High-Performance Resist Materials for ArF Excimer Laser and Electron Beam Lithography

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High-performance resist materials for ArF (argon fluoride) excimer laser (λ = 193 nm) and electron beam (EB) lithography for fabricating 100 nm-level and beyond ULSIs have been developed. For the base polymers of the ArF resists, a novel methacrylate was employed as a base polymer whose ester groups have chromophores with a low extinction coefficient at 193 nm. A polycyclic hydrocarbon substituent, called adamantyl, and lactone substituents were introduced for acid-labile ester groups in the methacrylate polymer. The alicyclic group provides superior sensitivity, resolution, and dry-etch resistance, while the lactone groups afford compatibility with a standard TMAH (tetramethylammonium hydroxide) developer, good resolution, and adhesion to Si substrates. For the base polymer of the EB resist, the above-mentioned adamantyl methacrylate unit was applied in a vinylphenol copolymer. By optimizing the compositions of these resists and the process conditions, we achieved a 100 nm line and space pattern by ArF excimer laser lithography and a 59 nm hole pattern by EB lithography.

1. Introduction

Increasing demands for devices with higher circuit densities have led to the use of shorter-wavelength light sources in optical lithography. KrF (krypton fluoride) excimer laser lithography (λ = 248 nm) has been used for the production of devices having design rules ranging from 250 to 130 nm. For even smaller dimensions, an ArF (argon fluoride) excimer laser will be needed$^{1)}$ because it has a shorter wavelength (λ = 193 nm) than a KrF laser and offers a superior resolution of around 90 nm.

The photoresists used for microlithography must have a high resolution, high sensitivity, and good dry-etch resistance as basic properties. Resists based on phenolic resins are well balanced in terms of the above-mentioned properties and have therefore been widely used for g-line (436 nm), i-line (365 nm), and KrF lithography. The phenolic rings in these resists give them moderate solubility in an alkali developer as well as a good dry-etch resistance.$^{2)}$ Phenolic resists cannot be used in ArF lithography, however, because they are completely opaque at 193 nm. In contrast, it is well known that aliphatic polymers such as methacrylates have low absorption at 193 nm, but they also have a poor dry-etch resistance.$^{3),4)}$ Therefore, new resist materials must be developed which have both transparency at 193 nm and a dry-etch resistance comparable to that of KrF resists.

For the next-generation lithography, whose target dimensions are below the 100 nm realm, EB lithography is considered to be a promising technique. EB lithography does not require consideration of the resist's absorbance, because an EB has a very short wavelength (λ = 3.7 pm at 100 keV). Therefore, there are few limitations on the composition of an EB resist. Electron beam projection lithography (EPL), which uses high-speed EB exposure systems such as SCALPEL,[5] PREVAIL,[6] and BAA,[7] can overcome the low throughput problem in a conventional EB direct-write lithography.

To incorporate high-speed EB exposure systems into a mass-production process, highly sensitive EB resists that have a high resolution capability need to be developed. Resolution and sensitivity can be improved very effectively by using a resist film that is thin but has a lowered dry-etch resistance. Polyvinylphenol (PVP)-based resists are generally used in EB lithography and consist of a variety of protective groups (acetals,[8],[9] tert-butoxycarbonyl,[10] tert-butyl [tBu],[11] etc.), but these protective groups have a poor dry-etch resistance because of their aliphatic structures. Therefore, the use of such protective groups deteriorates the dry-etch resistance of the resist. To overcome this problem, acid-sensitive and dry-etch-resistant protective groups are required. These requirements can be met by incorporating the acid-cleavable alicyclic substituents used for ArF resists into the base polymer.[12],[13] This paper describes our approach and development of novel, chemically amplified resists for use in ArF and EB lithography.

2. Experiments

2.1 Materials

Mevalonic lactone, 2-methyl-2-adamantanol, and 4-acetoxystyrene (AS) were used as received. 2-Ethyl-2-adamantyl methacrylate (EAdMA) was synthesized according to the patent manuscript.[14] Methacryloyl chloride was distilled under reduced pressure. Dioxane, methylene chloride, and triethylamine were distilled over CaH_2. Other solvents were used as received. AIBN (2,2'-azobisisobutironitrile) was purified by recrystalization in methanol.

2.2 Synthesis

2.2.1 Monomers

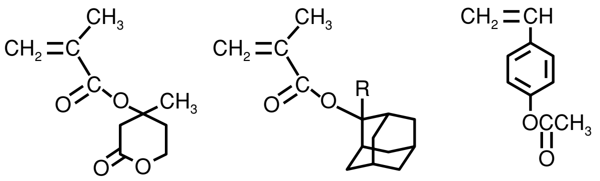
Mevalonic lactone methacrylate (MLMA) and 2-methyl-2-adamantyl methacrylate (MAdMA) were prepared as follows.

Methacryloyl chloride was added dropwise to a stirred solution of an equimolar amount of alcohol (mevalonic lactone or 2-methyl-2-adamantanol), excess triethylamine, and methylene chloride in a dry, cooled (–30 to 0°C) nitrogen atmosphere. Then, the reaction mixture was stirred for several hours while maintaining the lowered temperature. The resultant mixture was filtered, and the filtrate was concentrated *in vacuo*. The concentrated mixture was washed with water and brine. The water layer was extracted with methylene chloride. The organic layer and the extracts were combined, dried with anhydrous Na_2SO_4, and concentrated *in vacuo*. The purification of the crude monomers by silica gel chromatography (EtOAc/hexane or ether/hexane) gave satisfactory yields. The yields for MLMA and MAdMA were 70% and 87%, respectively. The chemical structures of the monomers are shown in **Figure 1**.

Analytical data

MLMA: ^{1}H-NMR ($CDCl_3$, ppm, J in hertz) 1.66, 1.91 (each singlet [s], 3H, CH_3), 2.48 (multiplet [m], 2H, CH_2), 2.87 (double doublet [dd], J = 20, 2H, CH_2), 4.39 (m, 2H, CH_2), 5.58, 6.05 (each s, 1H, = CH_2). IR (neat, KBr, cm^{-1}) 1743, 1714, 1637, 1173, 1160.

MAdMA: ^{1}H-NMR ($CDCl_3$, ppm) 1.65, 1.93 (each s, 3H, CH_3), 2.35 (m, 3H, CH), 1.34-2.35 (m, 10H, CH_2), 5.49, 6.05



MLMA

MAdMA (R = Me)
EAdMA (R = Et)

AS

Figure 1
Chemical structures of the monomers.

(each s, 1H, = CH_2). IR (neat, KBr, cm^{-1}) 2912, 1712, 1637, 1172, 1105.

2.2.2 Polymers

The series of polymers for ArF resists were synthesized with various feed ratios using 15 mol% of AIBN as the initiator in 3 mol/l of dioxane solution at 70°C for 8 hours. The polymers were isolated by precipitation into a large amount of methanol. In the case of MLMA-rich polymers, γ-butyrolactone was used as the polymerization solvent and THF was employed as a poor solvent in the precipitation procedures. The resultant precipitate was filtered and dried *in vacuo* at 45°C for 8 hours. The collected polymers were purified by reprecipitation three times. The polymers for EB resists were prepared using the same conditions for ArF resists. In the case of poly (AS-MAdMA), deacetylation reaction was performed according to the literature[15)] to yield poly (VP-MAdMA). The chemical structures of the polymers are shown in **Figure 2**.

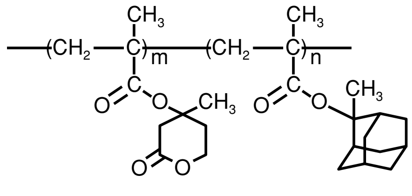
2.3 Analytical measurements

NMR spectra were obtained using a JEOL GX500 spectrometer at a resonance frequency of 500 MHz for protons. IR spectra were measured by a JEOL JIR-100 spectrometer. The molecular weights were determined using a TOSOH SC-8020 chromatograph. The molecular weights are linear polystyrene standard (TOSOH)-equivalent. DSC and DTA were measured on a DuPont thermal analyzer with a 10°C/minute heating rate. Vacuum ultraviolet (VUV) spectra were obtained from a 0.5 µm-thick film spin-coated on a quartz substrate.

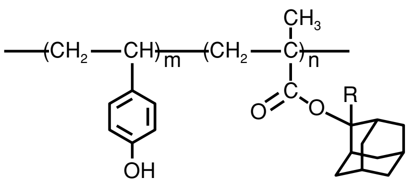
2.4 Resist formulation, lithographic evaluation, and dry-etch rate

The resist used for ArF evaluation consisted of the copolymer 2 wt% of TPSOTf (triphenylsufoniumtriflate) and PGMEA (propyleneglycol-1-methylether-2-acetate) and also ethyl lactate as an auxiliary solvent. The resist used for EB evaluation consisted of the copolymer 5 wt% of TPSOTf and PGMEA. The well-mixed resist solution was filtered through a series of 0.5 µm and 0.2 µm Teflon membrane filters, spun onto HMDS-primed Si substrates, and baked for 60 seconds on a hot plate to form 0.4 µm-thick or 0.5 µm-thick films. The resist-coated substrates were exposed with an ArF excimer laser exposure system (Nikon, NA = 0.55) or an ArF excimer laser step-and-scan system (Nikon, NA = 0.6) or an EB exposure system (50 keV) followed by a post-exposure baking (PEB) on a hot plate. Finally, the films were developed in a 2.38% TMAH aqueous solution and rinsed in deionized water. The alkali dissolution rate (ADR) of the resist films was measured in a 4% TMAH solution to enhance the dissolution rate of the unexposed regions.

The relative dry-etch rates compared to a novolak resist were determined in Ar, CF_4, and Cl_2 plasmas using a reactive ion etcher that was constructed in-house. The etching conditions were 0.02 Torr at 200 W. The flow rates of the gases were 100 sccm for Ar and CF_4 and 30 sccm for Cl_2. The film thickness loss was measured with an Alpha-step 200 profilometer (Tencor Instruments) after etching for 5 minutes.



(a) poly (MAdMA-MLMA)



(b) poly (VP-RAdMA), R = Me, Et

Figure 2
Chemical structures of the polymers.

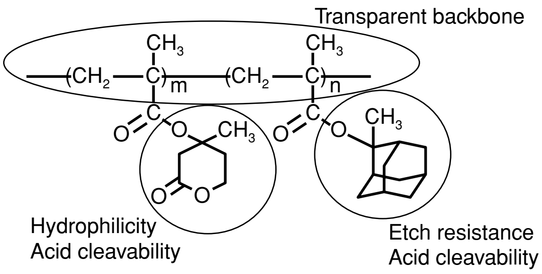


Figure 3
Functions of poly (MLMA-MAdMA).

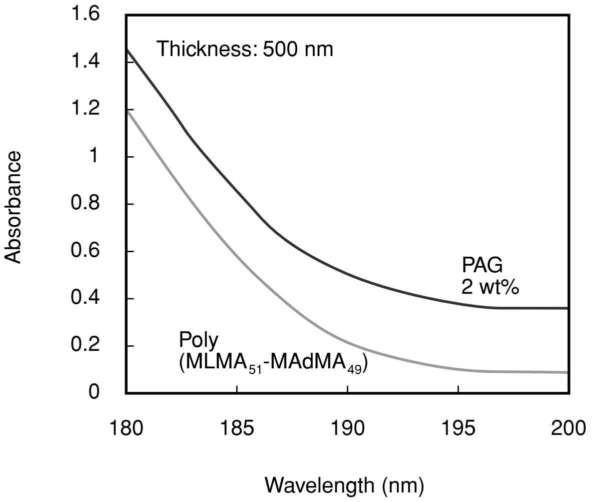


Figure 4
VUV spectra of 500 nm-thick films of poly ($MLMA_{51}$-$MAdMA_{49}$) and formulated resist (PAG 2 wt%) on quartz substrate.

Table 1
Characteristics of the polymers.

	Monomer feed (MLMA/MAdMA)	Polymer composition	Mw (Mw/Mn)	Yield (%)	*Tg* (°C)	*Td* (°C)
A	0 / 100	0 / 100	9900 (2.14)	73	Not observed	216.9
B	20 / 80	22 / 78	15 100 (2.28)	72	Not observed	187.5
C	55 / 45	51 / 49	20 000 (2.19)	75	105	176.1
D	80 / 20	72 / 28		66	92	168.0
E	100 / 0	100 / 0		56	Not observed	150.5

Table 2
Preliminary imaging properties of resists based on the polymers.

	Polymer composition	Resist solvent	Imaging results[note)]
A	0 / 100	Cyclohexanone	Cracks, patterns peeled off
B	22 / 78	Cyclohexanone	Patterns peeled off
C	51 / 49	Ethyl lactate	Good
D	72 / 28	Ethyl pyruvate	Unexposed region dissolved
E	100 / 0	?-Butyro lactone	PAG separated out, unexposed region dissolved

note) PAG: TPSOTf 5 wt%

3. Results and discussions

3.1 ArF resist

3.1.1 Characteristics and VUV absorption

We designed a novel methacrylate copolymer for ArF resists, poly (MLMA-MAdMA), that includes two different acid-cleavable protective groups (**Figure 3**).[16)-18)] The hydrophilic mevalonic lactone group provides adhesion of the formulated patterns to Si substrates. It also has acid cleavability because it contains an acid-sensitive β-hydroxyketone structure and a tertiary alcohol structure. The alicyclic adamantyl group substituent imparts dry-etch resistance and also has acid cleavability derived from the tertiary alcohol structure. The acid cleavage of these groups affords uniform solubility in the exposed regions.

These protective groups eliminate chromophores that have a high extinction coefficient below 200 nm wavelengths (**Figure 4**). The absorbance of the copolymer and the resist are 0.14 μm^{-1} and 0.41 μm^{-1}, respectively. We believe that the resist is sufficiently transparent for imaging.

3.1.2 Syntheses

Each monomer synthesis gave satisfactory yields (> 70%) through a traditional esterification. Using these monomers, a series of five methacrylate polymers (A to E) were prepared (**Table 1**). The molecular weights of polymers D and E could not be determined because they were insoluble in THF (GPC eluate). DSC measurements made at temperatures up to 200°C revealed a *Tg* in polymers C and D but not in the other polymers. Polymer C has protective groups that are well-balanced for lithography and also has a *Td* of 176.1°C (5 wt% weight loss temperature); these two features of polymer C make it suitable for use as a resist base polymer.

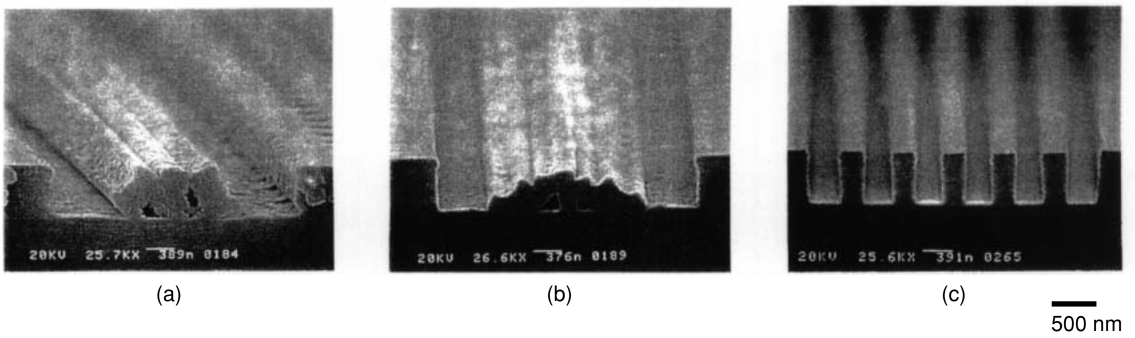


Figure 5
SEM micrographs of 300 nm L/S patterns obtained by KrF exposures.
The molar-ratio incorporations of MLMA into these resists were 0 (a), 22 (b), and 51 (c).

3.1.3 Imaging properties

The preliminary imaging results obtained from exposing resists based on polymers A to E on a KrF stepper are listed in **Table 2**. In MAdMA-rich resists A and B, the formulated resist patterns often peeled off the Si substrates, which suggests that the brittleness of the resist films derives from the dominant rigid adamantyl units. The MLMA-rich resists D and E were alkali soluble, so they did not resolve any resist patterns. Resist E was also difficult to spin-coat because the PAG was separated out. The 300 nm L/S patterns of resists A, B, and C, which demonstrated resist adhesion, were significantly improved by increasing the amount of MLMA (**Figure 5**). These results suggest that resist C has a promising composition. Based on these observations, the optimum composition for the base polymer should be about MAdMA/MLMA=1/1.

3.1.4 Deprotection of protective groups

The acid cleavage of the new protective groups was investigated using resists A and E by IR spectroscopy. **Figure 6** shows the IR spectra of the resist films before and after exposure and post-exposure baking. Carboxylic acid absorption at around 3200 cm^{-1} and 1700 cm^{-1} was clearly observed in the spectra after exposure and baking, which proved that acid catalyzed cleavage of the protective groups was achieved.

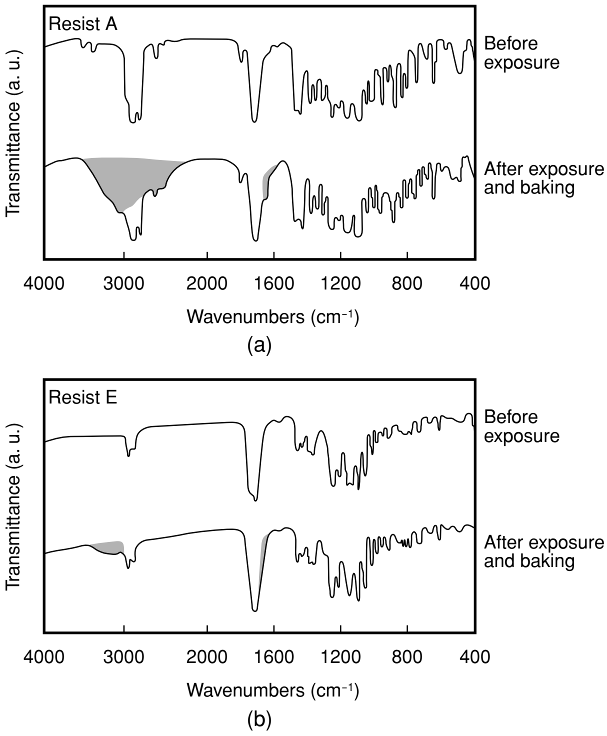


Figure 6
IR spectra of resists A (a) and E (b) containing 2 wt% of TPSOTf before and after DUV exposures (20 mJ/cm^2). The resists were spin-coated on KRS-5 plates and baked at 120°C for 60 seconds and the postexposure baking was conducted at 100°C for 60 seconds.

3.1.5 Lithographic evaluation on ArF

A high contrast and a high sensitivity of 2.5 mJ/cm^2 were observed in the exposure response curve (**Figure 7**). Using a 2/3 annular illumination (NA = 0.6, σ = 0.75) and a binary mask, 100 nm line and space (L/S) patterns were resolved with an optimized resist at 15.5 mJ/cm^2 (**Figure 8**). The formulated resist patterns did not peel off the Si substrates in the 100 nm dimension. Thus, the acid cleavage of the two protective groups proved to be extremely effective for achieving high sensitivity and high resolution.

3.1.6 Dry-etch resistance

A dry-etch resistance comparable to that of traditional "aromatic" resists is necessary for such an aliphatic resist. The dry-etch rates of polymer C, PMMA (aliphatic methacrylate), and a novolak resist were investigated in CF_4, Ar, and Cl_2 plasmas. The results indicated that polymer C has a dry-etch resistance that is nearly comparable to that of the novolak resist in CF_4 and Ar plasmas (**Table 3**). Hence, we believe that the resin has an acceptable dry-etch resistance for use as a photoresist.

3.2 EB resist

3.2.1 Polymer design

We incorporated the acid-cleavable adamantyl groups into our PVP-based polymers.$^{19),20)}$ As mentioned above, the incorporation of the adamantyl groups in PVP resists can be effective for use in EPL. These strongly hydrophobic groups reduce the ADR (alkali dissolution rate) of the resists with only a small amount of loading to the PVP-based polymer. As a result, there is a greater dissolution rate change at exposed regions, even though the deprotection of these strongly hydrophobic groups is small. This can be beneficial for both the resolution and the sensitivity. Furthermore, the etch resistance makes it easier to reduce the film thickness of the resist to attain superior resolution as well as higher sensitivity.

3.2.2 Dissolution inhibition

The ADRs of poly (VP_{50}-$tBuA_{50}$), poly (VP_{79}-$MAdMA_{21}$), and poly (VP_{79}-$EAdMA_{21}$) were measured in a 4% TMAH solution to compare the dissolution inhibitions. In the case of poly (VP_{50}-$tBuA_{50}$), the ADR decreased from 10^5 Å/s (PVP) to 4.7 Å/s when a 50 mol% tBu group was incorporated into the polymer. On the other hand, in the case of polymers containing MAd (2-methyl-2-adamantyl) and EAd (2-ethyl-2-adamantyl), it was possible to reduce

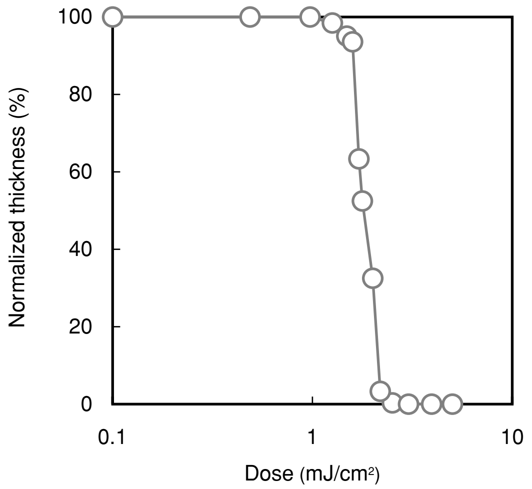


Figure 7
Exposure response curve for ArF exposures of poly ($MAdMA_{49}$-$MLMA_{51}$)-based resist.
The sensitivity was 2.5 mJ/cm^2.

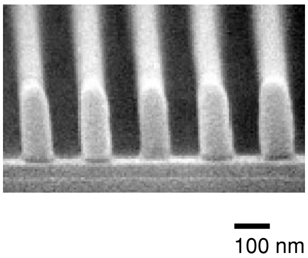


Figure 8
A 100 nm L/S pattern obtained with poly ($MAdMA_{49}$-$MLMA_{51}$)-based resist using 2/3 annular illumination.
The sensitivity was 15.5 mJ/cm^2.

Table 3
Dry-etch rates of polymer C and PMMA relative to Novolak resist.

Polymer	$CF_4$$^{\text{note 1)}}$	Ar$^{\text{note 1)}}$	$Cl_2$$^{\text{note 2)}}$
Novolak	1.0	1.0	1.0
PMMA	1.4	2.0	2.5
poly($MAdMA_{51}$-$MLMA_{49}$)	1.1	1.2	1.3$^{\text{note 3)}}$

note 1) 100 sccm, 0.02 Torr, 200 W, 5 minutes, note 2) 30 sccm, 0.02 Torr, 200 W, 3 minutes, note 3) MAdMA/MLMA = 56/44.

the ADRs to 5.9 Å/s and 2.0 Å/s, respectively, when 21 mol% of the adamantyl groups was incorporated (**Figure 9**). These results indicate that the adamantyl groups have a stronger dissolution inhibition than the tBu group. We consider that the highly hydrophobic nature and bulky structure of the adamantyl groups induce this stronger dissolution inhibition. Thus, a large polarity change can be obtained with a small amount of deprotection, and therefore a superior contrast between exposed and unexposed regions and a superior resolution can be achieved.

3.2.3 Deprotection of protective groups

The deprotection conversion induced by DCl treatment and heating was calculated for tBuMA, MAdMA, and EAdMA monomers using the integral values obtained in NMR spectroscopy. The deprotection conversion was calculated using the ratio of integral values obtained between the deprotected material and unchanged monomer (**Table 4**). The reactivity relative to the tBu group was 3.4 for the EAd group and 1.3 for the MAd group. The EAd group's deprotection conversion was 2.5 times higher than that of the MAd group under this condition. These results indicate that the high reactivity of the EAd group is produced by the stability of the intermediate in the deprotection reaction and the stability of the deprotected 2-ethenyladamantane. The MAd group has three protons in the methyl group which stabilize the carbonium ion on the intermediate by hyperconjugation, while the EAd has two protons and a methyl group in the ethyl substituent. The inductive effect of the methyl group in the ethyl substituent stabilizes the carbonium ion on the intermediate. We believe that the stabiliza-

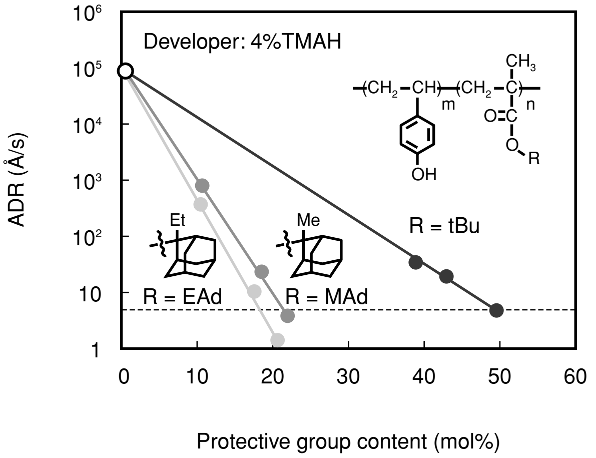
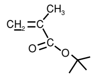
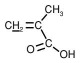
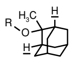
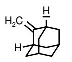
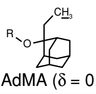
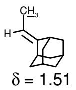
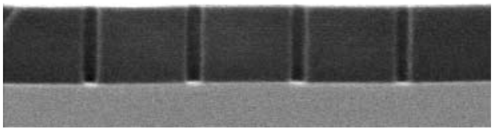


Figure 9
Dissolution rate changes of VP-protected methacrylate copolymers in a 4% TMAH solution.

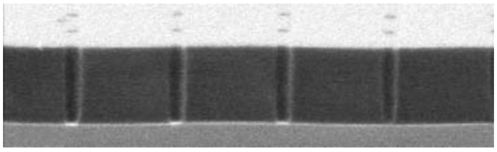
Table 4
Deprotection conversion of the protective groups.

Starting monomer (δ in ppm)	Product	Integral values monomer/product	Deprotection conversion (%)	Relative reactivity
 tBuMA (δ = 5.92)	 δ = 5.98	1.25/0.27	18	1.0
 MAdMA (δ = 2.27)	 δ = 2.46	0.38/0.12	24	1.3
 EAdMA (δ = 0.73)	 δ = 1.51	0.29/0.46	61	3.4

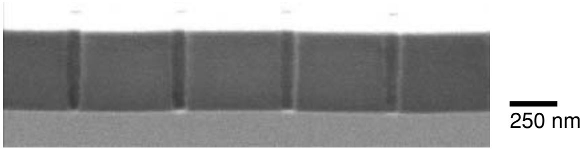
R = methacyl



(a) poly (VP$_{50}$-tBuA$_{50}$), 110 nm (9.0 μC/cm^2)



(b) poly (VP$_{79}$-MAdMA$_{21}$), 104 nm (9.0 μC/cm^2)



(c) poly (VP$_{79}$-EAdMA$_{21}$), 98 nm (6.0 μC/cm^2)

Figure 10
Hole patterns delineated by 50 keV EB exposures.

tion due to the inductive effect of the methyl group is stronger than that of the hyperconjugation of the protons. Additionally, the substituent-rich structure of 2-ethenyladamantane is more thermodynamically stable than that of 2-methyleneadamantane. Therefore, EAd shows a higher reactivity than MAd. Although these results imply acidic hydrolysis of the protective groups, they also to some extent elucidate the reactivity of the protective groups.

3.2.4 Lithographic performance for EB exposures

We made a preliminary investigation of the lithographic performance of the tBu-, MAdMA-, and EAdMA-incorporated resists. **Figure 10** shows SEM micrographs of delineated hole patterns. The poly (VP_{50}-$tBuA_{50}$)-based resist resolved 110 nm at 9.0 μC/cm^2, the poly (VP_{79}-$MAdMA_{21}$)-based resist resolved 104 nm at 9.0 μC/cm^2, and the poly (VP_{79}-$EAdMA_{21}$)-based resist resolved 98 nm at 6.0 μC/cm^2. The poly (VP_{79}-$EAdMA_{21}$)-based resist displayed the highest resolution and sensitivity, which is in accord with the descriptions of the EAd group's characteristics given in Sections 3.2.2 and 3.2.3. We also used the poly (VP_{79}-$EAdMA_{21}$)-based resist to produce line and space (L/S) patterns (**Figure 11**). The resist resolved 120 nm L/S patterns at 9.0 μC/cm^2 with a 0.5 μm thickness, which demonstrates that the resist can be used for both hole and L/S patterns. By optimizing the material composition of the poly (VP-MAdMA)-based resist and the process conditions, we resolved a 59 nm hole pattern at 6.0 μC/cm^2 (**Figure 12**).

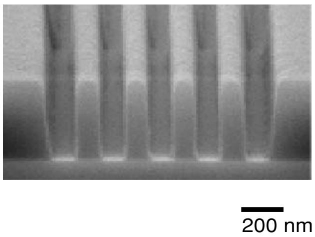


Figure 11
A 120 nm L/S pattern obtained for poly (VP_{79}-$MAdMA_{29}$)-based resist printed by 50 keV EB exposures.
The exposure dose was 9.0 μC/cm^2.

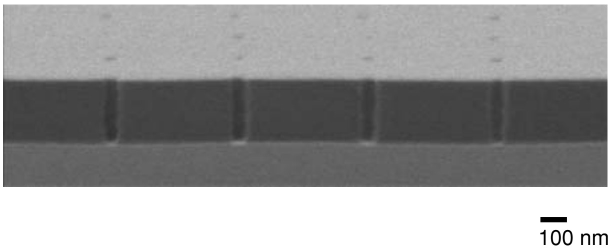


Figure 12
59 nm hole patterns for poly (VP-MAdMA)-based resist printed by 50 keV EB exposures.
The exposure dose was 6.0 μC/cm^2.

3.2.5 Dry-etch resistance

The dry-etch rates of poly (VP_{50}-$tBuA_{50}$), poly (VP_{79}-$MAdMA_{21}$), poly (VP_{79}-$EAdMA_{21}$), and PVP were investigated for comparison with novolak resist using a magnetron reactive ion etcher under oxide etch conditions (**Table 5**).

The acyclic tBu group resist showed the fastest dry-etch rate. On the other hand, the EAd group resist displayed a slower dry-etch rate than PVP. Note that the higher EAd unit concentration reduces the dry-etch rate. As a result, the dry-etch resistance of poly (VP_{79}-$EAdMA_{21}$) is about 1.3 times higher than that of poly (VP_{50}-$tBuA_{50}$) and 1.1 times higher than that of PVP. These results indicate that, compared with the poly (VP_{50}-$tBuA_{50}$)-based resist, we can use the new resist in pattern fabrication at a 30% reduced film thickness and consequently achieve a higher sensitivity and higher resolution.

Table 5
Relative etch rates of VP-based resists.

Polymer	Relative etch rate$^{note)}$
Novolak	1.00
PVP	1.07
poly (VP_{50}-$tBuA_{50}$)	1.33
poly (VP_{79}-$EAdMA_{21}$)	0.98
poly (VP_{56}-$EAdMA_{44}$)	0.96

note) Ar 200 sccm, C_4F_8 10 sccm, O_2 20 Sccm, 0.5 Pa, 400 W

4. Summary

High-performance resist materials for ArF and EB lithography were described. The base polymer for the ArF resist comprises two different acid-cleavable protective groups, 2-methyl-2-adamantyl and mevalonic lactone, in the side chain of a methacrylate polymer. The impact of these protective groups on lithography are that they 1) are compatible with the standard 2.38% TMAH developer, 2) provide good adhesion to resist patterns, 3) resolve 100 nm L/S patterns, and 4) provide an acceptable dry-etch resistance comparable to that of a novolak resist. The acid cleavage of both the adamantyl and the lactone groups induces a large polarity change in the exposed regions, yielding a high contrast and resolution.

For the EB resist, ethyl- or methyl-substituted adamantyl groups were applied to the base polymer. The strong hydrophobicity and bulky structure of these groups afford a strong dissolution inhibition, which enables us to obtain a greater change in the alkali dissolution rate, even with the small deprotection of these groups. NMR spectroscopy revealed that the adamantyl groups have a higher acid-reactivity than the tBu group. These characteristics contribute toward a high resolution as well as a high sensitivity. The adamantyl groups also impart a higher etch-resistance, enabling film thickness to be reduced for superior resolution and higher sensitivity. An optimized poly (VP-MAdMA)-based resist can clearly resolve 59 nm hole patterns.

These ArF and EB resists are already being used to fabricate devices having 100 nm dimensions and beyond.

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