Articles

Molecular Design and Synthesis of 3-Oxocyclohexyl Methacrylate for ArF and KrF Excimer Laser Resist

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We originally designed 3-oxocyclohexyl methacrylate (OCMA) for an acid-labile component in chemical amplification. The key concept of the molecular design of the 3-oxocyclohexyl substituent was the introduction of acidic protons at the α position of the elimination site by using a ketone functional group. OCMA was synthesized by esterification of 1,3-cyclohexanediol and methacryloyl chrloride followed by pyridinium dichromate oxidation. Using AIBN as an initiator, we also prepared Poly(OCMA-*co*-AdMA) (AdMA: adamantyl methacrylate) by a thermally induded radical copolymerization of OCMA and AdMA. The resist comprises the copolymer and 10 wt % of triphenylsulfonium hexafluoroantimonate as a photoacid generator (PAG). This resist has high sensitivity, good thermal stability, good dry etch resistance, and good postexposure delay durability. Using a KrF excimer laser stepper (NA = 0.45) and 2-propanol mixed aqueous alkali developer, we obtained 0.3-μm line and space patterns with our resist. A resist with 1 wt % of the PAG has an acceptable transmittance at 193 nm, so we believe this resist is suitable for ArF excimer lithography.

Introduction

As circuit integration increases in microelectronic devices, lithographic technologies using short-wavelength light sources have been developing. Deep-UV lithography employing KrF excimer laser light (248 nm) is expected to be used for the production of smaller features. Chemical amplification for excimer laser lithography resists has been reported as a promising approach to the quarter-micron range. Many chemically amplified resist systems have been presented for 248-nm lithography, and some are used in fabrication or on a pilot line for fabricating DRAMs.[2,3] Prototype steppers using ArF excimer laser light (193 nm) for more advanced ULSIs, such as 256-Mbit or 1-Gbit DRAMs, have also been tested.[4,5]

Chemically amplified resists for 248-nm radiation usually comprise *tert*-butoxycarbonyl (*t*BOC) protected poly(vinylphenol) (PVP) and a PAG.[6–11] PVP-based resists have been studied for KrF lithography because of material availability, well-known physical and chemical properties of the resins, good dry etch resistance derived from their aromatic rings, and moderate transparency (40% transmittance through a 1-μm-thick film on a quartz substrate) at that wavelength. These resists cannot be used at 193 nm, however, because their aromatic rings have a high extinction coefficient ($\epsilon > 10^5$) at that wavelength. PVP resins are completely opaque at 193 nm. In contrast, aliphatic methacrylates, such as poly(methyl methacrylate) (PMMA) or poly(*tert*-butyl methacrylate) (PTBMA), have low absorption at 193 nm, but they also have poor etch resistance.

We have been investigating alicyclic polymers, e.g., adamantane or norbornane containing polymers, for excimer laser lithography because we thought rigid structures are effective for the etch resistance. The absence of conjugated double bonds in such alicyclic components is also favorable for transparency at shorter

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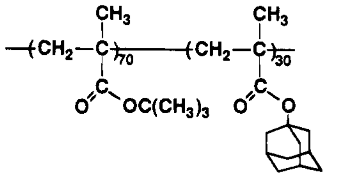
wavelengths. We found they had good etch resistance and high transmittances at 248 and 193 nm.[12] Even a polymer composition with 50 mol % alicyclic component, we obtained good dry etch resistance in CF_4 and Ar plasmas comparable to that of Novolak resists. We considered latitude in designing materials with controlled properties and transparency. Methacrylate monomers are suitable for our resist because of their clean copolymerization behavior and well-known physical and chemical properties.

We prepared a copolymer of *tert*-butyl methacrylate (TBMA) and adamantyl methacrylate (AdMA), **1**, and its transmittances are 87% at 248 nm and 82% at 193 nm (1-μm-thick film on a quartz substrate) with acceptable etch resistance in CF_4 and Ar plasmas. We proposed a resist for excimer lithography, which comprised this copolymer and triphenylsulfonium hexafluoroantimonate (TPSHA) as a PAG.[13] However, the resist needed 70 mol % TBMA loading in the polymer and 15 wt % TPSHA for a practical sensitivity of about 50 mJ/cm^2 at 248 nm because of the poor reactivity of *tert*-butyl (*t*Bu) substituents toward the acid photogenerated. Adamantyl substituents' concentration was limited to 30 mol % in this resist, and it was not enough to obtain etch resistance comparable to that of Novolak resists. Since 15 wt % of TPSHA loading deteriorates the transparency at 193 nm, the adaptability of this resist does not extend into 193-nm exposures.



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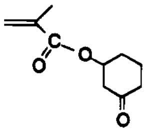

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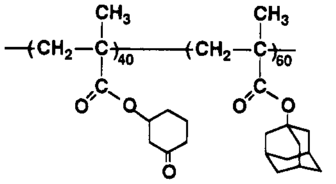

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For 193-nm lithography, bilayer or top-surface imaging approaches have usually been used.[14,15] Recently, methacrylate-based single-layer resists at 193 nm were reported by researchers at Matsushita and IBM-MIT's collaboration.[16,17] The former used norbornyl pendant substituents for the ester and nonaromatic PAG to obtain an etch-resistant resist with low absorption at 193 nm. The latter used TBMA-based terpolymers having a methacrylic acid component to obtain high resolution, high sensitivity, and good postexposure delay durability. They also have been trying to improve the etch resistance in CF_4 and halogenated gases' plasmas by introducing isobornyl pendant substituents instead of *t*Bu without deformation of the profile.

The chemically amplified resists reported are restricted in the selection of protective groups for acidic functional groups (i.e., phenolic or carboxylic hydroxyl groups) because they require moderate acid lability, proton reproducibility, and thermal and storage stability. Although many protective groups have been reported in synthetic organic chemistry,[18] there are few appropriate protective groups which meet the abovementioned requirements. The majority of protective groups for chemically amplified resists are *t*BOC,[19] *t*Bu,[20,21] dimethylbenzyl (DMBn),[20,21] or tetrahydropyranyl (THP).[22,23] We cannot use *t*BOC for methacrylate because it is difficult to synthesize. We also cannot use DMBn because the aromatic rings greatly absorb deep UV light, and THP is unstable in storage. Therefore, we need a new protective group for methacrylate.

Our approach for 193- and 248-nm photoresists is to replace the less acid labile *t*Bu substituent with a more reactive one in our alicyclic methacrylate system, which reacts effectively even with small amounts of the PAG. With such reactive substituents, we can introduce a 50 mol % alicyclic component in the polymer for higher dry etch resistance and 193-nm exposures. In this paper, we report on our approach for an excimer laser resist with the introduction of an originally designed 3-oxocyclohexyl substituent as a new acid labile protective group in our methacrylate system.

Experimental Section

Materials. 1,3-Cyclohexanediol (Kodak) was used as received. Methacryloyl chloride (Tokyo Kasei Kogyo) was distilled under reduced pressure in the presence of excess hydroquinone. Methylene chloride and triethylamine were distilled over CaH_2. Tetrahydrofuran (THF) and dioxane were distilled over $LiAlH_4$ prior to use. Pyridinium dichromate (PDC),[24] obtained from Tokyo Kasei Kogyo, was dried *in vacuo* at 40 °C for 8 h. 4A molecular sieves were activated in a 300 °C oven and then allowed to cool to room temperature *in vacuo*. Adamantyl methacrylate (Hakusui Kagaku Kogyo) was used as received. Triphenylsulfonium hexafluoroantimonate was purchased from Midori Kagaku and purified as described in the literature.[25]

Synthesis of 3-Oxocyclohexyl Methacrylate (OCMA), 2. To a 500-mL, three-necked flask fitted with a dropping funnel, a rubber septum, a drying tube filled with calcium chloride, and a magnetic stir bar, was added 21.3 g (183.4 mmol) of 1,3-cyclohexanediol, 18.8 mL (192.5 mmol) of meth-

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acryloyl chloride, 150 mL of methylene chloride, 50 mL of THF, and 10 g of activated 4A molecular seives. The suspension was then stirred at 0 °C. To this mixture, 28.2 mL (202 mmol) of triethylamine was slowly added through the dropping funnel over 20 min and stirred for 1 h at 0 °C. Then the reaction mixture was allowed to warm to room temperature and stirred for 3 h. The resultant mixture was filtered through a Celite pad, and the pad was washed with several portions of ether. The filtrate was concentrated *in vacuo* at 35 °C. The concentrated mixture was washed with 100 mL of dilute aqueous HCl solution. The organic layer was separated and the water layer was extracted with ethyl acetate (EtOAc) three times. The organic layer and the extracts were combined, washed with brine, dried with anhydrous Na_2SO_4, and concentrated *in vacuo* at 35 °C. Purification of the residue by silica gel chromatography (500 g of silica gel, 32% EtOAc/hexane–50% EtOAc/hexane) gave 10.47 g (31%) of 3-hydroxycyclohexyl methacrylate as a colorless oil. ^1H NMR ($CDCl_3$, ppm, J in hertz) 1.2–2.35 (m, 8 H, CH_2), 1.94 (m, J = 1.3, 3 H, CH_3), 3.65–4.1 (m, 1 H, HOC*H*), 4.7–5.3 (m, 1 H, OCH), 5.55, 6.09 (each m, 1 H, $=CH_2$). IR (neat, KBr, cm^{-1}) 3420 (OH), 1718 (C=O), 1637 (C=C).

To a well dried 500-mL, three-necked flask fitted with a dry nitrogen gas inlet, a rubber septum, a drying tube filled with calcium chloride and a magnetic stir bar was added 10 g of activated 4A molecular sieves, 10.47 g (56.8 mmol) of 3-hydroxycyclohexyl methacrylate, and 100 mL of methylene chloride. The flask was then purged with dry nitrogen and the suspension was stirred vigorously. To this was added 64.14 g (170.5 mmol) of PDC and stirred vigorously for 3 h. The reaction mixture was filtered through a Celite pad, and the pad was washed with several portions of ether. The filtrate was concentrated *in vacuo* at 35 °C. Purification of the residue by silica gel column chromatography (500 g of silica gel, 8% THF/hexane–16% THF/hexane) afforded 8.42 g (81%) of **2** as a colorless oil. ^1H NMR ($CDCl_3$, ppm, J in hertz) 1.8–2.15 (m, 6 H, CH_2), 1.92 (m, J = 1, 3 H, CH_3), 2.40 (m, 2 H, CH_2), 2.55 (dd, J = 6.0 and 14.7, 1 H, OCHCH_2C(O) axial), 2.68 (dd, J = 4.4 and 14.7, 1 H, OCHCH_2C(O), equatorial), 5.33 (m, 1 H, OCH), 5.57, 6.08 (each m, 1 H, $=CH_2$). ^{13}C NMR ($CDCl_3$, ppm) 18.03 (CH_3), 20.69, 29.12, 40.82 (each CH_2), 46.32 (C(=O)CH$_2$), 71.69 (CH), 125.77 ($=CH_2$), 136.07 ($H_2C=C$), 166.12 (ester C=O), 208.17 (ketone C=O). IR (neat, KBr, cm^{-1}): 1718 (ester C=O), 1687 (ketone C=O), 1637 (C=C).

Synthesis of Poly(3-oxocyclohexyl methacrylate-*co*-adamantyl methacrylate), 3. A solution of 8.42 g (46.2 mmol) of 3-oxocyclohexyl methacrylate and 6.42 g (30.8 mmol) of adamantyl methacrylate in 21.9 mL of dry dioxane was stirred and heated to 80 °C under a dry nitrogen atmosphere. To this mixture was added 1.9 g (11.6 mmol) of 2,2′-azobis(isobutyronitrile) (AIBN). After 7 h, the mixture was precipitated in 4 L of methanol containing a small amount of hydroquinone. The precipitate was filtered off with a glass filter and dried *in vacuo* at 45 °C for 6 h. The resultant white powder was dissolved in THF and then reprecipitated in 4 L of methanol, filtered off using a glass filter, and dried again. This repricipitation procedure was repeated one more time to provide 9.88 g (66.6%) of **3** as a white powder. ^1H NMR analysis of the copolymer showed the molar composition 4:6 (OCMA:AdMA). IR (thin film, KRS-5, cm^{-1}) 1721 (C=O). GPC: M_n = 10 470, M_w = 15 500, M_w/M_n = 1.48. DSC: T_g = not observed below 156 °C, TDA: T_d = 189 °C.

Analytical Measurements. NMR spectra were obtained using a Varian Gemini-200 spectrometer at resonance frequencies of 200 MHz for protons and 50 MHz for carbons. The glass transition temperature (T_g) of the polymer was measured on a SII DSC-220 differential scanning calorimeter and the thermal decomposition temperature (T_d) was measured on a TG/DTA-320 thermogravimetric analyzer. Molecular weight determination was performed by gel permiation chromatography (GPC) at 40 °C in THF elution using a Tosoh Model HLD-803D chromatograph equipped with a TSK-GEL G2500HR and a G4000HR (Tosoh) column. The molecular weights reported are linear polystyrene standard (Tosoh)-equivalent. IR spectra were obtained using a Perkin-Elmer 1760X spectrometer. VUV and UV absorption spectra were recorded on JASCO VUV-200 and a Shimazu UV-3100 spectrophotometer, with a 1-μm-thick film spincoated on a quartz substrate.

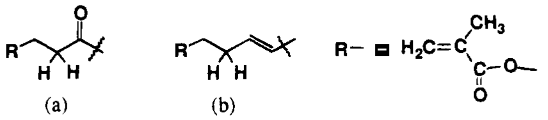

Figure 1. Favorable functional groups for the protective group possessing acidic protons at (a) the ketone's α position and (b) allylic position.

Lithographic Performance Evaluation. We prepared resist solution by dissolving the copolymer in cyclohexanone (15 wt/wt %) and added TPSHA 10 wt % (vs polymer weight). The solution was then filtered through a series of 0.45- and 0.2-μm Teflon membrane filters, spun onto cured Novolak resists on silicon substrates (*vide infra*) or on silicon substrates, and baked at 100 °C for 60 s on a hot plate equipped with a vacuum holddown chuck. The resist-coated substrates were exposed by using a KrF excimer laser stepper (Nikon, NA = 0.45). Then the exposed substrates were postexposure-baked at 150 °C for 60 s on a hot plate equipped with a vacuum holddown chuck. The films were then developed in dip mode using a 2.38% tetramethylammonium hydroxide aqueous solution (TMAH, Tokyo Ohka Kogyo) or a mixed solution of 20 vol % IPA (2-propanol)/TMAH for 60 s and rinsed in deionized water.

We measured the plasma etching rates using in-house made reactive ion etchers for CF_4, Ar, and Cl_2 and a Plasma Therm A-360 etcher for HBr. The etching conditions were (1) 100 sccm of Ar, 0.02 Torr, at 200 W, (2) 100 sccm CF_4, 0.02 Torr, at 200 W, (3) 30 sccm Cl_2, 0.02 Torr, at 200 W, and (4) 25 sccm HBr, 0.025 Torr, at 150 W. The film thickness loss was measured with an alpha-step 200 profilometer (Tencor Instruments) after etching for 5 min. Sensitivity was determined to the minimum irradiation dose required to completely remove the film in the exposed regions without loss of film thickness in the unexposed regions. Resist patterns were examined with Hitachi Model S-450 and Akashi DS-130F scanning electron microscopes (SEM).

Results and Discussion

Molecular Design. Protective groups for acidic functional groups in chemical amplification must fill the above-mentioned requirements. Our protective group should also have higher acid lability than that of *t*Bu substituent for higher sensitivity and should not have conjugated double bonds or aromatic rings so that the absorption of deep-UV light is low. Initially, we thought that the stability of the carbonium ions generated after deprotection of the protective groups was the most important factor in reactivity. However, we examined various compounds for the protective group and found that both proton acidity at the α position of the carbonium ion and carbonium ion stability were very important. The acidic proton was removed easily in the transition state, so the reaction proceeded smoothly.

We thought that a ketone or a double bond was a key functional group for the protective group because they have acidic protons at the α or allylic positions without a loss of transparency at KrF and ArF wavelengths (Figure 1). Table 1 shows pK_a[26] of the α protons of acetone, a representative ketone, and the allylic protons of propylene, a representative double bond, and the λ_{max} wavelengths with ϵ.[27] Acetone has more acidic protons

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Table 1. pK_a and λ_{max} Wavelengths with ϵ of Acetone and Propylene

compounds	pK_a	λ_{max} (nm) [ϵ][a]
acetone	20 (α protons)	189 [794] 278 [12.6]
propylene	35 (allylic protons)	176 [12600][b]

[a] Measured in heptane. [b] 1-Octene's values were applied.

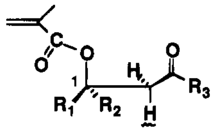
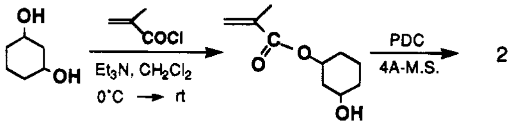


Figure 2. Schematic view of an antiperiplanar position of the ketone's α proton (wavy underline) to the C_1–O bond.

Scheme 1. Synthetic Route for OCMA



than propylene as well as the low ϵ of the carbonyl chromophore at 193 nm (λ_{max} = 189 nm, ϵ = 794). Hence, we selected a ketone for the functional group in the protective group.

We considered the substituent's structure regarding smooth deprotection with the materials availability in the synthesis. We thought that smooth elimination of the acidic proton at the ketone's α position required an anti-periplanar position to C_1–O bond (Figure 2). Ring structures are more favorable than chain structures for this requirement because the proton occupies the antiperiplanar position by ring flip. Additionally, we expect greater etch resistance by introducing the ring structure. A cyclohexyl ring is superior to other ring structures in material availability and cost. For a cyclohexyl ring, 3-oxocyclohexyl is the substituent's structure, and a product of deprotection will be 2-cyclohexen-1-one (bp 168°). We thought that a high boiling point for the deprotected product was favorable for critical dimension (CD) control because it would decrease film shrinkage at the PEB step. Thus we selected a cyclohexyl ring for the base structure and designed the 3-oxocyclohexyl substituent for the protective group in our alicyclic methacrylate-based resist.

Monomer and Polymer Syntheses. We used two-step syntheses to prepare **2** (Scheme 1). Esterification of 1,3-cyclohexanediol and methacryloyl chloride, followed by oxidation gave **2** in moderate yield. We often obtained, however, a mixture of **2**, about 20 mol % methacrylic acid, and 2-cyclohexen-1-one (3-oxocyclohexyl deprotected product) due to the product's thermal instability. We could not purify the mixture by vacuum distillation or silica gel column chromatography. Distillation temperatures over 90 °C caused thermally induced polymerization in the flask even with excess inhibitor. Considering the boiling point of trimethylsilyl methacrylate (51 °C/20 mmHg), we purified the mixture by *in situ* trimethylsilylation of methacrylic acid by adding excess *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) and dry ether under a nitrogen atmosphere. After stirring for 15 min at 0 °C, the reaction mixture was allowed to warm to room temperature, and then stirred for 3 h. The excess BSTFA, trifluoroacetamide, ether, 2-cyclohexen-1-one and resultant trimethylsilyl methacrylate were evacuated *in vacuo* at room temperature to give pure **2**. Since **2** is unstable at room temperature, the monomer must be stored below −20 °C under a dry nitrogen atmosphere. We used this purification procedure prior to polymerization.

Table 2. Relative Dry Etch Resistance of OCMA Copolymer, PMMA, and Novolak Resist

films	CF_4[a]	Ar[a]	Cl_2[b]	HBr[c]
Novolak resist	1.0	1.0	1.0	1.0[d]
PMMA	1.4	2.0	2.5	
poly(OCMA$_{40}$-AdMA$_{60}$)	0.9	1.1	1.3	0.8

[a] The following etching conditions were employed: (a) 100 sccm, 0.02 Torr, 200 W, 5 min, (b) 30 sccm, 0.02 Torr, 200 W, 5 min, and (c) 25 sccm, 0.025 Torr, 150 W, 5 min. (d) UV-cured Novolak resist was used as a reference.

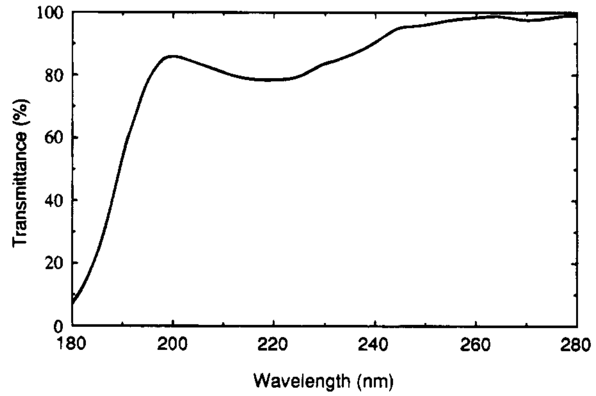


Figure 3. VUV–UV spectrum of a 1-μm thick poly(OCMA$_{40}$-*co*-AdMA$_{60}$) film on a quartz substrate.

The thermally induced free radical polymerization of AdMA and **2** was carried out using AIBN as the initiator. Although **2** is temperature sensitive, we obtained a pure copolymer without the methacrylic acid component at a polymerization temperature of 80 °C. To confirm this, we employed the following procedure. Excess trimethylsilyldiazomethane was added to a THF solution of the copolymer and allowed to stand for a few hours at room temperature. The reaction mixture was then poured into a large amount of methanol and the resultant precipitate was filtered through a glass filter. The precipitate was dried *in vacuo* at 45 °C and was ^{1}H NMR analyzed. There is no methyl ester peak in the NMR spectrum.

Dry Etch Resistance. We investigated the etch rates of **3**, PMMA, and Novolak resist (NPR-820, Nagase & Co.). This copolymer has etch resistance to CF_4, Ar, and HBr etching gases comparable to or better than Novolak resist (Table 2). The etch rate in Cl_2 plasma is slightly lower; however, we think the copolymer still has acceptable etch resistance for this severe plasma exposure. The copolymer has better dry etch resistance than that of **1** because the adamantyl methacrylate concentration is higher than in **1**.

VUV–UV Absorption. Figure 3 shows the VUV–UV spectrum of a 1-μm-thick film of **3** on a quartz substrate. It indicates that the polymer composition and the introduction of 3-oxocyclohexyl substituents do not effect photoabsorption. The transmittances are 95% at 248 nm and 70% at 193 nm.

Deprotection and Imaging. We evaluated the deprotection and imaging primarily by IR spectroscopy. A 5 wt % TPSHA-loaded resist was spun onto a KRS-5 plate and baked at 100 °C for 60 s. The film was exposed to deep-UV light (Ushio UXM-501MA) with a

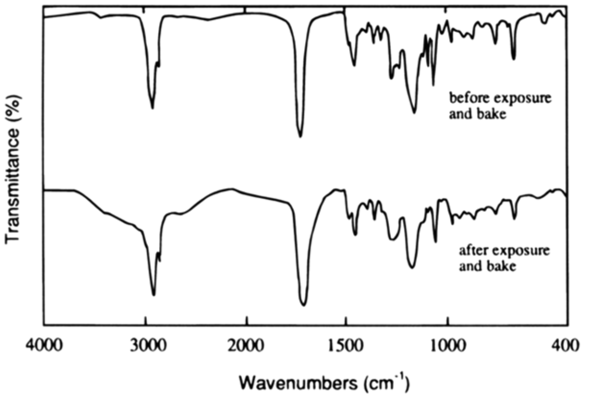
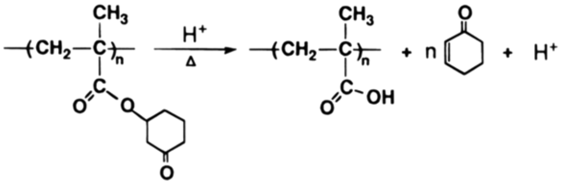


Figure 4. IR spectra of a poly(OCMA$_{40}$-*co*-AdMA$_{60}$) film containing 5 wt % of Ph_3SSbF_6 before and after deep-UV exposure (~50 mJ/cm^2) followed by postexposure baking at 100 °C for 60 s.

Scheme 2. Pathway for the Acid–Catalyzed Deprotection and Regeneration of a Proton



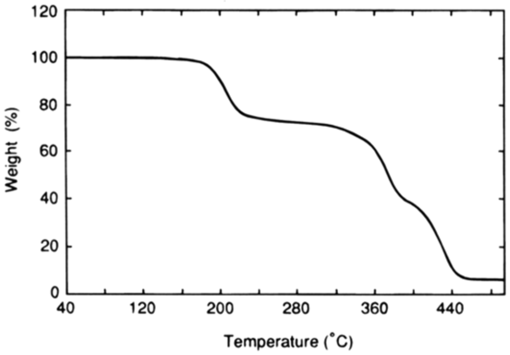


Figure 5. TGA curve at 10 °C/min of poly(OCMA$_{40}$-*co*-AdMA$_{60}$).

dose of about 50 mJ/cm^2 and postexposure-baked at 100 °C for 60 s. The IR spectrum indicated over 80% deprotection of 3-oxocyclohexyl substituents after the exposure and postexposure baking (Figure 4). In contrast, we did not obtain any resist patterns in a resist containing 10 wt % of TPSHA after a 248-nm exposure and a postexposure bake at 80 °C. This result indicates that the deprotection was not enough to resolve the patterns at this PEB temperature and the resist has a deprotection threshold temperature between 80 and 100 °C.

We have stored the resist for over 6 months at room temperature without any problems. Although **2** was unstable at room temperature, **3** was stable even as a resist solution. We attribute the difference in the stability of the monomer and the polymer to the electron density variation at the ester carbonyl groups after polymerization. We believe the pathway of the acid-catalyzed deprotection is as shown in Scheme 2. The acidic C_2 protons are readily removed from 3-oxocyclohexyl substituents to form carboxylic acid and 2-cyclohexen-1-one. Hence, the acid-catalyzed deprotection, which is assisted by the acidic proton of the 3-oxocyclohexyl substituent, proceeds as expected.

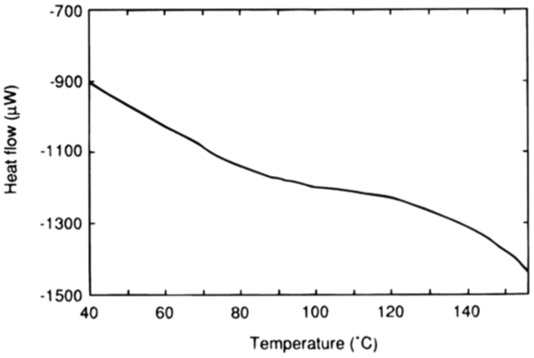


Figure 6. Second heating DSC curve at 20 °C/min of poly(OCMA$_{40}$-*co*-AdMA$_{60}$).

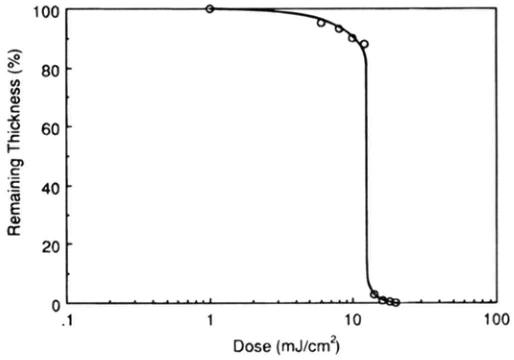


Figure 7. Sensitivity curve plotting percentage of remaining thickness versus log dose of 248-nm radiation for poly(OCMA$_{40}$-*co*-AdMA$_{60}$) resist containing 10 wt % of Ph_3SSbF_6.

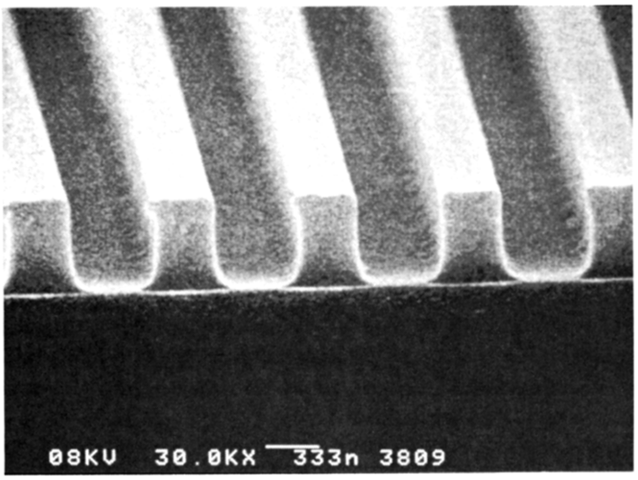


Figure 8. SEM micrograph depicting positive image of 0.5-μm L/S patterns in 0.7-μm-thick film of poly(OCMA$_{40}$-*co*-AdMA$_{60}$) resist containing 10 wt % of Ph_3SSbF_6 on a cured Novolak on Si substrate followed by postexposure baking at 100 °C for 60 s and developing in 2.38% TMAH solution. The sensitivity was 20 mJ/cm^2.

The TGA curve exhibits weight loss at the 3-oxocyclohexyl substituents deprotection temperature at 189 °C (Figure 5). The DSC curve does not show any endothermic peaks (Figure 6). Since we did not see the copolymer's T_g below 156 °C, we limited the postexposure bake temperature to the pattern edges' melting temperature of about 160 °C. For postexposure baking at 150 °C, we obtained fine-pattern profiles without problems. We attribute the resist's high thermal resistance to the adamantyl methacrylate component. The rigidness of the polymer film caused by the bulky adamantyl substituents may prevent T_g appearance below 156 °C. The wide range of postexposure bake

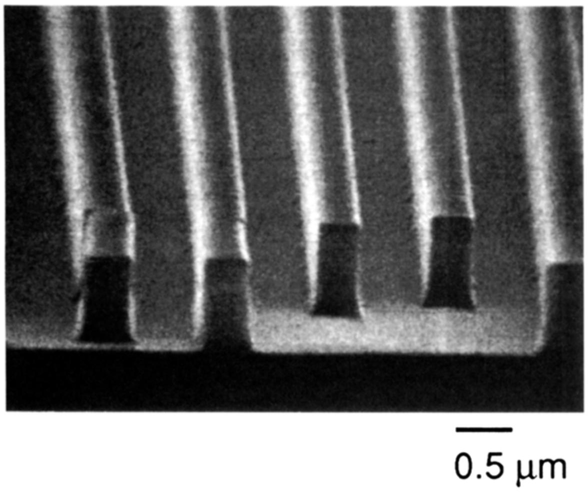


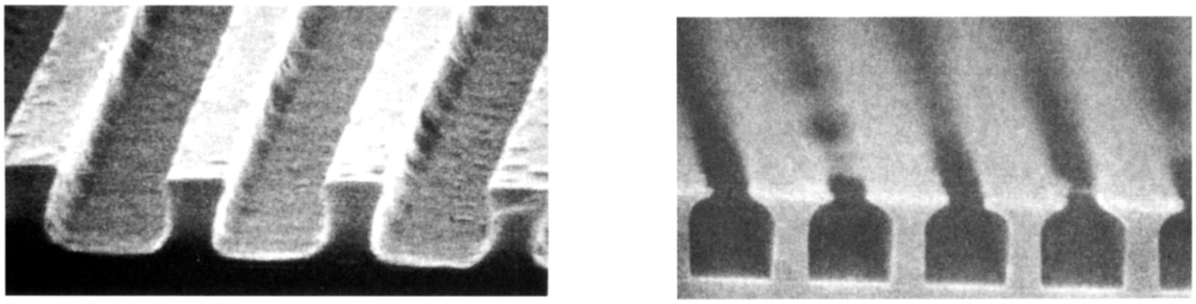
Figure 9. SEM micrograph depicting improved positive image of 0.3-µm L/S patterns in a 0.7-µm-thick film of the same resist as Figure 8 on a Si substrate followed by postexposure baking at 100 °C for 60 s and developing in 20 vol % IPA/TMAH. The sensitivity was 8 mJ/cm^2.

temperatures, 90−150 °C, is useful for a variety of process conditions.

We evaluated the lithographic performance of a **3**-based resist containing 10 wt % of TPSHA. We investigated the sensitivity curve for the resist formation and the line and space (L/S) pattern profiles after exposure using a KrF excimer laser stepper followed by a postexposure bake and development in 2.38% TMAH solution (Figure 7). Figure 8 shows a micrograph of 0.5-µm L/S patterns at a dose of 36 mJ/cm^2. In standard TMAH development, the formulated sub-half-micron patterns often peel off the Si substrates because of film rigidness. Hence we used substrates made from cured Novolak resist on silicon (Novolak on Si) for this evaluation. The resist with 10 wt % of the PAG resolved more precise profiles than with 5 wt %. The resist with 5 wt % of the PAG also resolved 0.5-µm L/S patterns and the sensitivity was 55 mJ/cm^2. The transmittance of this resist at 248 nm was 42% (1-µm-thick film on a quartz substrate). Film shrinkage at this PEB condition (100 °C) was 11%. We did not optimize the PAGs for this evaluation and the optimization of PAGs will be a future subject.

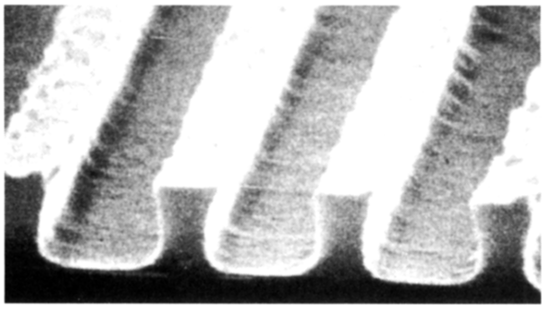
We improved the lithographic performance on Si substrates by mixing IPA into the alkali developer.[28] Figure 9 shows 0.3-µm features on a Si substrate using 20 vol % IPA/TMAH developer. The imaging dose was 24 mJ/cm^2. Sub-half-micron patterns did not peel off the substrates with this developer. We did not observe film thickness loss at the unexposed region in this development process. We attribute these improvements to a decrease of stress on the resist film, which was probably caused by rapid penetration of the aqueous alkali developer into the exposed regions, and to the variation of osmotic pressure of the developer by IPA mixing. We could decrease the PAG loading in our resist to 1 wt % using 50 vol % IPA/TMAH developer. At this loading, we also obtained 0.3-µm patterns at a dose of 38 mJ/cm^2 without deformation of the profiles. The transmittance of this resist was 40% at 193 nm (1-µm-thick film). This indicates that this resist has potentiality for 193-nm exposures.

We compared the postexposure delay (PED) durability of this resist and a PVP-based (about 16% *t*BOC



after 1 min

after 1 min



after 45 min

Figure 10. SEM micrographs depicting positive images of L/S patterns obtained on (a, left) poly(OCMA$_{40}$-*co*-AdMA$_{60}$) resist containing 10 wt % of Ph_3SbF_6 with a 50 mJ/cm^2 exposure dose after 1- and 45-min delays, (b, right) PVP (ca. 16% *t*BOC blocked) resist containing 5 wt % of $Ph_3SCF_3SO_3$ with a 10 mJ/cm^2 exposure dose after a 1-min delay. The following baking conditions were employed: (a) Prebake; 100 °C for 60 s, postexposure bake: 100 °C for 60 s. (b) Prebake; 90 °C for 60 s, postexposure bake: 90 °C for 120 s.

blocked) resist containing 5 wt % triphenylsulfonium triflate. With each resist, approximately 0.7-μm-thick films were formed by spin-coating on Novolak on Si substrates for the **3**-based resist and on Si substrates for the PVP resist and then baked. The resist-coated wafers were then exposed with a KrF excimer laser stepper. Delay interval was introduced into a process between exposure and PEB. As shown in Figure 10b, "T-top" profiles appeared even after a 1-min delay in the PVP resist. The PVP resist did not resolve any patterns after a 5-min delay. The delay time resistance of the **3**-based resist is superior to that of the PVP resist. This result indicates that the polymer matrix significantly affects PED durability. We attribute the superior delay time durability to the adamantyl components because the bulky hydrophobic substituents prevent the uptake of "airborne contamination".[29] We believe that the hydrophobic resist absorbs less contaminant than hydrophilic resists, such as the PVP resist because amines or other organic alkalis, the major contaminants, are hydrophilic.

We expect this resist to be suitable for 193-nm lithography as well as 248-nm lithography because the reactivity of 3-oxocyclohexyl is better than *t*Bu and the transmittance of the base resin is high at 193 nm. Currently, we are trying to evaluate 193-nm exposures of the resist, and the result will be presented at a later date.

Conclusion

We described an approach to creating highly transparent and etch-resistant methacrylate resist for excimer lithography. We designed and synthesized OCMA for the acid sensitive component in a new chemically amplified resist. The new resist comprised poly(OCMA$_{40}$-*co*-AdMA$_{60}$) and 10 wt % of TPSHA. Using this resist, we could delineate 0.3-μm L/S patterns by KrF excimer laser exposures and using IPA mixed developer. The resist is suitable for excimer laser lithography because it has (1) high sensitivity (8 mJ/cm^2), (2) good thermal stability, (3) good dry etch resistance, comparable to that of Novolak resist, and (4) good PED durability. The resist's PED durability suggests that the polymer's hydrophobicity is very important for longer delay times. A resist even with 1 wt % of TPSHA has an acceptable transmittance at 193 nm, so we believe that it is suitable for ArF excimer lithography.

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Registry No. 1,3-Cyclohexanediol, 504-01-8; methacryloyl chloride, 920-46-7; PDC, 20039-37-6; BSTFA, 25561-30-2; HMDS, 999-97-3; 2-propanol, 67-63-0.

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