

Alicyclic Polymers for 193 nm Resist Applications: Lithographic Evaluation

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Photoresist compositions designed for 193 nm lithography were formulated from a series of cycloaliphatic co- and terpolymers of 2-methylpropyl bicyclo[2.2.1]hept-5-ene-2-carboxylate (trivial name, carbo-*tert*-butoxynorbornene), bicyclo[2.2.1]hept-2-enecarboxylic acid (trivial name, norbornene carboxylic acid), 8-methyl-8-carboxytetracyclo[4.4.0.1,^{2,5}1^{7,10}]dodec-3-ene (trivial name, methyltetracyclododecene carboxylic acid), 5-norbornene-2-methanol, and maleic anhydride, which were synthesized by free radical, Pd(II)-catalyzed addition and ring-opening metathesis polymerization techniques. The cycloaliphatic polymer backbones provide etch resistance, mechanical properties, and stability to radiation. The lithographic function is provided by carefully tailored pendant groups, which include an acid functionality that is masked by protecting groups that undergo acid-catalyzed thermolysis, as well as polar groups that influence the adhesion, wettability, and dissolution properties of the polymer. The polymers are soluble in common organic solvents and have glass transition temperatures ranging from less than 60 °C to higher than 250 °C depending on the specific structure and mode of polymerization. The polymers are as transparent at 193 nm as the corresponding acrylics. The dry etch resistance of these polymers varies with the formulation, but the polymers etch more slowly than APEX-E, a commercial deep UV photoresist under conditions typically used to pattern polysilicon. Upon exposure and baking, the resists have demonstrated high sensitivities (3–15 mJ/cm²), and 0.16 μm features have been resolved.

Introduction

Photolithography at 193 nm lithography based on ArF lasers¹ is a promising technology for printing devices with 130 nm dimensions.² Printing sub-100 nm features using 193 nm lithography will most likely be possible with the aid of resolution enhancement techniques involving phase shift mask³ and optical proximity correction. Most of the integrated circuits that are produced today are printed with I-line (365 nm) exposure technology and have minimum dimensions of around 350 nm. The very latest generation of integrated circuits are being printed with 248 nm light from KrF lasers at minimum dimensions of approximately 250 nm. Manufacturing devices with minimum features of 150 nm is planned, but considered to be beyond the limits of both the I-line and KrF lithographic technologies.

The basis of the relentless drive to develop lithographic technologies using ever shorter wavelengths can be understood on the basis of eq 1, which relates the resolution (R) of the lens at the diffraction limit to the exposure wavelength (λ), the numerical aperture (NA), and a proportionality constant (k_1). Under practical

$$R = k_1 \frac{\lambda}{NA} \quad (1)$$

conditions, k_1 depends on factors such as lens aberrations, illumination, mask, patterns, exposure tool conditions, resist process, and even the operator.⁴ In theory, the value of k_1 must be greater than 0.5.

Reduction in the exposure wavelength provides higher resolution. The ability to manufacture devices with smaller circuit elements enables improved integration with corresponding increases in performance—at lower cost. The drive for improved resolution is well justified.

The implementation of lithography at 193 nm is a major technological challenge. Even the best lens materials absorb significantly at this wavelength. Excellent 193 nm lens systems have been constructed but the damage threshold for the glass limits the exposure power that can be delivered to the wafer.⁵ Hence, highly sensitive resists will be required to enable 193 nm imaging technology.

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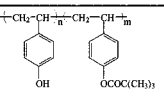
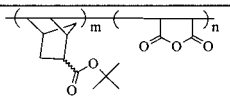
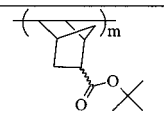
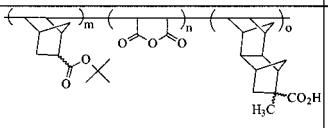
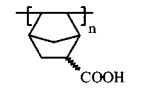
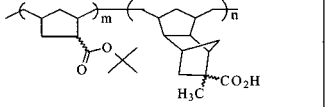
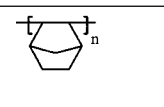
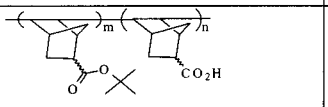
(1) Unfortunately, the widely used misnomer “excimer laser” appears in the literature to describe ArF*, KrF* (lasing at 248 nm), and XeCl* (lasing at 308 nm). These lasers are more accurately described as “exciplex lasers.”

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Table 1. Etch Rate Data of Representative Resist Polymers^a

Resist Material	Etch Rate	Resist Material	Etch Rate
 APEX-E	1.00	 Poly(CBN- <i>alt</i> -MAH)	1.05
 Poly(CBN)	0.85	 Poly(CBN- <i>alt</i> -MAH- <i>alt</i> -MTDC)	0.94
 Poly(NBCA)	0.75	 Poly(CBN- <i>co</i> -MTDC)	0.80
 Poly(NBE)	0.31	 Poly(CBN- <i>co</i> -NBCA)	0.90

^a Measurements were made relative to APEX-E DUV resist.

Resist materials designed for 193 nm exposure must have not only very high sensitivity, the resists must have high transparency at the exposure wavelength and stability to reactive ion and plasma etching conditions. The discovery of dry etch-resistant, nonaromatic materials by Kaimoto et al.⁶ in 1992 created a new perspective on the design of resist materials and has had a particularly important influence on the design of materials for 193 nm lithography. In this paper, we report lithographic studies of a series of new, single-layer, chemically amplified, positive tone resists for 193 nm imaging. These resists were formulated from a series of cycloaliphatic co- and terpolymers synthesized by (1) Pd(II)-metal-catalyzed addition polymerization, (2) free radical polymerization, and (3) ring-opening metathesis polymerization (ROMP). The ROMP polymers were hydrogenated, using diimide, produced in situ from hydrazine. The structures of typical resist polymers are shown in Table 1. The cycloaliphatic backbone of these polymers provides dry etch-resistance and thermal stability and serves to tether the pendant functionalities required for imaging.

Photoresist Chemistry. In general, photoresists function by radiation-induced changes in the dissolution rate of the polymer resin from which they are made. Negative resists become less soluble upon exposure to

radiation; that is, the unexposed areas can be selectively removed by immersion in an appropriate solvent (developer.) Positive resists undergo an increase in solubility rate upon exposure, enabling the exposed areas to be selectively removed by the developer. Both types of resists are formulated from polymers designed to have physical and chemical properties consistent with semiconductor processing. Details of these processes are described by Moreau⁷ and Thompson, Willson, and Bowden.⁸

The new alicyclic polymer resist systems incorporate a *tert*-butyl ester pendant group and either a maleic anhydride or carboxylic acid comonomer. The role of the polar comonomers is to enhance the adhesion, wettability and the solubility of the resist material in aqueous base. The *tert*-butyl ester-protected carboxylic acid reacts with photogenerated acid in a catalytic fashion to undergo thermolysis generating acid functionality. This is the basis of the chemical amplification concept.⁹

In chemically amplified resist systems, photogenerated species within the resist catalyze subsequent chemical events that in turn modify the solubility of the resist polymer in aqueous base developer. In this way, the overall quantum efficiency of the reactions responsible for modifying the solubility of the resist polymer in the developer is greater than 1. Chemically amplified resist systems therefore have very high sensitivity. A recent review of chemically amplified resist systems has been provided by Ito.¹⁰

The alicyclic polymer-based photoresists are formulated by dissolving the polymer and a photoacid generator (PAG) such as triphenylsulfonium hexafluoroantimonate in an appropriate solvent such as propylene glycol monomethyl ether acetate (PGMEA). Spin coating the photoresist solution on a silicon wafer substrate affords a thin, uniform film. Baking at around 150 °C for 60 s removes residual solvent from the resist film. Irradiating the resist film with 193 nm light decomposes the PAG in the exposed portions of the film generating a latent image of a strong Brønsted acid. During subsequent postexposure bake at around 150 °C for 60 s, the photogenerated acid catalyzes the thermolysis of the *tert*-butyl ester pendant group (as illustrated in Scheme 1). This leads to the formation of isobutylene (a gas) and a carboxylic acid group. The deprotected polymer has a higher solubility in aqueous base than its protected precursor. Immersing the silicon wafer on which the exposed and baked photoresist is coated into an aqueous base such as tetramethylammonium hydroxide (TMAH) selectively dissolves away the exposed portions of the film, providing patterned access to the underlying substrate.

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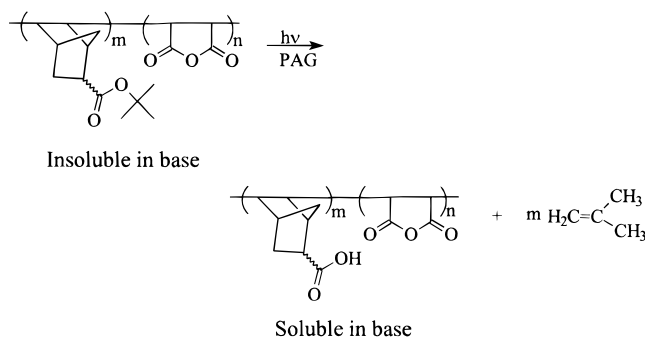
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Scheme 1



Experimental Section

Materials. Cycloaliphatic co- and terpolymers of carbo-*tert*-butoxynorbornene (CBN), norbornene carboxylic acid (NBCA), methyltetracyclododecene carboxylic acid (MTDCA), maleic anhydride (MAH), and 5-norbornene-2-methanol (NM) were synthesized by free radical, Pd(II)-complex-catalyzed addition, and ring-opening metathesis polymerization techniques, the details of which are given in an accompanying paper¹¹ and in ref 12. Triphenylsulfonium hexafluoroantimonate was prepared according to the literature procedure.¹² DUV-18 antireflection coating was obtained from Shipley Company. BARL antireflective coating was obtained from IBM Corporation. PD-523AD developer, 0.26 N aqueous tetramethylammonium hydroxide solution with surfactant, was supplied by Japan Synthetic Rubber Company. LDD-26W developer, 0.26 N aqueous tetramethylammonium hydroxide (TMAH), was supplied by Shipley Company.

Material Characterization. *IR Analyses of Resist Films.* Infrared spectra were measured using a Nicolet Magna-IR FTIR/550 spectrometer. The resist solutions were spin coated at 2500 rpm to produce $\sim 0.7 \mu\text{m}$ thick films on 8 in. double-polished silicon wafers and heated at 150 °C for 60 s (unless otherwise stated) in hard contact with the bake plate. Following exposure to known doses ranging from 0 to 50 mJ/cm² on a GCA XLS KrF (248 nm) or an ISI MicroStep (193 nm) excimer laser stepper, the wafer was baked with minimal delay (<5 min) for 60 s at 150 °C. This experiment was repeated for postexposure bake temperatures of 140, 130, and 120 °C.

Etch Rate Measurements. The dry etch-resistance of the resist polymers was determined using Lam Research Rainbow Model Plasma Etcher under Cl₂/HBr plasma conditions that are used to etch polysilicon as follows: The resist was coated on 8 in. silicon wafers to a thickness of 0.6–0.7 μm , baked at 150 °C for 60 s, and then etched under Cl₂/HBr plasma. The Cl₂ and HBr flow rates were 280 and 125 sccm, respectively. The top and bottom electrodes were maintained at 60 °C. Two samples of each resist polymer were etched for 60 s. The film thickness was measured before and after etching on a Prometrix SM-200 film thickness probe. The etch rate for each run was calculated by dividing the decrease in the thickness of the resist film by the etching time. The etch rate is reported as the average obtained from two runs on each polymer sample.

Optical Measurements. A Hewlett-Packard 8450A diode array spectrophotometer was used to obtain UV absorption spectra as follows: Polymers were dissolved in PGMEA at 16 wt % relative to solvent and spin coated at 2500 rpm on 1 in. quartz wafers and then heated at 150 °C for 60 s, after which, the thickness of the film and the UV absorbance were recorded. The film thickness was measured on a Tencor Instruments Alpha-Step 2000 profilometer. Thickness is reported as the

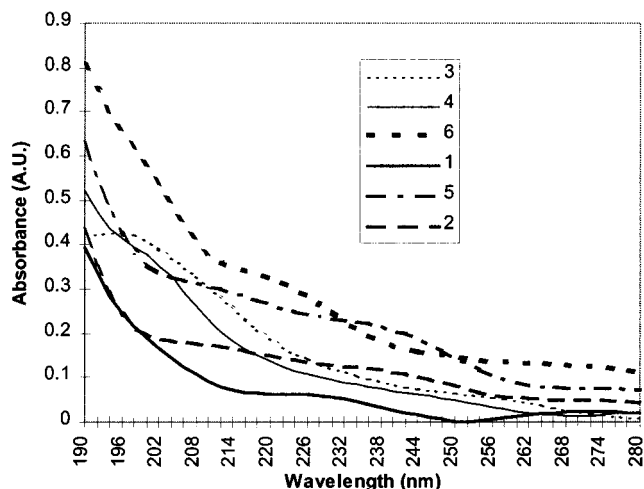


Figure 1. UV absorption spectra of 1.0 μm thick films of typical resist polymers: (1) poly(CBN-*co*-NBCA); (2) poly(CBN-*alt*-MAH); (3) poly(CBN-*co*-MTDCA), a hydrogenated ROMP polymer; (4) poly(CBN-*co*-NME); (5) poly(CBN-*alt*-MAH-*alt*-MTDCA); (6) poly(CBN-*alt*-MAH-*alt*-NBE).

average of at least three values obtained at different positions on the wafer.

A Woollam variable angle scanning ellipsometer (VASE) was used to measure the Cauchy coefficients of the photoresist compositions as follows: The photoresist solution consisting of 15 wt % of polymer relative to solvent and 3 wt % of triphenylsulfonium hexafluoroantimonate (relative to polymer weight) in PGMEA was filtered through a 0.45 μm Teflon filter. The formulations were spin coated at 2500 rpm to provide $\sim 0.4 \mu\text{m}$ thick films on silicon wafers. The postapply-bake process was 150 °C for 60 s in hard contact with the bake plate. Postexposure bake of the wafer was conducted with minimal delay (<5 min) for 60 s at 140 °C, after which the wafer was placed on the VASE tool and scanned to measure the refractive index of the film as a function of wavelength from 190 to 800 nm.

Lithographic Evaluation. All photoresist exposures were made using either an ISI MicroStep stepper with a 193 nm ArF excimer laser illumination source or a 248 nm GCA-XLS stepper with KrF excimer laser illumination source. The 193 nm stepper has a variable NA lens (experiments were conducted at 0.6 NA), a field size of 1.5 \times 1.5 mm and partial coherence of 0.7. The 248 nm stepper has a 0.53 NA lens and experiments were conducted using annular illumination with 0.5 and 0.73 inner and outer sigma. Scanning electron micrographs were recorded on an AMRAY Instruments scanning electron microscope.

The photoresist solutions were prepared as follows: The resist polymer (13–16 wt % relative to solvent) and triphenylsulfonium hexafluoroantimonate (3 wt % relative to polymer weight) were dissolved in PGMEA and filtered through a 0.45 μm Teflon filter. Several surface preparation methods were studied. These included hexamethyldisilazane (HMDS) prime, DUV-18 antireflection coatings and IBM-BARL antireflective coatings. The resists were spin coated at 2500 rpm to ~ 0.4 – $0.7 \mu\text{m}$ thickness. The postapply-bake process was 150 °C for 60 s (unless otherwise stated) in hard contact with the bake plate. Postexposure bake of the wafer was conducted with minimal delay (<5 min) for 60 s at 140 °C. The development processes consisted of two 15 s puddles with either 0.065, 0.13, or 0.26 N TMAH developer solution diluted from LDD-26W or JSR PD-523AD developer, followed by a deionized water rinse.

Results and Discussion

Dry Etch-Resistance of the Resist Polymers.

The dry etch-resistance of some representative polymers

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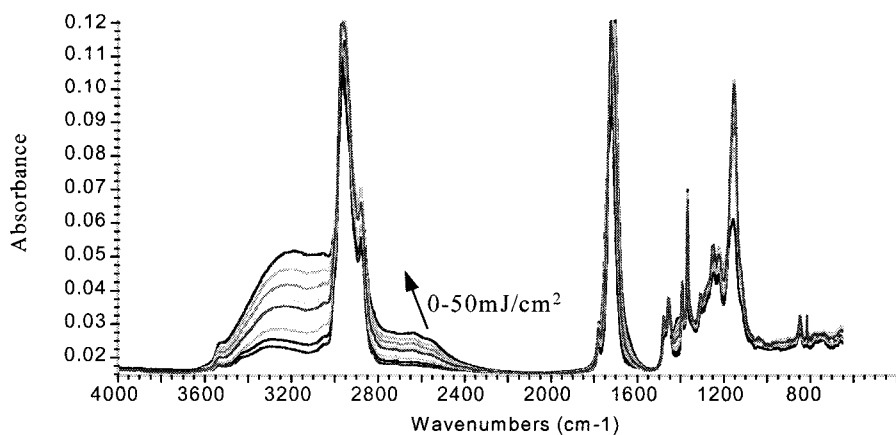


Figure 2. Change in FTIR spectra of a typical resist copolymer (poly(CBN-*co*-NBCA)) as a function of dose. Postexposure bake temperature = 130 °C, time = 60 s. Exposure was made with a 248 nm GCA-XLS stepper with NA = 0.53.

Table 2. Optical Properties of Typical Photoresists^a

polymer	A	B Å ² ^a	C Å ⁴
poly(CBN- <i>alt</i> -MAH)	1.48	4.24 × 10 ⁵	9.06 × 10 ¹¹
poly(CBN- <i>co</i> -NBCA)	1.48	4.01 × 10 ⁵	1.54 × 10 ¹¹

^a These coefficients were used in the calculation of the resist film thickness.

is shown in Table 1. On the average, these polymers etch slower than APEX-E (a commercial deep UV resist). The high etch resistance of our alicyclic polymers confirms reported empirical relations between etch rates and carbon/hydrogen ratio¹³ and between etch rates and "ring parameter".¹⁴ Also, unlike methacrylate-based resists, the alicyclic polymers do not unzip and depolymerize under exposure to plasma. However, depending on the etch chemistry employed, there is evidence for some plasma-induced deprotection of the pendant *tert*-butyl group on the alicyclic polymer matrix.

Optical Study of the Photoresist Compositions.

The UV absorption spectra of typical resist polymers at 193 nm are shown in Figure 1. Most of the resist polymers have acceptable transparency at 193 nm.

Over a limited wavelength range, the function relating the index of refraction of the photoresist to wavelength, the dispersion curve, can be adequately described by the Cauchy relation (eq 2):

$$n(\lambda) = A + B/\lambda^2 + C/\lambda^4 \quad (2)$$

The Cauchy coefficients of typical photoresists determined with the VASE tool are summarized below in Table 2. The values are valid for the 400–800 nm spectral region.

IR Study of the Exposed Resist Films. When the photoacid generator, triphenylsulfonium hexafluoroantimonate is irradiated, it decomposes to release hexafluoroantimonic acid in the resist film. This photochemical reaction occurs at room temperature. The acid-catalyzed deprotection of the *tert*-butyl ester that masks the pendant carboxylic acid group of the polymer occurs at a significant rate only at elevated temperature. It is therefore necessary to heat the resist film to an ap-

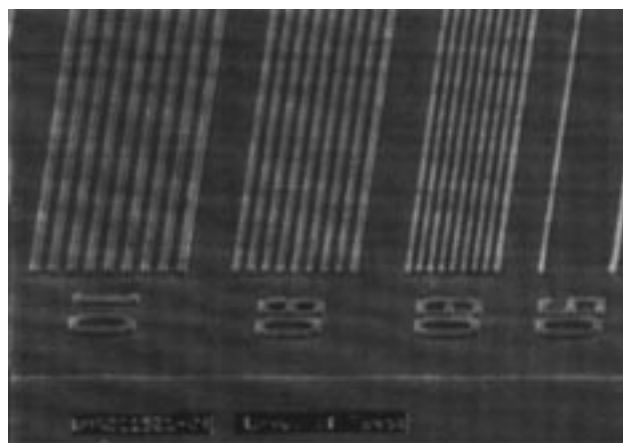


Figure 3. Scanning electron micrograph of 0.5–1.0 μm lines and spaces printed in resist formulated with poly(CBN-*co*-NBCA) made by Pd(II)-catalyzed addition polymerization. The image was printed at 248 nm.

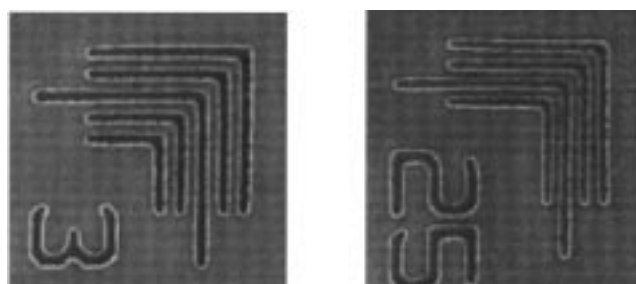


Figure 4. Top-down SEM of images printed in a hydrogenated ROMP terpolymer. Conditions: PAB = 150 °C for 60 s; PEB = 150 °C for 60 s. Developer: TMAH (8.67 × 10⁻³ N) for 30 s. The exposure was done with the 193 nm ISI Microstepper. The structure of the resist polymer is shown in Figure 5.

propriate temperature (postexposure bake) to provide the energy required for the acid-catalyzed thermolysis. For a given formulation at a particular thickness, the extent of deprotection is dependent on the exposure dose, postexposure bake temperature, and postexposure bake time. By monitoring the carboxylic acid OH stretch at 3000–3600 cm⁻¹, the ester carbonyl (C=O) around 1735 cm⁻¹, acid carbonyl (C=O) around 1705 cm⁻¹, and ester C–O–C stretch around 1105 cm⁻¹, it is possible to determine the dose dependence of the deprotection reaction, as well as the influence of baking temperature on the extent of deprotection for each resist

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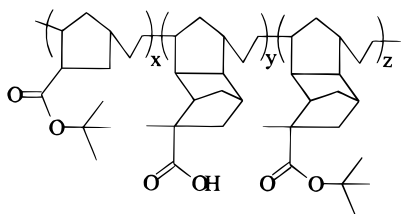


Figure 5. Polar ROMP terpolymer.

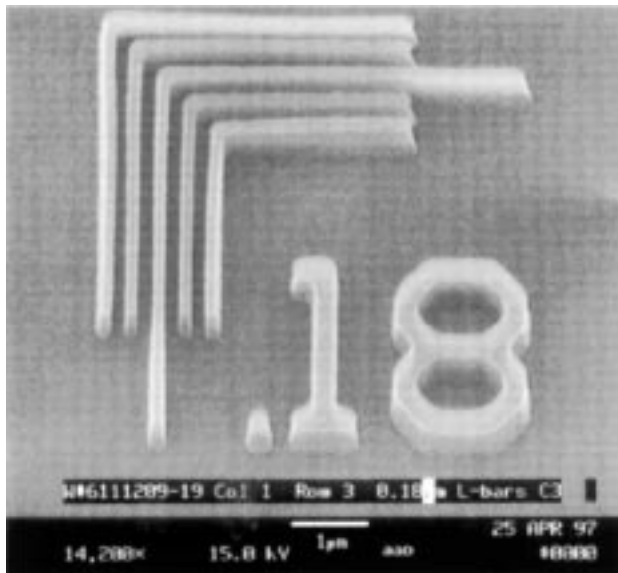


Figure 6. Scanning electron micrograph of $0.18 \mu\text{m}$ features printed in resist formulated with poly(CBN-*alt*-MAH). The resist thickness is $0.62 \mu\text{m}$. The image was printed with an ISI MicroStep stepper at 193 nm.

system. Doses ranging from 0 to 50 mJ/cm^2 were applied to each resist system, after which the samples were baked at 120, 130, 140, and 150°C and then analyzed by FTIR.

Figure 2 shows typical IR spectra of resist formulated with triphenyl sulfonium hexafluoroantimonate and poly(carbo-*tert*-butoxynorbornene-*co*-norbornene carboxylic acid) exposed to $0\text{--}50 \text{ mJ/cm}^2$ of 248 nm radiation and postbaked at 130°C for 60 s. Similar spectra were collected at 120, 140, and 150°C .

The intensities of the carboxylic acid OH stretch ($3100\text{--}3600 \text{ cm}^{-1}$) and the carboxylic acid carbonyl ($\text{C}=\text{O}$) stretch ($1695\text{--}1705 \text{ cm}^{-1}$) both increase upon exposure while the ester carbonyl ($\text{C}=\text{O}$) stretch (ca. 1720 cm^{-1}) decreases, indicating the deprotection of the *tert*-butyl ester group and the consequent conversion to a carboxylic acid. The $\text{C}-\text{O}-\text{C}$ (1150 cm^{-1}) stretch of the ester also decreases with exposure dose.

Lithographic Evaluation. Preliminary evaluations of the resists formulated with poly(CBN-*co*-NBCA) and poly(CBN-*co*-MTDCA) using 248 nm KrF excimer laser exposure tool resulted in excellent performance with dose to clear (E_0) in the range of $5\text{--}25 \text{ mJ/cm}^2$. Resists formulated with poly(CBN-*co*-NBCA) had cracking and adhesion problems. A scanning electron micrograph showing $0.5\text{--}1.0 \mu\text{m}$ lines and spaces printed at 248 nm in a poly(CBN-*co*-NBCA) (made by Pd(II)-catalyzed addition polymerization) resist formulation is shown in Figure 3. Note that the image quality is excellent, but features with dimensions below $0.6 \mu\text{m}$ have lost adhesion to the substrate.

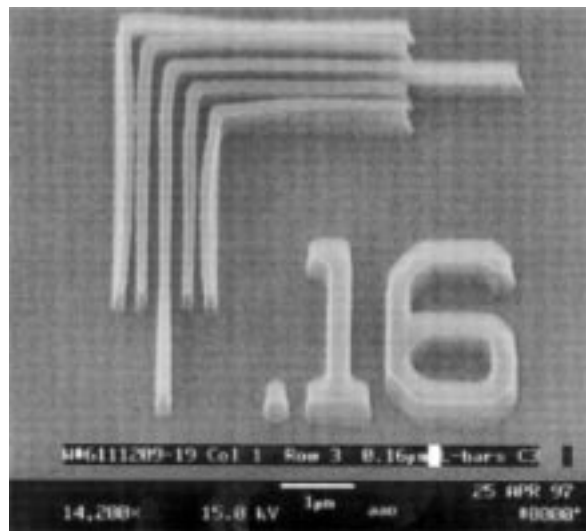


Figure 7. Scanning electron micrograph of $0.16 \mu\text{m}$ features printed in $0.62 \mu\text{m}$ resist formulated with poly(CBN-*alt*-MAH). The image was printed with an ISI MicroStep stepper at 193 nm.

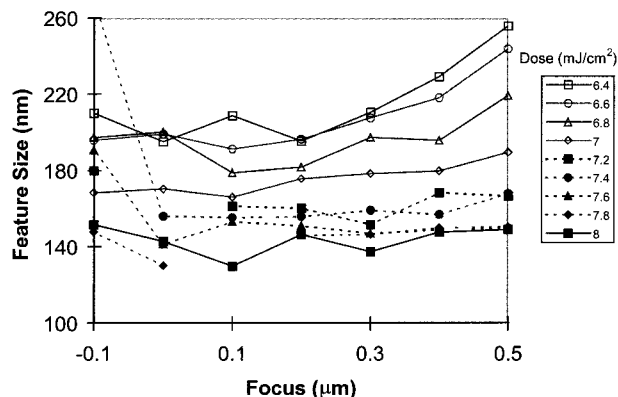


Figure 8. Focus-exposure characteristics of $0.18 \mu\text{m}$ nested lines. The resist was $0.4 \mu\text{m}$ thick poly(CBN-*alt*-MAH), and the antireflection coating was 670 nm DUV-18. The images were printed with an ISI MicroStep stepper at 193 nm.

The hydrogenated ROMP-derived polymers showed phase incompatibility with common PAGs such as triphenylsulfonium hexafluoroantimonate. Therefore, terpolymers which incorporate more polar comonomers were prepared. A typical terpolymer is shown in Figure 5. Increasing the polarity of the hydrogenated, ROMP-derived polymers does allow formation of homogeneous films, but these polar terpolymers swell during development with TMAH solution. Figure 4 is a SEM micrograph of a resist formulated with a typical hydrogenated ROMP polymer. The resist was developed with an extremely weak developer solution (0.008 N TMAH) to minimize the swelling problem.

The incorporation of more polar monomers such as maleic anhydride into the polymers made by free radical polymerization, such as poly(CBN-*alt*-MAH) and poly(CBN-*alt*-MAH-*alt*-NBE), dramatically improved the adhesion and cracking problem without creating resolution loss due to swelling. Exposure of the resist formulated with poly(CBN-*alt*-MAH) at 193 nm provided resolution down to $0.16\text{--}0.18 \mu\text{m}$ (images with sizing doses in the range of $3\text{--}15 \text{ mJ/cm}^2$ (see Figures 6 and 7).

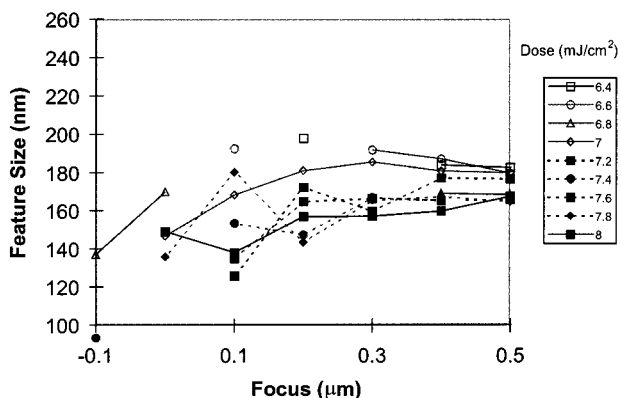


Figure 9. Focus-exposure characteristics of 0.16 μm isolated lines. The resist was 0.4 μm thick poly(CBN-*alt*-MAH), and the antireflection coating was 670 nm DUV-18. The images were printed with an ISI MicroStep stepper at 193 nm.

The improvement in adhesion is demonstrated by the resolution of the small decimal point in front of the numbers in Figures 6 and 7 and the resolution of 0.16 μm lines/space patterns. Note that in Figure 7 the outermost lines in the array have been distorted due to capillary action during the development in aqueous base and water rinse.

Figures 8 and 9 are plots of the focus-exposure characteristics of 0.18 and 0.16 μm nested lines and isolated lines, respectively. The images were printed in poly(CBN-*alt*-MAH) on DUV-18 antireflection coating. The depth of focus for both the nested and the isolated 0.18 μm lines is greater than 0.6 μm at 7.0 mJ/cm². The depth of focus for 0.16 μm lines is ca. 0.3 μm at a dose of 7.0 mJ/cm². Figure 10 is a linearity plot for the nested and isolated lines that shows the printed feature size versus the feature size on the mask. The nested lines are linear down to 0.18 μm and the isolated features to 0.15 μm .

Conclusions

A series of alicyclic polymers for 193 nm resist applications have been evaluated and some show significant promise. These polymers were synthesized by free radical, Pd(II)-complex-catalyzed addition, and ring-opening metathesis polymerization techniques. Resists

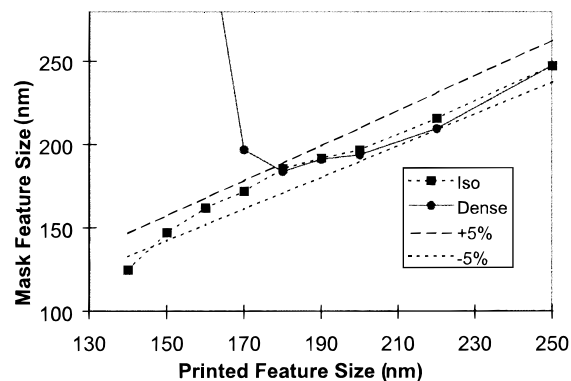


Figure 10. Linearity plot at 7.0 mJ/cm² for isolated and nested lines. The resist was 0.4 μm thick poly(CBN-*alt*-MAH); the antireflection coating was 670 nm DUV-18. The images were printed with an ISI MicroStep stepper at 193 nm.

formulated from free radical polymers containing maleic anhydride units show the best resolution and adhesion. Those made from Pd(II)-catalyzed addition polymerization have the best contrast, but suffer from adhesion problems. The resists formulated from ROMP-derived polymers have poor resolution and also suffer from phase incompatibility with conventional onium-based PAGs. All of the polymers have low absorbance at 193 nm and high dry etch resistance. The best of these photoresists have demonstrated resolution down to 0.16 μm and have significant process latitude at 0.18 μm . We are continuing to study the influences of material, process, and formulation variables on the lithographic and etch performance of these promising new resists.

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