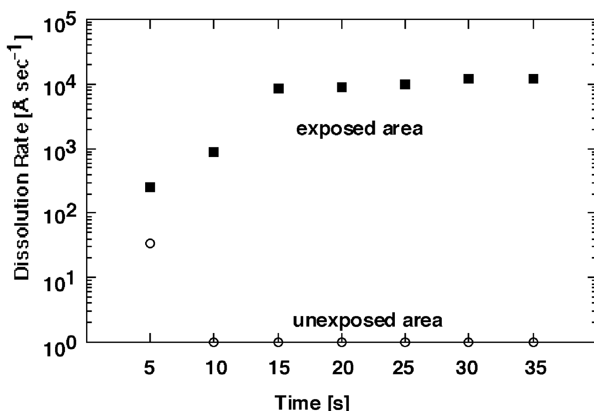


Fig. 4 Effect of PEB time on the dissolution rate of average 60 mol% ***t*-Boc C-4-R** film containing DIAS. Exposure 30 mJ cm^{-2} (365 nm); PEB temperature 105 °C; developer 2.38 wt% aqueous TMAH solution.

intensity, postbaked at various temperatures for various times and developed with a 2.38 wt% aqueous TMAH solution. The difference of dissolution rate between exposed and unexposed areas increased rapidly at 100 °C and 15 s, respectively. This indicates that deprotection of *t*-Boc groups occurs mainly at this temperature and time in the presence of acid.

After these preliminary optimization studies involving PEB temperature and time, adhesion, and dissolution rate contrast, we formulated a resist system consisting of average 60 mol% ***t*-Boc C-4-R** (95 wt%) and DIAS (5 wt%) in cyclohexanone. The film spin-cast on HMDS treated silicon wafer was prebaked at 100 °C for 3 min (thickness of 1.8 μm), exposed to 365 nm UV irradiation, postbaked at 105 °C for 90 s, and developed in positive mode with the 2.38 wt% aqueous TMAH solution at room temperature. The sensitivity curve shown in Fig. 5 indicates that the sensitivity and contrast are 13 mJ cm^{-2} and 12.6, respectively. This good sensitivity and contrast is thought to be due to the ease of changing polarity in the whole molecule, stemming from the small size of the resist molecule and good permeation of developer into the resist film.

Fig. 6 presents a scanning electron micrograph of the contact-printed image that was obtained using the resist described above after exposure to 20 mJ cm^{-2}, post-exposure baked at 105 °C for 90 s, and developed with the 2.38 wt% aqueous TMAH solution. The clear positive pattern with 1.5 μm resolution, which is the limitation of our exposure system, was obtained.

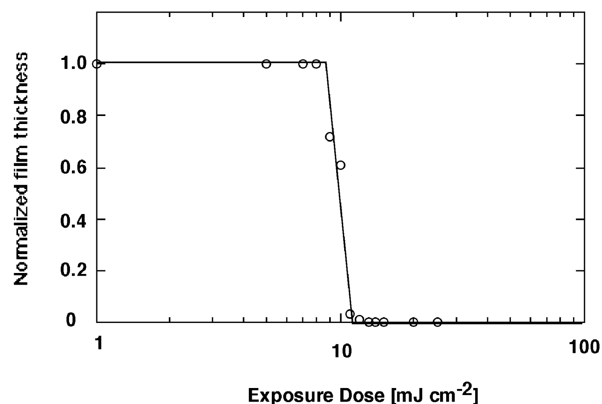


Fig. 5 Exposure characteristic curves for average 60 mol% ***t*-Boc C-4-R** film containing DIAS.

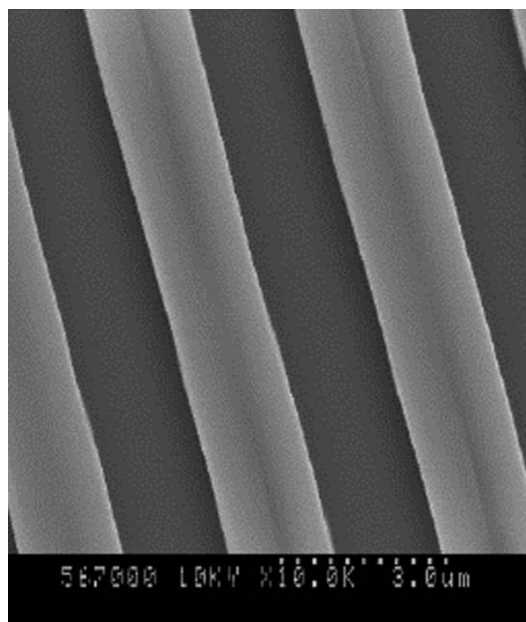


Fig. 6 Scanning electron micrograph of the contact-printed positive image obtained from the average 60 mol% ***t*-Boc C-4-R** film containing 5 wt% of DIAS.

Conclusions

A positive working low-molecular-weight photoresist based on ***t*-Boc C-4-R** and DIAS as a PAG has been developed. ***t*-Boc C-4-R**s with various protecting ratios were synthesized and evaluated as a chemically amplified resist. The appropriate *t*-Boc protecting ratio was an average of 60 mol% in view of adhesion and dissolution rate contrast. The photoresist consisting of average 60 mol% ***t*-Boc C-4-R** (95 wt%), and DIAS (5 wt%) showed a sensitivity of 13 mJ cm^{-2} and a contrast of 12.6 when it was exposed to 365 nm light and postbaked at 105 °C for 90 s, followed by developing with the 2.38 wt% aqueous TMAH solution at room temperature.

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