Design and Synthesis of New Photoresist Materials for ArF Lithography

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ABSTRACT: A new class of photoresist matrix polymers based on vinyl ether–maleic anhydride (VEMA) alternating copolymers was developed for ArF single-layer lithography. These polymers were synthesized by copolymerization of alkyl vinyl ether and maleic anhydride alternating copolymers with acrylate derivatives containing bulky alicyclic acid-labile protecting groups. The resulting polymers showed good control of polymerization and high transmittance. Also, these resists exhibited good adhesion to the substrate, high dry-etching resistance against CF_4 mixture gas (1.02 times the etching rate of deep UV resist), and high selectivity to silicon oxide etching. Using an ArF excimer laser exposure system with 0.6 NA, 120-nm L/S patterns were resolved under conventional illumination. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 165–170, 2004

Key words: block copolymers; lithography; photochemistry; photoresists

INTRODUCTION

ArF lithography using chemically amplified resists has been regarded as one of the most promising technologies for producing patterns below 0.15 μm.[1–11] However, a number of fundamental challenges exist in designing photoresist materials for 193-nm lithography such as transmittance, dry-etch resistance, adhesion, resolution, contrast, and line-edge roughness (LER). Currently, one of the most crucial challenges among them is the reactive ion-etch (RIE) resistance. Another important challenge is the LER for patterned resist film in the dry-etching process.

During the last several years, researchers have developed several classes of new polymer-functionalized polymethacrylate, cycloolefin–maleic anhydride (COMA), and polynorbornene chemistry for use in 193-nm lithography.[12–18] Generally, polymethacrylates are readily synthesized with good control and exhibit excellent resolution. However, these polymers are quite limited in oxide-etch resistance, with difficulty in controlling the LER. On the other hand, compared to polymethacrylates, COMA-based alternating copolymers show good oxide etch resistance, but the latter have some significant problems such as difficult control of the polymerization and molecular weight and poor polymerization yields and low transmittance of the resin.

Previously, we reported COMA-based alternating copolymers with functionalized norbornene derivatives, which showed good lithographic performance.[19] However, these designs showed moderate dry-etching resistance and poor shelf-life stability, due to the hydrolysis of the maleic anhydride moiety with the hydroxy group in the resin system.[13,14] Also, the glass transition temperature (T_g) of these COMA systems were in the range of 200–230°C, due to a rigid polymer backbone, and they are inappropriate for the high baking process, which prevents airborne contamination of the resist film and shows a good postexposure baking (PEB) delay effect. Thus, new polymers having a more flexible backbone than that of a COMA-based polymer are needed to lower the T_g.

To solve the above problems, we designed and synthesized new chemically amplified ArF single-layer photoresist materials based on vinyl ether–maleic anhydride (VEMA) alternating copolymers for 193-nm lithography. Compared to COMA systems, these VEMA systems have a more flexible backbone, better adhesion, and higher polymerization yields.

EXPERIMENTAL

Materials

The photoacid generators (PAGs), triphenylsulfonium (TPS) triflate, and TPS nonaflate were purchased from

(a)

Poly(DHP-*alt*-MA-co-ETCDA)   Poly(DHEP-*alt*-MA-co-ETCDA)
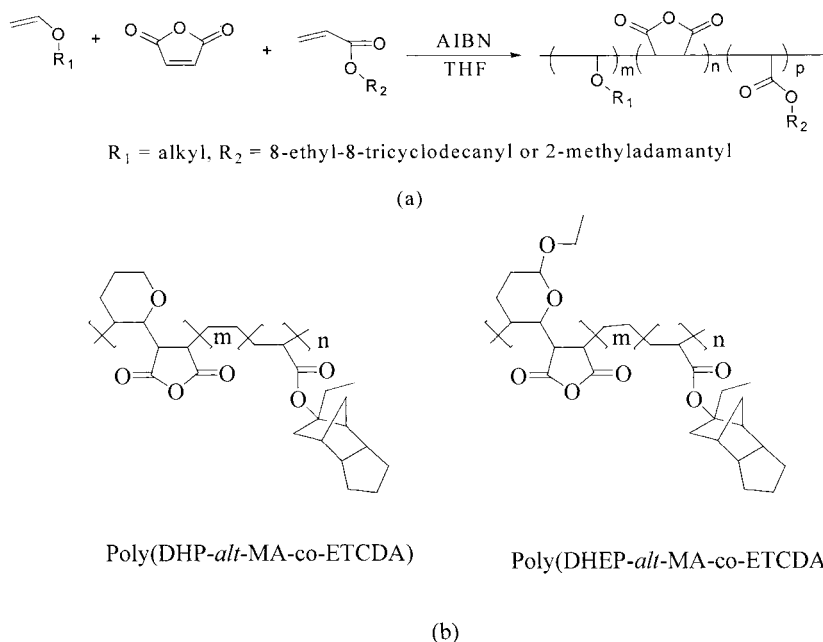
(b)

Figure 1 Chemical structures of (a) poly(VE-*alt*-MA-*co*-tAA) and poly(DHP-*alt*-MA-*co*-ETCDA) and (b) poly(DHEP-*alt*-MA-*co*-ETCDA).

the Midori Kagaku Co., and the radical initiator, 2,2′-azobisisobutyronitrile (AIBN), was purchased from the Aldrich Chemical Co. Maleic anhydride (MA), 3,4-dihydro-2-ethoxy-2*H*-pyran (DHEP), and 3,4-dihydro-2*H*-pyran (DHP) were purchased from the Aldrich Chemical Co. and used without further purification. 8-Ethyl-8-tricyclodecanyl acrylate (ETCDA) and 2-methyl-2-adamantyl acrylate were synthesized by a one-step esterification reaction of the corresponding alcohols with acryloyl chloride in the presence of triethylamine and purified by column chromatography.

Synthesis of poly(vinyl ether-*alt*-maleic anhydride-*co-tert*-alkyl acrylate) [poly(VE-*alt*-MA-*co*-tAA)]

Chemical structures of poly(VE-*alt*-MA-*co*-tAA) are shown in Figure 1(a). In Figure 1(a), alkyl vinyl ethers were linear, and cyclic vinyl ether and the alkyl group were acid-labile alicyclic groups such as the 8-ethyl-8-tricyclodecanyl and 2-methyl-2-adamantyl groups. The polymers were synthesized by free-radical terpolymerization using AIBN as the polymerization initiator in THF. The monomers were mixed at the desired ratios and dissolved in a solvent to obtain a monomer concentration of 20–50% by weight. Free-radical initiators, 2–6 mol % (versus monomer), were added to the monomer solution, if needed, along with small amounts of a chain-transfer agent. The polymerization was carried out at 65°C for 24 h and then the polymers were separated by repeated precipitation in isopropyl alcohol and subsequently dried at 50°C under a vac-
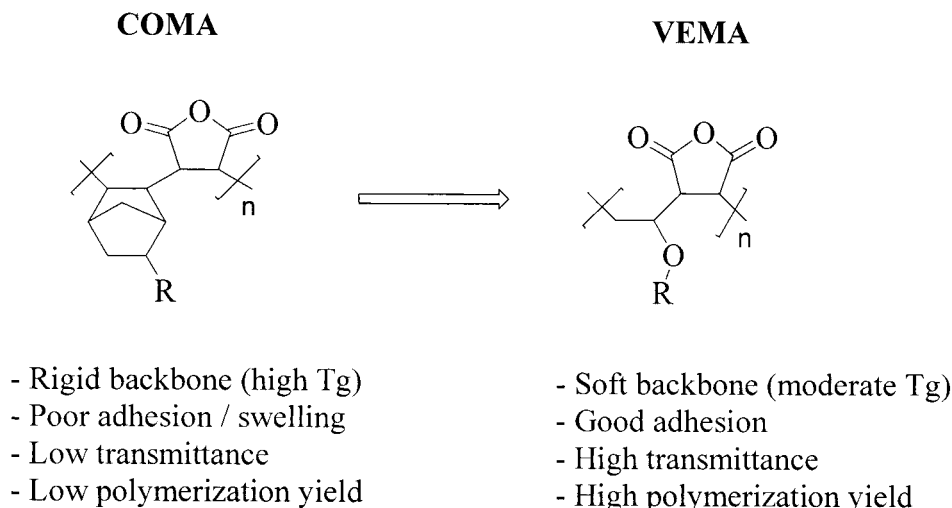
uum [yield: 65–75%, weight-average molecular weight (M_w): 7,000–13,000, polydispersity: 1.8–2.0].

Characterization

A ^{1}H-NMR spectrum was obtained by a Bruker AC 300-MHz instrument. UV-visible absorption spectra were measured by a Jasco V-560 spectrometer, and FTIR spectra were obtained by a Nicolet Magna 550 instrument. The weight-average molecular weights (M_w) and polydispersities were determined in the THF solvent with a Hewlett–Packard 1050, calibrated with polystyrene standards. Thermal properties were analyzed with a Polymer Laboratories STA 625 at a heating rate of 10°C/min. Dry-etching was performed with an RIE system (Rainbow 4500: $CF_4/CHF_3/Ar$ = 10/10/300 sccm, 700 W, 150 mTorr, 120 s).

Lithography

Resists were formulated by dissolving the polymer (12–15 wt %), TPS triflate or TPS nonaflate (1–2 wt % for the polymer), and a base additive (10–30 mol % for PAG) in propylene glycol monomethyl ether acetate; then, the solution was filtered in a 0.2-μm Teflon membrane filter. Resist films were coated to a 0.25–0.35-μm thickness on a silicon substrate and soft-baked at 120–140°C for 90 s. Exposure was conducted using an ArF exposure system (ISI, NA 0.6). Exposed resists were baked at 110–140°C for 60 s on a hot plate,

COMA   **VEMA**

- Rigid backbone (high Tg)
- Poor adhesion / swelling
- Low transmittance
- Low polymerization yield

- Soft backbone (moderate Tg)
- Good adhesion
- High transmittance
- High polymerization yield

Scheme 1

then developed in a 2.38 wt % tetramethylammonium hydroxide (TMAH) aqueous solution for 60 s.

RESULTS AND DISCUSSION

There has been much interest in the radical copolymerization of MA with cycloolefins such as norbornene derivatives, which yield an alternating copolymer, probably via the formation of a donor–acceptor complex between both monomers. As a rule, COMA-based alternating copolymers yield a high glass transition temperature (T_g) with a 1:1 alternating structure, which are in the range of 200–230°C. On the other hand, copolymerization of MA with vinyl ether (VE) derivatives yields a more flexible VEMA-based copolymer backbone, which has a moderate T_g, such as 160–180°C, with a perfect 1:1 alternating structure.

Scheme 1 shows the design concept of our base polymer, a VEMA-based alternating copolymer. Generally, in the case of COMA-based copolymers, some problems exist in the physical properties, such as a high T_g, poor adhesion to a substrate, and a low polymerization yield. To solve these problems, it is necessary to change the physical properties of the COMA-based copolymer to the more flexible alkyl vinyl ether

backbone, which results in a moderate T_g. Therefore, our study used a VEMA-based alternating copolymer as the base resin, which has a more flexible backbone than that of a COMA-based copolymer. It also showed good adhesion to the substrate and a high polymerization yield, compared to COMA-based copolymers. We also introduced terpolymer systems to improve the dry-etch resistance and resist performance. The terpolymers consisted of VEMA-based alternating copolymers and bulky acid-labile alicyclic acrylate derivatives.

Figure 1(b) shows the chemical structures of terpolymer systems. DHP and DHEP were used as an alkyl vinyl ether. The bulky protecting groups, 8-ethyl-8-tricyclodecanyl and 2-methyl-2-adamantyl groups, were introduced to improve the dry-etch resistance of the resists. The terpolymers were synthesized by radical polymerization of DHP, MA, and ETCDA using AIBN as an initiator. The feed ratios of the monomers during the polymerization reaction were important for achieving good adhesion and high etch resistance of the resist. In particular, the feed ratio of DHP:ETCDA was very important for obtaining good lithographic performance. The polymerization results of poly-(DHP-alt-MA-co-ETCDA) are summarized in Table I.

TABLE I
Polymerization Results of DHP, MA, and ETCDA

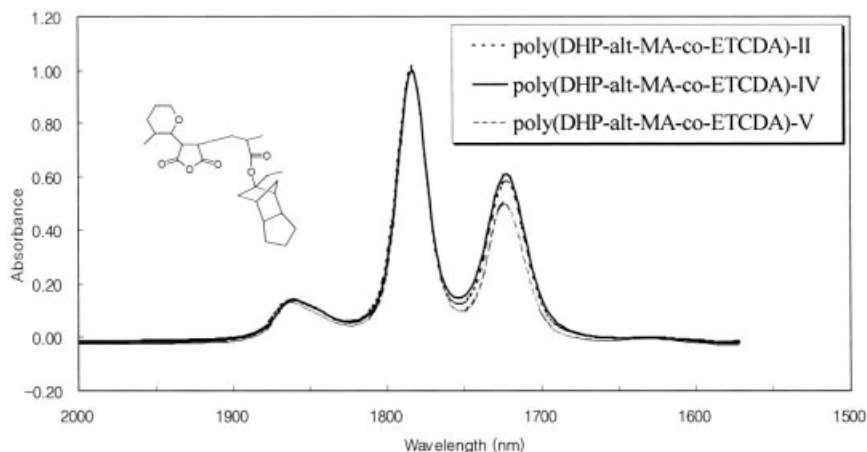| Polymer	Feed ratio	AIBN (mol %)	M_w	PDI	Yield (%)	Transmittance (%/0.5 μm)
Poly(DHP-alt-MA-co-ETCDA)-I	1:8:4	2	12,200	1.8	70	72
Poly(DHP-alt-MA-co-ETCDA)-II	1:8:3	2	11,690	1.7	73	70
Poly(DHP-alt-MA-co-ETCDA)-III	1:8:5	2	13,300	1.9	70	74
Poly(DHP-alt-MA-co-ETCDA)-IV	1:6:3	2	8400	1.8	69	71
Poly(DHP-alt-MA-co-ETCDA)-V	1:1:1	4	7900	1.8	66	70
Poly(DHEP-alt-MA-co-ETCDA)-I	1:6:3	5	8100	1.9	69	71

Figure 2 FTIR spectra of poly(DHP-*alt*-MA-*co*-ETCDA).

Poly(DHP-*alt*-MA-*co*-ETCDA) showed a good polymerization yield (~70%) and the molecular weights of the polymers were also controllable. The weight-average molecular weight (M_w) and the polydispersity of the terpolymers were in the range of 8.1–13.3 × 10³ and 1.7–1.9, respectively. The UV transmittance at 193 nm was sufficient to be used for ArF single-layer resists.

Figure 2 shows the FTIR spectra of poly(DHP-*alt*-MA-*co*-ETCDA). The strong carbonyl bands at 1860, 1780, and 1725 cm^{-1} indicate the successful formation of the terpolymer, as shown in Figure 1(b). The intensity of the ETCDA peaks in the FTIR spectra shows a relative quantity of ETCDA in the terpolymer, based on the quantity of the MA. The lithographic performance of the resist was also evaluated. The contrast of the resists based on poly(DHP-*alt*-MA-*co*-ETCDA)-II, -IV, and -V were measured. Figure 3 shows the contrast curves of the resists [130°C–90 s for soft baking and 110°C–60 s for postexposure baking, (PEB)]. TPS triflate (1 wt % for the resin) was used as a PAG. The
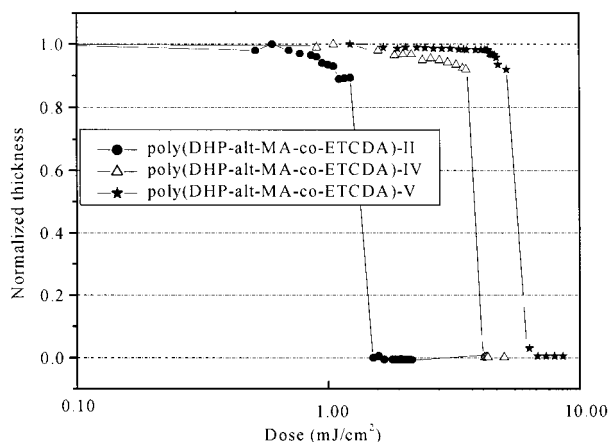
resists showed good contrast and sensitivity. The lithographic performance was studied using an ArF exposure system (ISI, NA 0.6) with a conventional illumination.

Figure 4(a) shows an SEM micrograph of the poly(DHP-*alt*-MA-*co*-ETCDA)-IV resist formulated with TPS triflate/nonaflate (1.0/1.0 wt % for the resin) and a base additive having thicknesses of 3400 and 2700 Å. AR-19 (Shipley Co.) was used as a bottom antireflection coating (BARC). The optimum PEB temperature was 110°C. Good pattern profiles with vertical sidewalls were achieved at 17 mJ/cm² with a 2.38 wt % TMAH aqueous solution for 60 s. It was clearly shown that the resist has good sensitivity and high performance as a single-layer resist for ArF lithography. The 120-nm L/S patterns were resolved at a 2700-Å film thickness. The minimum resolution was increased to 120 nm with a decreasing resist thickness. Figure 4(b) shows an SEM micrograph of the poly(DHP-*alt*-MA-*co*-ETCDA)-V resist with TPS triflate/nonaflate (1.0/0.5 wt %) of a 3000-Å thickness at a 36 mJ/cm² dose. The resolution was similar to that of the poly(DHP-*alt*-MA-*co*-ETCDA)-IV resist, meaning that the alkyl vinyl ether moiety in our terpolymer systems works well as an adhesion promoter regardless of the portion of the acrylate. Instead of DHP, DHEP was tested as an adhesion promoter in the terpolymer systems. Figure 4(c) shows the patterning result of the poly(DHEP-*alt*-MA-*co*-ETCDA) resist with TPS triflate (1.0 wt % for the resin) using conventional illumination. The profile of the resist showed a T-top profile, due to the hydrophobicity of the resin compared to the poly(DHP-*alt*-MA-*co*-ETCDA)-IV resist.

The dry-etch resistance of poly(DHP-*alt*-MA-*co*-ETCDA) was investigated under a silicon oxide-etching condition. Figure 5 shows the relative etch rate of the polymers to the deep UV (DUV) resist and SEPR-430S (ShinEtsu Chemical Co.) for comparision. Under
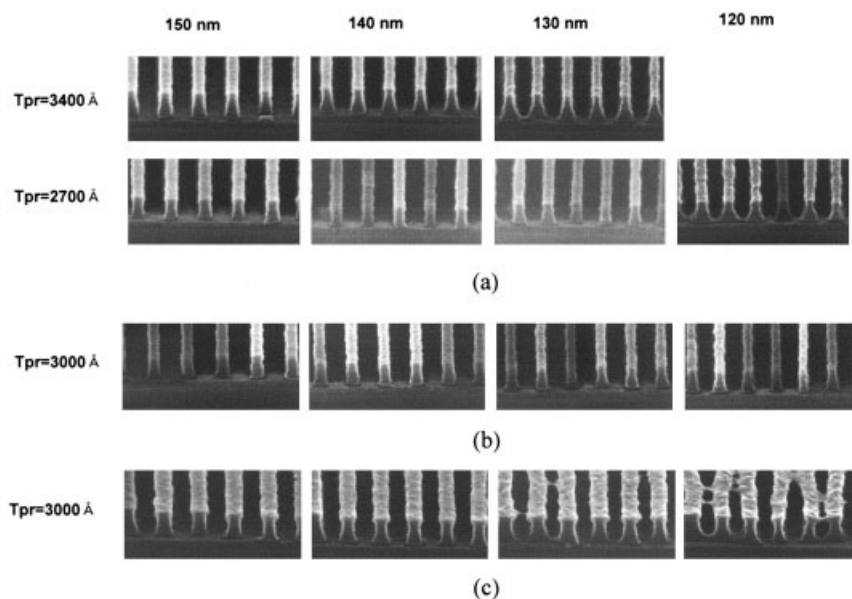

Figure 3 Contrast curves of poly(DHP-*alt*-MA-*co*-ETCDA).

Figure 4 Lithographic performance of (a) poly(DHP-*alt*-MA-*co*-ETCDA-IV, (b) poly(DHP-*alt*-MA-*co*-ETCDA)-V, and (c) poly(DHEP-*alt*-MA-*co*-ETCDA) on the BARC (BARC: AR19, S/B: 130°C–90 s, PEB: 110°C–60 s).

conventional etch conditions, the etch rates of some ArF resists are usually similar to that of the Novolak resin. However, under oxide-etch conditions, most ArF resists are weaker than are DUV resists. As shown in Figure 5, the etch-rate ratio of our terpolymers [poly(DHP–MA–ETCDA)-II, -IV, and -V] is about 1.02–1.08 times greater than that of a DUV resist, while the methacrylate-based polymer (MAP; Fujitsu) and the COMA-based copolymer (tBNC-MA; IBM, Almaden, CA) have less dry-etch resistance (1.23 and 1.38 times, respectively). This demonstrates that the etch
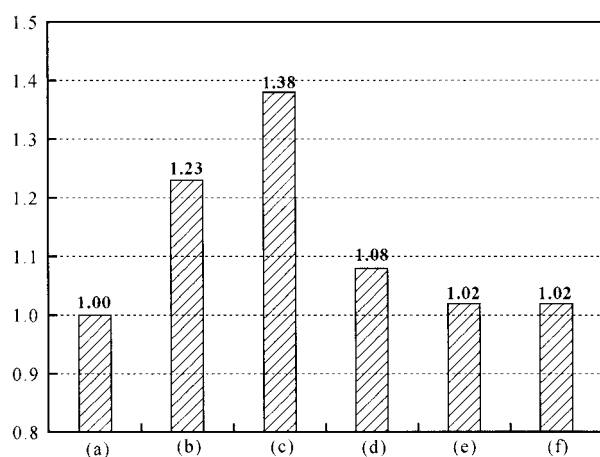

Figure 5 Etching rate of poly(DHP-*alt*-MA-*co*-ETCDA) normalized to DUV resist (condition: $CF_4/CHF_3/Ar = 10/10/300$ sccm, 150 mTorr, 700 W, 120 s): (a) SEPR-430S; (b) MAP; (c) tBNC; (d) poly(DHP-*alt*-MA-*co*-ETCDA)-II; (e) poly(DHP-*alt*-MA-*co*-ETCDA)-IV; (f) poly(DHP-*alt*-MA-*co*-ETCDA)-V.

resistance of poly(DHP-*alt*-MA-*co*-ETCDA) is sufficient for application in the real printing of a device. Under oxide-etching conditions, the first obvious discrimination in the resists is the difference in the relative etching rates, with the COMA-based resists etching up to 40% faster than VEMA-based resists. Although some improvement has been made in the oxide-etching rate for more advanced acrylate-based resists, etching rates are 20% faster than those of VEMA-based resists.

Figure 6 shows the L/S patterns of poly(DHP-*alt*-MA-*co*-ETCDA)-IV and MAP that were obtained before and after the etching under oxide-etch conditions. The tetraethylorthosilicate (TEOS) thickness was 5000 Å. The thickness of the resist was 4000 and 2700 Å for poly(DHP-*alt*-MA-*co*-ETCDA)-IV and MAP, respectively. The etching depth was 3000 Å. In the case of MAP, most of the oxide patterns eroded due to the poor dry-etch resistance of the resist patterns with 3000 Å of the P-TEOS layer being etched. In contrast, all the resist patterns of poly(DHP-*alt*-MA-*co*-ETCDA)-IV with vertical oxide patterns remained during the oxide etching, due to good dry-etch resistance. We also investigated line-width slimming for a VEMA- and an acrylate-based resist under the beam power of 400 eV. The acrylate-based resist performed rather poorly with over 20 nm of line slimming occurring. However, the VEMA-based resist performed much better than that of the acrylate-based resist with about 10 nm of line slimming occurring. The etch condition was optimized to obtain the better profiles. It is believed that our new VEMA-based polymer system is a
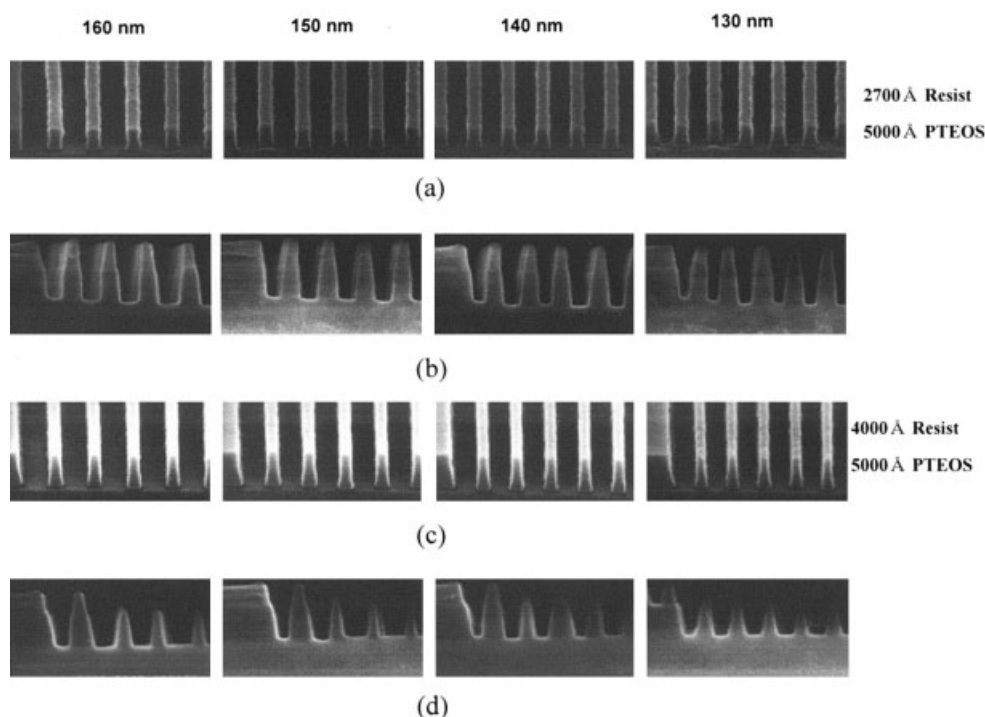
Figure 6   SEM images of L/S patterns of poly(DHP-*alt*-MA-*co*-ETCDA)-IV and acrylate-based resist (MAP) (a,c) before and (b,d) after oxide etching (etching condition: $CF_4/CHF_3/Ar$ = 10/10/300 sccm, 150 mTorr, 700 W, 60 s).

strong candidate for an ArF single-layer system.

CONCLUSIONS

This study synthesized novel resist materials based on VEMA-based alternating copolymers with excellent dry-etch resistance and high resolution. VEMA-based terpolymers were synthesized by radical polymerization of VEMA-alternating copolymers, and bulky acid-labile alicyclic acrylates showed good adhesion to the substrate and good control of the polymerization. The resists with VEMA-based terpolymers exhibited good resolution down to 120-nm L/S patterns with conventional illumination. Also, these resists showed good dry-etch resistance with 1.02 times the etch rate of the DUV resist using an oxide-etching condition, and the pattern profiles were maintained during P-TEOS etching.

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