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Patternable block copolymers with high transparency at 157 nm: Fluorocarbinol functionalized poly(isoprene-*b*-cyclohexane)

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Summary

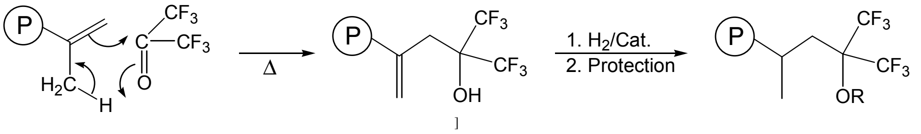
A three-step polymer modification reaction was developed to prepare polydiene-based patternable block copolymers with high transparency at 157 nm wavelength. In the first step, the ene reaction of poly(isoprene-*b*-cyclohexadiene) with hexafluoroacetone was carried out to incorporate a pendent hexafluoro-2-hydroxy-2-propyl functional group in the polyisoprene block. Subsequently, the hexafluorocarbinol functionalized block copolymer was hydrogenated to enhance transparency at 157 nm and finally the fluorocarbinol was protected with an ethoxymethyl group to induce a solubility switch after exposure. The final block copolymer exhibited an absorption coefficient of 3.30 μm^{-1} at 157 nm. Exposure was carried out on a 248 nm stepper and feature sizes down to 0.5 μm were resolved prior to optimization of exposure and formulation conditions.

Introduction

Protected acidic groups, such as phenols and carboxylic acids, are indispensable structural units in the design of chemically amplified photoresists for deep-UV lithography (248 and 193 nm). However, in the vacuum-UV (VUV) region, these acidic groups limit the film thickness due to their strong absorbance and, therefore, a paradigm shift in the resist design was thought necessary to continue the use of organic polymers as photoresists in the VUV region such as in 157 nm lithography.

Recently, fluorocarbinol functionalized polymers have garnered much interest due to their high transparency at 157 nm wavelength combined with their acidity comparable to that of phenols. It has been reported that fluorocarbinols can be used as acidic functional groups in the design of chemically amplified and aqueous base developable resists [1-3]. Przybilla et al. introduced this novel concept in the design of polystyrene-based photoresists and dissolution inhibitors for 248 nm lithography [2]. Further extension to 193 nm lithography was made by Ito et al. during the preparation of poly(norbornene sulfone)-based resists [3].

In order to incorporate a fluorocarbinol functional group within the polymer backbone, we studied the *ene* reaction of hexafluoroacetone (HFA) with double bond containing polymers. This reaction was first reported by Urry et al. [4], and they reported that the *ene* reaction of HFA with olefins results in the formation of hexafluoro-2-hydroxy-2-propyl functionality with a double bond migration. The polymer analogous reactions were also studied by Snow et al. [5] and Coleman et al. [6] using 3,4-polyisoprene (PIP) and 1,4-*cis*-PIP, respectively, to prepare PIP's with a pendent hexafluorocarbinol group. As shown in Scheme 1, it was conceived that the hydrogenation of the residual double bond, followed by protection of the fluorocarbinols with an acid-labile group, may provide a facile route for the synthesis of highly transparent and chemically amplified photoresists for 157 nm lithography.



Scheme 1. The *ene* reaction of HFA with a double bond containing polymer

Preliminary studies were carried out using linear polydienes, such as PIP and polybutadiene, and it was found that the resulting hexafluorocarbinol functionalized polydienes are soluble in a 0.26 *N* tetramethylammonium hydroxide (TMAH) solution [7]. However, these aqueous base soluble polydienes exhibited relatively low glass transition temperatures (T_g) and improvement in etch resistance was required for photoresist applications. These shortcomings were overcome by the cyclization reaction before the ene reaction, and the cyclized PIP exhibited high T_g (120 ~ 170 °C) as well as excellent etch resistance after the *ene* reaction with HFA. In this study, we designed a model block copolymer which closely resembles cyclized PIP, and report a new design concept towards the development of patternable block copolymers with high transparency at 157 nm wavelength.

Experimental

Materials

Isoprene (IP) and 1,3-cyclohexadiene (CHD) were purified by successive distillation from calcium hydride and dibutylmagnesium. Cyclohexane was dried by successive distillation from calcium hydride and 1,1-diphenylhexyllithium. HFA, ethoxymethyl chloride (EOMCl), and *sec*-butyllithium were used as received from Aldrich.

Synthesis of block copolymer

Poly(IP-*b*-CHD) was prepared by living anionic polymerization using a standard high vacuum technique. The synthesis was carried out using a *sec*-butyllithium/*N,N,N',N'*-tetramethylenediamine (TMEDA) system reported by Natori et al. [8]. *sec*-Butyllithium (1.5 mmol) was added to 250 mL of cyclohexane and subsequently TMEDA was added to bring the molar ratio of *sec*-butyllithium/TMEDA to 4/5. The solution was stirred at room temperature for 10 min and then the temperature was raised to 40 °C. After 10 min, IP (21 mL, 0.21 mol) was added and polymerized for 2 h. A small quantity of the polymerization mixture was withdrawn and quenched with degassed methanol for the characterization of the polyisoprene (PIP) block. Subsequently, CHD (11 mL, 0.12 mol) was added to the reactor for the block copolymerization, and the polymerization was continued for 4 h. After quenching with degassed methanol, the polymer was precipitated into acetone, filtered, and dried in a vacuum oven to yield 20.5 g of poly(IP-*b*-CHD) (85.7% yield). GPC: M_n = 12,100 and M_w/M_n = 1.16 for PIP and M_n = 16,500 and M_w/M_n = 1.27 for poly(IP-*b*-CHD).

Modification of block copolymer

Poly(IP-*b*-CHD) (5.12 g) was dissolved in 50 mL of toluene, degassed by bubbling with nitrogen, and charged into a pressure reactor. To this was added HFA (29 g, 0.17 mol), and the mixture was then heated at 180 °C for 36 h. The hexafluorocarbinol modified block copolymer was recovered by precipitation into petroleum ether and then freeze-dried to yield 11.45 g. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 0.5-3.5, 4.6-6.0 (alkenyl H), 7.5 (b, OH). FT-IR: 3594, 3491, 3011, 2938, 2861, 1656, 1620, 1509, 1367, 1210, 1131, 994, 849, 718 cm^{-1}.

Hydrogenation of the hexafluorocarbinol modified block copolymer was carried out in ethanol under 580 psi of hydrogen at 130 °C. A supported Pd catalyst (5 wt % on $CaCO_3$) was used after activation by heating to 100 °C under 100 psi of hydrogen for a few hours. Using this catalyst, only partial hydrogenation (~40%) was obtained and the partially hydrogenated block copolymer was used for the protection reaction.

A partially hydrogenated block copolymer (3.9 g) in dry THF (40 mL) was added over 1 h to sodium hydride (0.25 g) in dry THF (20 mL) at 0 °C. The suspension was stirred for 1 h, then EOMCL (0.78 mL) in dry THF (20 mL) was added dropwise over 90 min at 0 °C. The white suspension was allowed to warm to room temperature and stirred overnight. Distilled water was added carefully to stop the reaction and the product was recovered by precipitation into distilled water. After filtration, the product was dried under vacuum to give 3.2 g of a white powder.

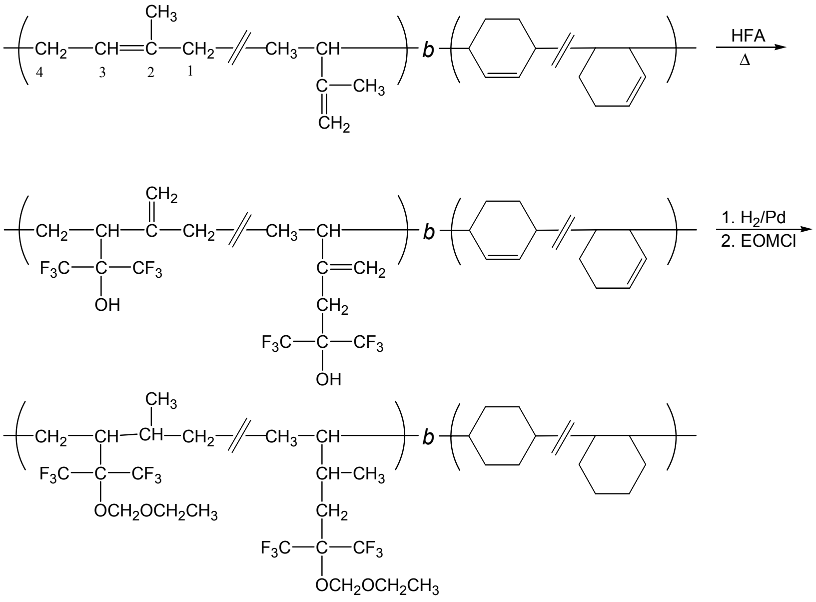
Lithographic Evaluation

The modified block copolymer was dissolved in propylene glycol methyl ether acetate (PGMEA) (12 wt/vol %) and to this was added triphenylsulfonium perfluoro-1-butanesulfonate (TPS-PFBS, 2 wt.% with respect to the polymer weight) as a photoacid generator (PAG). The solution was filtered through a 0.2 μm membrane filter and spin-coated onto hexamethyldisilazane primed silicon wafers at 2500 rpm to give ~0.3 μm thick resist films. The coated wafer was baked at 90 °C for 60 sec and exposure was carried out using a Nikon 248 nm stepper (*NA* = 0.42) equipped with a KrF excimer laser source. Post-exposure bake was carried out at 110 °C for 60 sec and development was conducted for 150 sec in a mixture of 0.26 *N* TMAH solution and isopropyl alcohol (5:1 by volume). The absorbance of the final block copolymer was measured on a VUV spectrometer at Intel Corporation. Measurements were carried out in the wavelength range of 115 to 300 nm under vacuum ($< 5 \times 10^{-5}$ Torr). The film thickness was measured on a Tenkor P-10 Surface Profiler. Developed patterns were imaged with a Leica 440 scanning electron microscope.

Results and discussion

Preparation of patternable block copolymers

Scheme 2 illustrates a three-step strategy for the preparation of patternable block copolymer with hexafluorocarbinol functionality, starting from poly(IP-*b*-CHD). In the first step, the *ene* reaction is carried out to incorporate hexafluorocarbinol functionality onto the polymer backbone. Subsequently, hydrogenation of residual double bonds was carried out to enhance the transparency of the polymer at 157 nm. Finally, the hexafluorocarbinol group was protected by an acid-labile group to yield chemically amplified positive tone photoresists.



Scheme 2. Preparation of patternable block copolymer

It should be noted that the structures shown in Scheme 2 are only representative. For instance, the HFA addition to the double bond renders the resulting structure more complicated, since the C-C bond formation between HFA and 4,1-regioisomer can occur at both C_2 and C_3 positions and allylic hydrogen shift can also occur at both methylene and methyl groups when the C_3 position is involved in the bond formation [4]. The starting block copolymer was prepared by living anionic polymerization using a *sec*-butyllithium/TMEDA system to yield a controlled molecular weight (M_n = 16,500) and a narrow molecular weight distribution (M_w/M_n = 1.27). The microstructure of PIP obtained under the given polymerization condition was reported to include 61% 4,3-, 25% 4,1-, and 14% 1,2-addition [9] and that of polycyclohexadiene was reported to include 52% 1,2- and 48% 1,4-addition [10]. The block composition was determined by ^{1}H NMR spectroscopy and the composition of CHD in the block copolymer was calculated to ~34 mol % (or ~38 wt %).

As previously reported [7], dramatic changes in solubility and T_g were observed after the incorporation of the hexafluorocarbinol group within the block copolymer. For example, the product was soluble in most polar organic solvents such as methanol or acetone, but not soluble in chlorinated solvents such as chloroform or dichloromethane. The T_g of a hexafluorocarbinol functionalized block copolymer was observed at 110.5 °C from DSC and the onset of decomposition was observed at 273.1 °C from TGA. The yield calculated by gravimetry indicated that only 57.8% of the reactive C=C bond was functionalized with HFA. This value is considerably lower than those obtained in the ene reaction of HFA with linear homopolymers, such as polybutadiene or PIP, where 80~90% functionalization was obtained [7]. The lower reactivity of the block copolymer can be attributed to the presence of sterically hindered methine hydrogens in the CHD block. It has been reported that the steric accessibility of the hydrogen abstracted plays an important role in the thermal ene reaction, and methyl and methylene hydrogens are abstracted more easily than methine hydrogens [11]. After the ene reaction, alkenyl protons in the IP block exhibited downfield shifts in the ^1H NMR spectrum possibly due to the presence of electron-withdrawing geminal CF_3 groups at a β position. However, no significant shifts were observed with alkenyl protons attached to the CHD block. Therefore, it appears that the ene reaction of the block copolymer occurs preferentially in the IP block as shown in Scheme 2, and the hexafluorocarbinol functionalized block copolymer is denoted as poly(IPF_6OH-*b*-CHD). Assuming that CHD block is not reactive in the ene reaction with HFA, it is calculated that ~81% of the reactive C=C bond in the IP block was reacted with HFA.

The hydrogenation of the double bond was carried out using a Pd catalyst supported on $CaCO_3$. Using this catalyst, partial hydrogenation was confirmed by ^1H NMR spectroscopy. On the basis of elemental analysis, it was determined that only 41% C=C bond was saturated. The alkenyl protons of the CHD block exhibited significant loss in intensity from ^1H NMR spectrum indicating the formation of a cyclohexane (CH) block. Therefore, it was concluded that olefins with β hexafluorocarbinol are less reactive in the hydrogenation reaction. Assuming that residual double bonds will not critically hinder the imaging process, the partially saturated block copolymer, poly(IPF_6OH-*b*-CH), was used in the protection reaction. Since the *tert*-butyloxycarbonyl (t-BOC) group, used by Przybilla et al. in the protection reaction of the hexafluorocarbinol based photoresists [2], is extremely absorbing at 157 nm, EOMCl was chosen to protect an acidic hexafluorocarbinol group. Aoai et al. used EOMCl for the protection of carboxylic acid in 193 nm resists [12] and Willson et al. demonstrated that ethoxymethyl (EOM) protected hexafluorocarbinols can be cleaved by PAG in a chemically amplified mode [13].

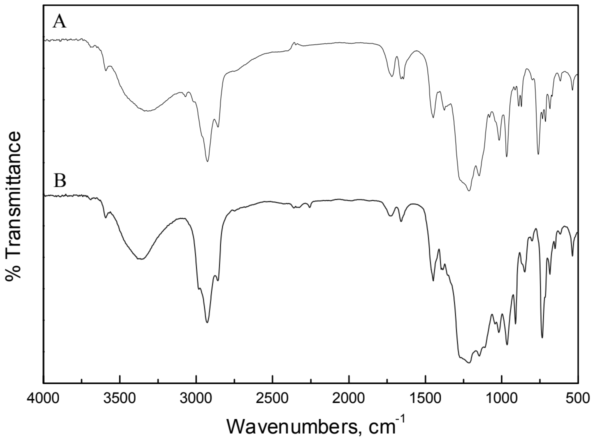


Figure 1. FT-IR spectra of poly(IPF_6OH-*b*-CH) before (A) and after EOM protection (B).

In Figure 1, are shown FT-IR spectra of poly(IPF_6OH-*b*-CH) before (A) and after EOM protection (B). Both block copolymers absorb strongly over a wide range between 1400 and 800 cm^{-1} due to the characteristic C–F stretching modes. The free hydroxyl group of fluorocarbinols exhibits O–H stretching at 3590 cm^{-1} and the intermolecularly hydrogen bonded hydroxyl group exhibits a broad peak at 3360 cm^{-1}. By comparison of absorbances due to the O–H stretching and the C–F stretching (1220 cm^{-1}), it was calculated that ~20% of the hydroxyl group was protected with EOM. After protection, a significant change in solubility was observed. While poly(IPF_6OH-*b*-CH) was soluble in DMSO but not soluble in chloroform before the EOM protection, it became soluble in chloroform but not in DMSO after EOM protection.

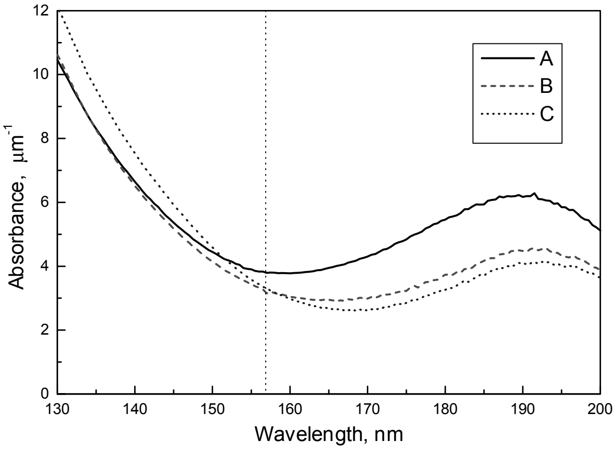


Figure 2. VUV spectra of poly(IPF_6OH-*b*-CHD) (A), poly(IPF_6OH-*b*-CH) (B), and EOM protected poly(IPF_6OH-*b*-CH) (C)

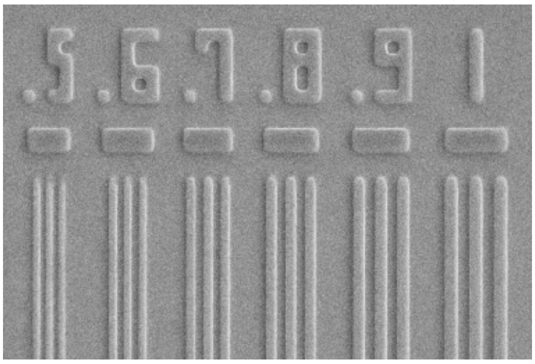


Figure 3. SEM image of 0.5~1 μm lines with EOM protected poly(IPF_6OH-*b*-CH) at 30 mJ/cm^2

Lithographic Evaluation

Absorbance of the block copolymers were measured on a VUV spectrometer in the wavelength range of 115 to 300 nm under vacuum ($< 5 \times 10^{-5}$ Torr) and VUV spectra of the block copolymers are compared in Figure 2. Figure 2(A) shows VUV spectrum of poly(IPF$_6$OH-*b*-CHD) before the hydrogenation reaction and its absorbance was measured to be 3.79 μm^{-1} at 157 nm. After hydrogenation, the absorbance was reduced down to 3.18 μm^{-1} at 157 nm, and this was slightly increased to 3.30 μm^{-1} after the EOM protection.

Before the EOM protection, aqueous base solubility of poly(IPF$_6$OH-*b*-CH) was tested in 0.26 *N* TMAH solution. Samples were prepared by spin-coating the polymer solution in PGMEA on a Si wafer at 3000 rpm to give ~3000 Å film thickness. It was found that poly(IPF$_6$OH-*b*-CH) is sparingly soluble in 0.26 *N* TMAH solution. It appears that the hydrophobic CH block exerts a strong dissolution inhibition effect in aqueous base. Therefore, in order to find optimum developing conditions, dissolution rates of poly(IPF$_6$OH-*b*-CH) and EOM protected poly(IPF$_6$OH-*b*-CH) were studied in a mixture of 0.26 *N* TMAH solution and isopropyl alcohol (IPA). When the volume ratio of 0.26 *N* TMAH solution and IPA reached 5:1, large differences in dissolution rates were observed between poly(IPF$_6$OH-*b*-CH) and EOM protected poly(IPF$_6$OH-*b*-CH). For example, poly(IPF$_6$OH-*b*-CH) exhibited a dissolution rate of 1720 Å/min and the EOM protected poly(IPF$_6$OH-*b*-CH) exhibited a nominal dissolution rate less than 10 Å/min. After finding optimum conditions for development, the EOM protected poly(IPF$_6$OH-*b*-CH) was formulated with TPS-PFBS in PGMEA and spin-coated on silicone wafers to yield ~0.3 μm film thickness. Exposure was carried out on a 248 nm stepper using exposure dosages starting from 3 mJ/cm^2 to 40 mJ/cm^2 with a 0.5 mJ/cm^2 increment. A clearing dosage was found at 25 mJ/cm^2 and, without formulation optimization, sub-micron lines/spaces patterns were obtained at 30 mJ/cm^2 as shown in Figure 3.

Conclusion

A new concept was developed for the preparation of patternable block copolymers. It was demonstrated that this new concept can provide a route for the synthesis of photoresist platforms transparent at 157 nm and, without formulation optimization, sub-micron lines/spaces patterns were obtained by exposure at 248 nm.

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