Lithographic Properties of Poly(*tert*-butyl methacrylate)-Based Block and Random Copolymer Resists Designed for 193 nm Wavelength Exposure Tools

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Received January 5, 1996. Revised Manuscript Received May 2, 1996[⊗]

Block and random copolymers were prepared using the monomers *tert*-butyl methacrylate and [3-(methacryloxy)propyl]pentamethyldisiloxane. The polymers have low absorption at 193 nm wavelength, making them attractive candidates for 193 nm wavelength imaging. The resists have a high resistance to oxygen reactive ion etching, making them suitable for the imagable layer of a bilevel resist system. After exposure, the block copolymers have better development behavior in aqueous base than that of the corresponding random copolymers even though they have a long hydrophobic siloxane block.

1. Introduction

Photoresist and exposure tool development coupled together allow the microelectronics industry to continue to decrease the smallest features of semiconductor devices. Because the smallest feature an exposure tool can resolve is proportional to the wavelength of radiation used, it is highly desirable to develop new exposure tools that use shorter wavelength radiation.[1] Currently there is a shift taking place in industry from 365 nm wavelength (Hg lamp) exposure tools to 248 nm wavelength (KrF excimer laser) exposure tools. The change in exposure tools also makes it necessary to change the imaging polymers because novolak-based photoresists have high absorption at 248 nm wavelength (the resist should not absorb so strongly that the effective dose varies greatly as a function of depth in a resist film).[2] Also, for reasonable wafer throughput to be achieved with the step-and-scan type 248 nm wavelength exposure tools, more sensitive resists are needed. It is expected that the next shift in exposure tools will be to those operating at 193 nm wavelength (ArF excimer laser). The ArF excimer laser-based exposure tools will also require a change in the resist used because the resists developed for use with 248 nm wavelength exposure tools [usually based on *tert*-butyloxycarbonyl (*t*-BOC) protected poly(vinylphenol)] absorb strongly at the 193 nm wavelength. High absorption of the matrix polymer causes conversion of the photoacid generator (PAG) to decrease significantly with depth from its maximum at the air−resist interface.

Researchers at IBM and MIT Lincoln Labs have published results of poly(*tert*-butyl methacrylate) [P(*t*-BMA)] based resists that have very low absorption at

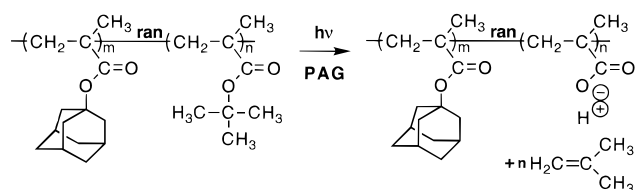

Figure 1. *tert*-Butyl component of an adamantyl methacrylate and *t*-BMA random (ran) copolymer cleaved catalytically by photogenerated acid.

193 nm wavelength.[3,4] The P(*t*-BMA)-based resists become soluble in aqueous base when photogenerated acid catalyzes the deprotection of the carboxylic acid and the liberation of isobutylene. Imaged at 193 nm wavelength, these materials have good sensitivity, contrast, and resolution. However, as the developers of the resist point out, the resist does not have sufficient dry etch resistance to be compatible with the processing associated with modern device manufacturing. Thus, a large amount of research aiming to introduce dry etch resistance into the *t*-BMA-based polymers is being performed. Much of this research focuses on introducing alicyclic methacrylate monomers into P(*t*-BMA)-based resists.[5−9] The structure of one of these types of copolymers, consisting of both adamantyl and *t*-BMA, is shown in Figure 1. Also shown in Figure 1 is the deprotection of the carboxylic acid, catalyzed by photogenerated acid. The alicyclic copolymers can have resistance to halogen-gas reactive ion etch (RIE) sufficient for modern device manufacturing.[6] While the copolymers have low absorption at 193 nm wavelength,

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⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.

(1) Thompson, L. F.; Bowden, M. J. In *Introduction to Microlithography*; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; American Chemical Society: Symposium Series 219; ACS: Washington DC, 1983; Vol. 219, p 20.

(2) Bowden, M. J. In *Materials for Microlithography; Radiation Sensitive Polymers*; Thompson, L. F., Willson, C. G., Frechet, J. M. J., Eds.; American Chemical Society: Washington DC, 1984; Vol. 266, p 39.

(3) Kunz, R. R.; Allen, R. D.; Hinsberg, W. D.; Wallraff, G. M. *SPIE* **1993**, *1925*, 167.

(4) Wallraff, G. M.; Allen, R. D.; Hinsberg, W. D.; Simpson, L. L.; Kunz, R. R. *CHEMTECH* **1993**, *23(4)*, 22.

(5) Kaimoto, Y.; Nozaki, K.; Takechi, S.; Abe, N. *Proc SPIE* **1992**, *1672*, 66.

(6) Allen, R. D.; Wallraff, G. M.; DiPietro, R. A.; Hofer, D. C.; Kunz, R. R. *J. Photopolym. Sci. Technol.* **1994**, *7(3)*, 507.

(7) Nakano, K.; Maeda, K.; Iwasa, S.; Yano, J.; Ogura, Y.; Hasagawa, E. *Proc. SPIE* **1994**, *2195*, 194.

(8) Allen, R. D.; Wallraff, G. M.; DiPietro, R. A.; Hofer, D. C.; Kunz, R. R. *Proc. SPIE* **1995**, *2438*, 474.

(9) Takahashi, M.; Takechi, S.; Nozaki, K.; Kaimoto, Y.; Hanyu, I.; Abe, N. *Proc. SPIE* **1995**, *2438*, 422.

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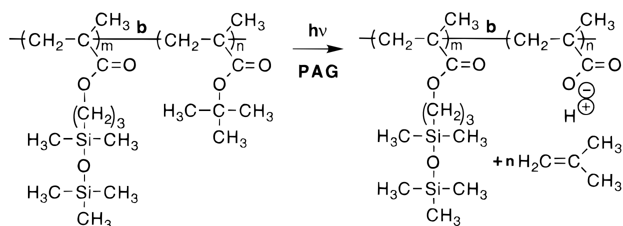

Figure 2. *tert*-Butyl component of a SiMA and *t*-BMA block copolymer cleaved catalytically by photogenerated acid.

many of the copolymers with adequate halogen-gas RIE resistance are not soluble in aqueous base developers after exposure.[8,9] Other possible resist systems capable of being imaged with ArF lasers and still compatible with modern nanofabrication methods include top surface imaging resists and bilevel resists. The bilevel approach has the advantage that the planarizing layer can be chosen to offer superb halogen-gas RIE resistance.

This paper discusses copolymers we prepared to be the imagable layer for a 193 nm wavelength bilevel resist. The copolymers use a *t*-BMA component for imagability. To give the *t*-BMA-based resists substantial resistance to oxygen RIE while still maintaining low absorption at 193 nm wavelength, they were copolymerized with a silicon-containing methacrylate. Along with designing and preparing the imagable layer for a 193 nm wavelength bilevel resist, we also wanted to continue our investigation of how the molecular architecture of a resist affects lithographic behavior.[10] To do this, block and random copolymers of the monomers *t*-BMA and [3-(methacryloxy)propyl]pentamethyldisiloxane (SiMA) were prepared.[11−13] Similar to the adamantyl methacrylate and *t*-BMA copolymer, the *tert*-butyl group of our copolymer can be cleaved to yield a polymer rich in methacrylic acid units (Figure 2). The block copolymer architecture has many advantages which were recently reviewed.[14] The rest of this paper gives a detailed account of the lithographic properties of the block copolymer resists. Comparisons between the lithographic properties of corresponding random and block copolymers having similar molecular weight and chemical composition are made.

2. Experimental Section

2.1. GPC, Thermal and UV Analysis. Number average molecular weight (M_n) and polydispersity (M_w/M_n) were found by GPC (THF) using PMMA standards, a Waters Associates 510 pump, a 410 refractive index detector and 4.6 × 300 mm Styragel HT3, HT4, HT5, and HT6E columns. A Seiko Instruments TTS220 differential scanning calorimeter was used to measure the glass transition temperatures (T_g's) of the polymers. For P(SiMA) and the block copolymers, the temperature cycle started at −110 °C and increased at 10 °C/min to 160 °C. For P(*t*-BMA) and the random copolymers the temperature cycle started at 0 °C and increased at 10 °C/min to 160 °C. Each sample was run twice. The T_g's reported, were determined using the second run for each sample. A Perkin-Elmer Lambda 4A UV/vis spectrophotometer was used to measure the UV absorbance of the polymers.

2.2. Materials. The THF used in the free-radical polymerizations was used as received in a SureSeal bottle from Aldrich. 2,2′-Azobisisobutyronitrile (AIBN) was obtained from Eastman Chemicals and recrystallized prior to use. The composition, molecular weight, and thermal behavior of the various copolymers used in this study are listed in Table 1. The procedures used to prepare the polymers (with the exception of the polymer prepared by free radical polymerization) are described in ref 13. Carbon tetrabromide, propylene glycol monomethyl ether acetate (PGMEA), and cyclohexanone were used as received from Aldrich, as were *t*-BMA from Scientific Polymer Products and SiMA from both Hüls America and Monomer-Polymer Dajac Laboratories. The *t*-BMA and SiMA were purified by drying over CaH_2,[15] using $CuCl_2$ as an inhibitor,[16] followed by distillation at reduced pressure. The triphenylsulfonium hexafluoroantimonate was donated by IBM Corp. The Silwet L-7604 and FC-431 surfactants were donated by OSi Specialties Inc. and 3M, respectively. Shipley MF321 was used as received for the 0.21 N tetramethylammonium hydroxide (TMAH) developer. For the 0.13 and 0.06 N TMAH developers, MF321 was diluted with DI water. Hoechst AZ 312 MIF developer was used as received for the 0.26 N TMAH. The isopropyl alcohol was reagent grade and used as received from JT Baker Inc. MXP-7 [poly(vinyl phenol)] was obtained from Microlithography Chemical Co.

2.3. Random Copolymerization of SiMA and *t*-BMA [P(*t*-BMA-ran-SiMA)III]. A 300 mL, three-necked round-bottom flask, with a stir bar, was fitted with a condenser and septum. Carbon tetrabromide (0.093 g, 0.28 mmol) and AIBN (0.135 g, 0.82 mmol) were added along with 100 mL of THF. After addition of 3.7 mL (12.3 mmol) of SiMA and 7.6 mL (46.7 mmol) of *t*-BMA, two freeze−thaw cycles were performed. The reaction vessel was heated to 65 °C for 44 h. The polymer was precipitated by pouring the solution into a mixture of 100 mL of water and 400 mL of methanol. The polymer was recovered by filtration, dissolved in 40 mL of THF, and reprecipitated in a mixture of 100 mL of water and 400 mL of methanol. The polymer was recovered by filtration and dried in vacuo at ambient temperature. The yield of the white, powdery polymer was 8.77 g (88%). Analysis of the NMR spectrum of the random copolymer revealed that the weight ratio of the SiMA to the *t*-BMA was 0.52 (theory 0.51).

2.4. Solution Preparation and Film Spinning/Postapply Baking. Solutions (10−15 wt %) of all the polymers were prepared with either PGMEA, cyclohexanone, or a mixture. The PAG (triphenylsulfonium hexafluoroantimonate) was used as needed. Surfactants such as Silwet L-7604 or FC-431 were added as specified to help decrease defects in spin-coated films. The solutions were passed through 0.2 μm pore size Teflon filters. Four inch silicon wafers were primed with hexamethyldisilazane vapor. Films of the polymers were made by manually dispensing approximately 1.25 mL of solution onto a silicon wafer, followed by spinning for 60 s using a MTI Flexifab coat-bake track. The spinning speed varied from 1000 to 3000 rpm depending on the thickness desired. Samples were then baked for 60 s at 145 °C. For exposing features and dose matrices, the thicknesses of the films were between 200 and 350 nm.

2.5. Lithographic Processing. All resist processing was done either in a class 100 clean room at The National Nanofabrication Facility (NNF) at Cornell University or in a class 10 clean room at MIT Lincoln Laboratory. Exposures were done using either a 193 nm wavelength excimer laser using 0.5 mJ/cm² pulses, or a GCA stepper with a 0.48 NA "Lotus" lens equipped with a Cymer KrF excimer laser operating at 248.4 nm wavelength. Exposure matrixes with doses ranging from 1 to 50 mJ/cm² with 1 mJ/cm² steps were used to determine the decrease in film thickness after a postexposure bake (PEB) for the various resists. The same

(10) Gabor, A. H.; Lehner, E. A.; Mao, G.; Schneggenburger, L. A.; Ober, C. K. *Chem. Mater.* **1994**, *6(7)*, 927.
(11) Gabor, A. H.; Ober, C. K. *Polym. Prepr.* **1993**, *34(2)*, 576.
(12) Gabor, A. H.; Ober, C. K. *Proc. A.C.S. Div. PMSE* **1995**, *72(1)*, 104.
(13) Gabor, A. H.; Ober, C. K. *Chem. Mater.*, preceding paper in this issue.
(14) Gabor, A. H.; Ober, C. K. In *Microelectronics Technology: Polymers in Advanced Imaging and Packaging*; Reichmanis, E., Ober, C. K., MacDonald, S. A., Iwayanagi, T., Nishikubo, T., Eds.; ACS Symposium Series; American Chemical Society: Washington DC, 1995; Vol. 614, p 282.
(15) Kraft, R.; Müller, A. H. E.; Warzelhan, V.; Hocker, H.; Schultz, G. V. *Macromolecules* **1978**, *11*, 1093.
(16) Bengough, W. I.; Fairservice, W. H. *Trans. Faraday Soc.* **1956**, *63*, 1206.

Table 1. Glass Transition Temperature (T_g), wt % Si, and M_n (GPC) for the Polymers Prepared for This Study[a]

polymer	wt % Si (NMR)	M_n (GPC, PMMA)	M_w/M_n (GPC)	T_g mid-pt (°C)	T_g onset (°C)	transition width (°C)[b]
P(SiMA)	20.4	8 960	1.08	-44	-53	17
P(*t*-BMA)	0.0	13 800	2.02	112	107	12
P(*t*-BMA−*b*-SiMA)I	6.9	13 140	1.31	61	42	45
P(*t*-BMA−*b*-SiMA)II	11.6	14 860	1.09	48	41	39
P(*t*-BMA−*b*-SiMA)III	10.0	15 230	1.34	31	−37	136
P(*t*-BMA−*b*-SiMA)IV	6.8	14 010	1.26	74	45	46
P(*t*-BMA−*b*-SiMA)V	4.1	10 030	1.64	75	40	56
P(*t*-BMA−*ran*-SiMA)I	4.3	16 560	1.63	84	50	43
P(*t*-BMA−*ran*-SiMA)III	7.0	13 020	2.24	68	52	30
P(*t*-BMA−*ran*-SiMA)II	9.7	21 310	1.67	50	22	44

[a] With the exception of P(*t*-BMA−*ran*-SiMA)III, the data presented here is discussed in detail in ref 13. [b] The transition width is the temperature difference between the onset of the T_g and the end of transition.

Table 2. First Cauchy Coefficient (A_0) Used in Determining the Film Thicknesses of the Various Resists[a]

polymer	A_0	n (636 nm)
P(*t*-BMA)	1.452	1.464
block, 10.0 wt % Si	1.429	1.441
block, 6.8 wt % Si	1.437	1.449
block, 4.1 wt % Si	1.443	1.455
random, 4.3 wt % Si	1.443	1.455
random, 9.7 wt % Si	1.429	1.441

[a] The index of refraction (n) at 636 nm wavelength was determined using the method described by Bicerano.[19]

dose matrix was used to determine the sensitivity and the contrast of the various resists using aqueous base, although occasionally a dose matrix from 1 to 99 mJ/cm^2 with 2 mJ/cm^2 steps was used. PEB was done for 60 s at 130 °C. Aqueous base development of films was done by submersion in the appropriate developer followed by rinsing with DI water.

2.6. Oxygen Reactive Ion Etch (RIE) Rate Study. Films, 500−650 nm thick, of each resist were spun (PGMEA solutions with 10^{-3} volume ratio of Silwet L-7604 relative to PGMEA) onto 4 in. silicon wafers. The film thicknesses were measured before and after etching on a Prometrix FT-650 film thickness probe with StatTrax version 6.0 software. By division of the thickness decrease by the etching time, an etch rate was obtained. The Prometrix uses the CARIS (constant-angle reflection interference spectroscopy) technique to measure the thicknesses of resist films. Afsar showed that the function relating the index of refraction to wavelength, for various polyacrylates is similar in the millimeter wavelength region.[17] For the *t*-BMA/SiMA copolymers the index of refraction was assumed to vary with the wavelength of the incident light in the same manner as poly(methyl methacrylate) [PMMA]. Thus, the function relating the index of refraction of the polymer films to the wavelength of the incident light was obtained by adjusting the function known for PMMA,[18] i.e., the A_1 Cauchy coefficient was kept at 466 100 Å^2 and the A_0 Cauchy coefficient was changed so that at 636 nm wavelength the index of refraction obtained using the Cauchy coefficients matched that calculated for the copolymers based on the method described by Bicerano.[19] The index of refraction predicted by this method and the A_0 Cauchy coefficient determined for the various polymers are shown in Table 2. The thickness of each film was determined by averaging the values measured from a 24-point matrix. The standard deviation of the film thickness was typically less than 0.25% of the film thickness and never more than 1.0%. The film thicknesses measured using the CARIS technique were confirmed by ellipsometry and were consistently within 5 nm of each other. Three samples of each polymer were etched for 2 min using a Lucas-Signatone etching system with a helicon plasma source which was previously described.[20] The system was operated with the source having 2000 W of rf power and the chuck having 50 W of rf power. The pressure was 2 mTorr, and the oxygen flow rate was 100 sccm. The backsides of the silicon wafers were maintained at 0 °C during each run. For the P(*t*-BMA) and MXP-7 samples, the time taken to etch through the film, to the silicon wafer, was measured, and etch rates were calculated based on the average of the three samples and the starting film thicknesses. The etch rate of each silicon-containing resist was determined from the average of the three samples etched.

2.7. M_n and M_w/M_n of Exposed P(SiMA). For studying the effect of the lithographic processing on the M_n and M_w/M_n of P(SiMA) homopolymer, films were exposed to a range of doses (248 nm wavelength) and the standard PEB. This was done both with and without PAG and with and without Silwet L-7604 surfactant using films approximately 600 nm thick. After the PEB, each polymer film was dissolved in THF, and the resulting solution collected and filtered though 0.2 μm pore size Teflon filters.

2.8. Determination of Thickness Changes after Exposure and Development. For measuring the thicknesses of the resists both for contrast curves and determining the decrease in the film thickness after PEB, a Tencor Instruments Alpha Step 200 profilometer was used. The exposed or partially developed polymer films were scratched and then the profilometer scanned over the scratch. Thicknesses were determined by an average of at least four scans at different positions along the scratch.

3. Results and Discussion

3.1. Polymerizations. Polymers were prepared using either group-transfer polymerization (GTP)[13] or free radical polymerization. GTP is a living polymerization method for acrylic and methacrylic type monomers in which the degree of polymerization is determined by the monomer to initiator molar ratio.[21] It is an excellent method for obtaining polymers of low polydispersity and of molecular weights ranging from 2000 to 60000 g/mol. This molecular weight range is ideal for resists. By adding two different monomers simultaneously to a reactor, random copolymers can be prepared. Alternatively, by adding two different monomers sequentially to a reactor, block copolymers can be prepared. If desired, the polymer chemist can control the addition of any number of monomers into a reactor to precisely tailor the molecular architecture of the polymer chain.

With the family of block and random copolymers (Table 1), we compared the lithographic properties and obtained information on the specific benefits that block copolymers offer. By using block copolymers and random copolymers of similar molecular weights, the effect of polymer structure on properties that are molecular

(17) Afsar, M. N. *IEEE Trans. Instrum. Meas.* **1987**, *IM-36(2)*, 530.
(18) Pliskin, W. A. *J. Electrochem. Soc.* **1987**, *134(11)*, 2819.
(19) Bicerano, J. *Prediction of Polymer Properties*; Marcel Dekker, Inc.: New York, 1993.
(20) Horn, M. W.; Hartney, M. A.; Kunz, R. R. *Proc. SPIE* **1992**, *1672*, 448.
(21) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.

Table 3. Oxygen RIE Resistance Measurements for Several Block Copolymers (BCP) and Random Copolymers

type	wt % Si	etch rate (Å/min)	normalized etch resistance[a] [P(*t*-BMA)]	normalized etch resistance[a] (MXP-7)
BCP	10	880	26.3	14.8
random	9.7	895	25.8	14.5
BCP	6.9	1 060	21.9	12.3
random	4.3	1 245	18.6	10.5
BCP	4.1	1 260	18.3	10.3
P(t-BMA)	0	23 100	1	0.56
MXP-7	0	13 000	1.78	1

[a] Normalized etch resistance is the etch rate of the reference polymer [either P(*t*-BMA) or MXP-7] divided by the etch rate of the polymer. The higher the normalized etch resistance is the more resistant the polymer is to the oxygen RIE.

weight sensitive, such as the time needed to clear an exposed resist with developer, can be compared.

3.2. Spin Coating of Resist Films. Films spun from polymer/solvent solutions had defects such as pinholes and striations. When additives were used, the quality of the spin-coated P(*t*-BMA) homopolymer and copolymer films improved. Low surface energy surfactants such as FC-431 (3M) and Silwet L-7604 (OSi Specialties) or the low surface energy molecule decamethyltetrasiloxane were added to 10 wt % polymer in cyclohexanone solutions. Qualitatively, films spun from these solutions had substantially fewer defects. The amounts of the surfactants and decamethyltetrasiloxane added to the polymer solution ranged from 10^{-2} to 10^{-6} volume fraction relative to the cyclohexanone solvent. The optimum volume fraction was found to be approximately 10^{-3} for all the additives tested. The surfactants were more effective than the decamethyltetrasiloxane at decreasing the number of defects. We are continuing to test other surfactants, but it is clear that using low surface energy surfactants can allow substantially higher quality films to be spun from P(*t*-BMA)-based resists. Spin-coated films of the P(SiMA) homopolymer were, by far, the lowest quality of all the polymers investigated.

The amount of PAG added to the solutions had a large effect on the quality of the spin coated films. The level of PAG added to the resist solutions varied from 2.5 to 10 wt % relative to the polymer. When 10 wt % PAG was added to the block and random copolymer resists, the spin-coated films cracked. When the level of PAG was decreased to 5 wt %, no cracking of the resist films was observed. With P(*t*-BMA), no cracking of the resist films was observed even when greater than 10 wt % PAG was used. We believe that this is an indication of decreased solubility of the PAG in *t*-BMA-based copolymers when SiMA is incorporated. This will be discussed in more detail in sections 3.6–3.8.

3.3. Oxygen RIE Resistance. The oxygen RIE resistance was determined using the method described in section 2.6. The results are shown in Table 3. At only 4 wt % silicon, the block copolymer has an oxygen RIE resistance 18 times greater than the P(*t*-BMA)-based polymer. The oxygen etch resistance of the polymers increases with the percentage of silicon in the polymer. A block copolymer with 10 wt % silicon has an etch resistance 26 times greater than that of the P(*t*-BMA)-based polymer. At the molecular weights of these copolymers, there is not an improvement in etch resistance by going from the random to the block copolymer

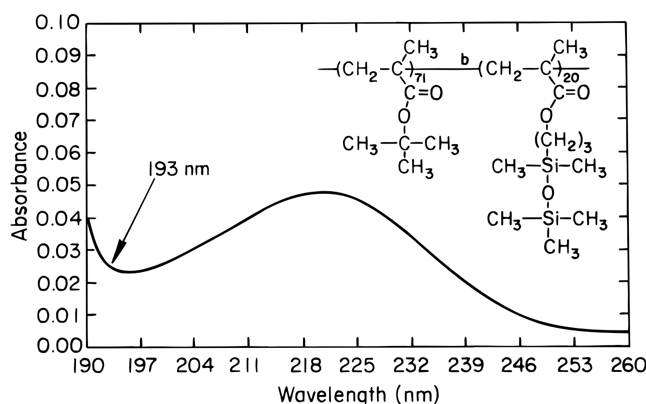

Figure 3. UV absorption spectrum of a 0.4 μm film of P(*t*-BMA-*b*-SiMA) with 6.9 wt % silicon.

architecture. Allen and MacDonald proposed that a block copolymer will offer superior etch resistance over a random copolymer only if the silicon-containing block is sufficiently long that it forms a thick silicon-enriched surface layer.[22] To obtain the greatest improvement in etch resistance compared to corresponding random copolymers, this layer should be thick enough that the RIE does not etch through it during processing. We believe that with our block copolymers, which range from 10 000 to 20 000 g/mol, a layer thick enough to cause an improvement is not formed. However, there are many other lithographic advantages of using block rather than random copolymers, including that the silicon-containing block copolymers can offer a high-T_g phase which can give the resist dimensional stability.[14]

3.4. Deep-UV Absorption. The copolymers have very low normalized optical absorption, at 193 nm wavelength. For example, the absorption of less than 0.1/μm for the block copolymer with 6.9 wt % silicon is similar to that of the first-generation 193 nm wavelength resist developed by IBM and MIT Lincoln Laboratory.[4] Thus, oxygen RIE resistance was imparted to the *t*-BMA-based copolymers while still achieving a polymer with low absorption at 193 nm wavelength. The UV absorption spectrum of the block copolymer with 6.9 wt % silicon is shown in Figure 3.

3.5. Aqueous Base Development. The aqueous base development of these resists was investigated during four different 3-day periods at MIT Lincoln Laboratory, spread over half a year. Throughout this time period we observed that the block copolymer resists required a dose substantially lower than the corresponding random copolymers to clear. The random copolymers with higher silicon concentrations did not clear even if doses up to 99 mJ/cm^2, stronger developers and longer development times were used. However, there were variations in the sensitivities measured from one 3-day period to the next for the random copolymers with lower silicon concentrations. These variations could be due to a number of factors, three of which are listed below:

1. The true normality of the aqueous base developer we were working with, on one or more of the visits, was different from the normality we report, perhaps due to different amounts of absorbed CO_2 in the developer.[23]

(22) Allen, R. D.; MacDonald, S. A. In *3rd Int. SAMPE Electronics Conf.*; 1989; pp 919–928.
(23) Moreau, W. M. *Semiconductor Lithography; Principles, Practices and Materials*; Plenum Press: New York, 1988; p 532.

Table 4. Comparison of Development Times and Doses Needed To Clear Both Corresponding Block and Random Copolymers under Various Conditions[a]

expt	type	λ (nm)	wt % Si	wt % PAG	TMAH[b]	IPA[b,c] (%)	dev time	dose to clear (mJ/cm²)
A1	random	193	7	9	100%, 0.26 N	0	>60 s	7.5
A2	BCP	193	6.9	9	100%, 0.26 N	0	20 s	4
B1	random	248	9.7	10	100%, 0.26 N	0	>5 min	did not clear
B2	BCP	248	10.0	10	100%, 0.26 N	0	20 s	23
B3	random	248	4.3	10	100%, 0.26 N	0	60 s	40
B4	BCP	248	4.1	10	100%, 0.26 N	0	20 s	27
C1	random	248	4.3	5	27%, 0.21 N	73	20 s	4
C2	BCP	248	4.1	5	27%, 0.21 N	73	20 s	1
C3	random	248	4.3	5	40%, 0.13 N	60	20 s	6
C4	BCP	248	4.1	5	40%, 0.13 N	60	20 s	2
C5	random	248	4.3	5	40%, 0.06 N	60	20 s	7
C6	BCP	248	4.1	5	40%, 0.06 N	60	20 s	1
D1	random	248	4.3	10	40%, 0.13 N	60	20 s	did not clear
D2	BCP	248	4.1	10	40%, 0.13 N	60	20 s	8
D3	random	248	4.3	10	60%, 0.13 N	40	20 s	did not clear
D4	BCP	248	4.1	10	60%, 0.13 N	40	20 s	22
D5	random	248	4.3	10	75%, 0.13 N	25	80 s	did not clear
D6	BCP	248	4.1	10	75%, 0.13 N	25	80 s	22
D7	random	248	4.3	5	40%, 0.13 N	60	20 s	did not clear
D8	BCP	248	4.1	5	40%, 0.13 N	60	20 s	12
D9	random	248	4.3	5	60%, 0.13 N	40	20 s	did not clear
D10	BCP	248	4.1	5	60%, 0.13 N	40	20 s	27

[a] The data which are "boxed" can be compared, but comparisons of data in different boxes are not valid (see discussion in the beginning of section 3.5). [b] The percentages for TMAH and IPA are in volume %. [c] IPA is isopropyl alcohol.

2. A change in the level of environmental contaminants in the clean room.[24]

3. Different amounts of reflected light being absorbed by the film, when the thickness of the resist is changed slightly (swing curve effects).

Because of the differences between the 3-day periods, we present the data collected during each period distinguished from the other visits (each experiment has been assigned an experiment number where the experiments that start with the same letter were performed during one visit). Also, we limit the data used to obtain comparisons between the different resists to that obtained during one 3-day period. The lithographic properties of the corresponding block and random copolymers can be compared using the data presented in Table 4.

The block copolymer architecture allows higher amounts of the hydrophobic silicon-containing units to be incorporated into the resists while still maintaining the ability to develop in aqueous base. For example, the block copolymer with 10 wt % silicon, cleared in 20 s with a dose of 23 mJ/cm² in 0.26 N TMAH (expt B2). The corresponding random copolymer (expt B1) did not clear, even with extended development times and doses as high as 99 mJ/cm². With the exception of visit D, the random copolymers with lower silicon concentrations did clear but required a higher dose and/or longer development times. For example, in experiments C5 and C6 the block copolymer with 4.1 wt % silicon cleared in 20 s with a dose of 1 mJ/cm² in a mixture of 0.06 N TMAH and 2-propanol, while the corresponding random copolymer required 7 mJ/cm² to clear with the same development conditions. During visit D the random copolymers with only 4.3 wt % silicon did not clear within a 20 s development cycle while the corresponding block copolymers consistently cleared.

While the block copolymers are capable of being developed with greater percentages of SiMA units, clearly there is a limit to the amount of SiMA units that the block copolymer can incorporate and still maintain aqueous base solubility after exposure (for example, the P(SiMA) homopolymer is a block of SiMA monomer units with no *t*-BMA block attached and is insoluble in aqueous base). We found that a block copolymer with 14.3 wt % silicon is not developable in aqueous base, even when exposed to doses as high as 50 mJ/cm². A block copolymer with 11.6 wt % silicon is developable with aqueous base after exposure to 15 mJ/cm². Therefore, in the molecular weight range we studied, the maximum amount of silicon that can be placed in a block copolymer resist, while still maintaining aqueous base developability, is between 11.6 and 14.3 wt % silicon.

Table 5. Doses Needed To Clear the BCP with 4.1 wt % Silicon When Mixed with 2.5 wt % PAG[a]

expt	TMAH[b]	IPA[b,c] (%)	dose to clear (mJ/cm²)
C7	27%, 0.21 N	73	2
C8	40%, 0.13 N	60	3
C9	40%, 0.06 N	60	4

[a] Exposures were done at 248 nm wavelength and the development time was 10 s for all the developers tested. [b] The percentages for TMAH and IPA are in vol %. [c] IPA is isopropyl alcohol.

The PAG concentration affects the dose needed to clear the resist. For example D2 and D8 were processed identically with the exception of the PAG concentration. Decreasing the PAG concentration from 10 to 5 wt % caused the dose needed to clear the resist to increase from 8 to 12 mJ/cm². D4 and D10 show similar response to changing the weight percent PAG. However, the higher concentrations of PAG have disadvantages which include the tendency for cracks to form in spin-coated films of the copolymers with 10 wt % silicon (as discussed in section 3.2). The doses needed to clear the copolymers with lower levels of PAG are still in the desired range for their use with step-and-scan type exposure tools. Even when only 2.5 wt % PAG was used (Table 5) the block copolymer with 4.1 wt % silicon required only a low dose to clear. Experiments C7–C9

(24) MacDonald, S. A.; Hinsberg, W. D.; Wendt, H. R.; Clecak, N. J.; Willson, C. G.; Snyder, C. D. *Chem. Mater.* **1993**, *5(3)*, 348.

Table 6. Effect on Development of Mixing a Block with a Parent Polymer[a]

expt	type	wt % Si	wt % PAG	TMAH[b]	IPA[b,c] (%)	dev time (s)	sensitivity (mJ/cm^2)
A3	BCP	11.6	6	100%, 0.26 N	0	60	15
A4	Pt-BMA	0	13	100%, 0.20 N	0	20	4
A5	25% BCP 75% P(t-BMA)	2.9	11	100%, 0.26 N	0	20	10

[a] Exposures were carried out using a 193 nm wavelength laser. [b] The percentages for TMAH and IPA are in vol %. [c] IPA is isopropyl alcohol.

also demonstrate that increasing the concentration of base decreases the dose needed to clear the resist.

Another advantage that block copolymers have over random copolymers is their ability not to macrophase separate when mixed with a parent polymer (a polymer the same as one of the blocks) of lower molecular weight than the corresponding block. This ability makes it possible to mix a block copolymer with another polymeric resist to improve lithographic properties, e.g., oxygen RIE resistance. Table 6 shows the results from experiments where a block copolymer with 11.6 wt % Si was mixed with P(*t*-BMA) homopolymer. Mixing one part of the block copolymer and three parts P(*t*-BMA) homopolymer resulted in a resist with a sensitivity between the two polymers. (It should be noted that the molecular weight of the P(*t*-BMA) homopolymer was higher than the molecular weight of the P(*t*-BMA) block. Therefore, it is possible that the homopolymer and block copolymer were macrophase separated from each other.)

3.6. Explanation of Observed Behavior Difference between Block and Random Copolymers. The solubility of P(*t*-BMA)-based resists after exposure is dependent on the acid-catalyzed cleavage of the *tert*-butyl groups which protect the methacrylic acid units of the copolymer. Thus, higher conversion of *tert*-butyl groups will result in a resist with greater solubility in aqueous base. The cleavage of the *tert*-butyl groups and the subsequent loss of isobutylene results in a decrease in the film thickness. We measured the decrease in film thickness as a function of dose for two sets of corresponding copolymers. We then related the thickness loss to the conversion of the *t*-BMA groups through eq 1 (derivation in ref 25). It should be noted that eq 1

$$\frac{\Delta t}{t} = r_{t\text{-BMA}} \times \text{conversion}_{t\text{-BMA}} \times \frac{\text{MW of isobutylene}}{\text{MW of } t\text{-BMA}} \quad (1)$$

where

Δt = change in thickness of the film after PEB

t = original thickness

$r_{t\text{-BMA}}$ = weight ratio of *t*-BMA in copolymer

MW of isobutylene = 56 g/mol

MW of *t*-BMA = 142 g/mol

could be made more accurate by including a ratio of the densities of the material both before and after the cleavage of *tert*-butyl groups. However, the function relating density to conversion of *tert*-butyl groups for these materials is not known. Therefore, the following simplifying assumption was made: the ratio of the densities of the material both before and after the cleavage of some *tert*-butyl groups is equal to 1. Figures 4 and 5 show the relation between dose and the conversion of *tert*-butyl groups for the block and random copolymers with approximately 4 and 10 wt % silicon, respectively. At every dose, the block copolymers have higher conversion of the *tert*-butyl groups than the corresponding random copolymers.

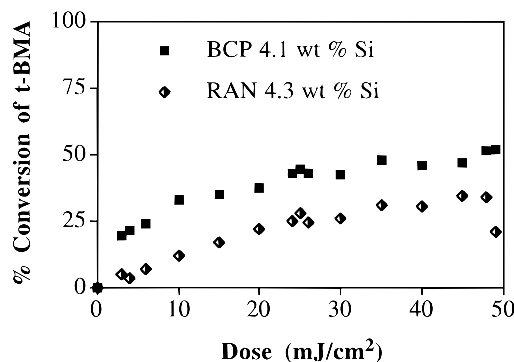

Figure 4. Plot of the conversion of *tert*-butyl groups vs dose for corresponding block (BCP) and random (RAN) copolymers with approximately 4 wt % Si.

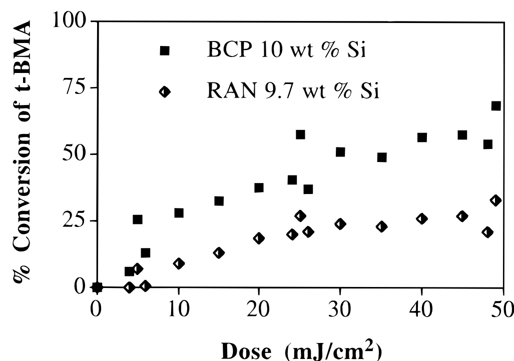

Figure 5. Plot of the conversion of *tert*-butyl groups vs dose for corresponding block (BCP) and random (RAN) copolymers with approximately 10 wt % Si.

The different ways that the block and random copolymers dissolve in aqueous base may also influence their development. Amphiphilic block copolymers form micelles when placed in a solvent that is a good solvent for one block but a bad solvent for the other block.[26,27] After a portion of the *tert*-butyl groups are cleaved the block copolymers consist of a P(SiMA) block which is extremely hydrophobic and a block rich in methacrylic acid units which is highly soluble in aqueous base. We assume that the exposed block copolymer forms micelles in aqueous base developer, with the silicon-containing block forming the core and the block rich in methacrylic acid units forming the corona (Figure 6). This is different from the exposed random copolymer which in order to be dissolved by a TMAH solution, has to have the inhibiting properties of the hydrophobic SiMA units overpowered by neighboring hydrophilic methacrylic

(25) Gabor, A. H. Ph.D. Thesis, Cornell University, 1996.
(26) Riess, G.; Rogez, D. *ACS Polym. Prepr.* **1982**, *23*, 19.
(27) Zhang, L.; Barlow, J.; Eisenberg, A. *Macromolecules* **1995**, *28*, 6055.

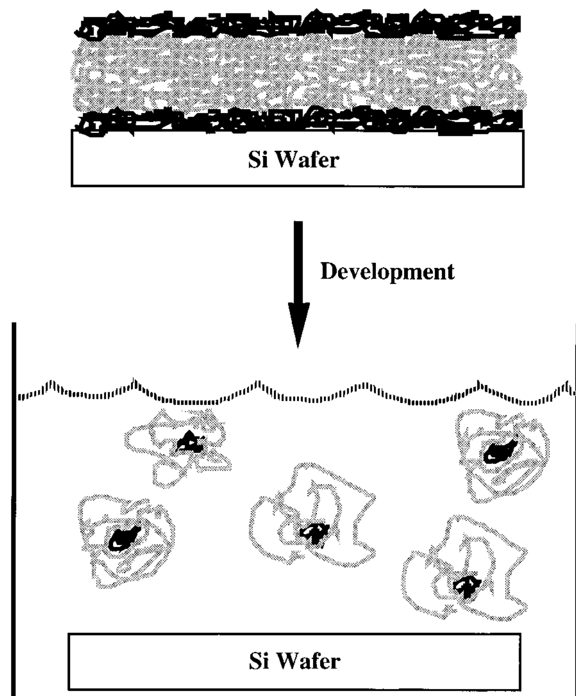

Figure 6. Schematic showing an exposed block copolymer with both a hydrophobic block (black) and a hydrophilic block (gray pattern). When developed using aqueous base, micelles can potentially be formed with the hydrophobic block forming the core of a micelle and the hydrophillic block forming the corona of a micelle.

acid units. The shorter development time needed to clear a block copolymer compared to the time needed to clear a corresponding random copolymer perhaps indicates that the proposed masking of the hydrophobic block, forming the core of a micelle, with a hydrophilic block that forms the corona of a micelle is a more effective mechanism for dissolution. We expect that the concept of incorporating a block that offers desired properties but is not by itself soluble can be extended to other resist systems.

Thus, there are probably at least two main causes for the differences in aqueous base development between the random and block copolymers. The first is that with the block copolymers, a higher percentage of the *tert*-butyl units are cleaved than in the corresponding random copolymers. The second is that the block copolymers can potentially develop in a micellar fashion, where only one block needs to be soluble in the aqueous base, while the entire random copolymer must be soluble in order for development to occur. The differences in conversion of the *t*-BMA are probably due to PAG efficiency in the two different polymer matrixes. It was previously shown that the degree of PAG miscibility with the polymer matrix is a critical factor in determining the efficiency of the photogenerated acid.[28] The effect of PAG concentration on the quality of the spin-coated films of the copolymers and P(*t*-BMA) homopolymer (section 3.2) indicates that the silicon-containing units cause the solubility of PAG in the polymers to decrease. In the block copolymer case, if the thin film of resist is microphase separated and the PAG preferentially segregates to the P(*t*-BMA)-enriched phase, it is probable that a higher percentage of the *tert*-butyl groups will be converted. Also, there is the possibility of a chainlike reaction occurring where it is more efficient for the acid to catalyze cleavage of neighboring *tert*-butyl groups than cleavage of *tert*-butyl groups that are separated by SiMA units.

3.7. Effect of Developer and Dose on the Dissolution of Copolymers. With TMAH developers there was a substantial amount of raggedness to the edges of features imaged with the copolymers. It appeared that with the TMAH developers, swelling of the exposed regions was followed by irregular development. Because of this, it was not possible to obtain meaningful contrast values for the resists developed with unmodified TMAH developer. Past researchers have added isopropyl alcohol to TMAH-based developers to improve aqueous base developability,[9] and this approach worked for us as well. Adding isopropyl alcohol to the TMAH-based developer substantially decreased the raggedness of the features at higher doses. At lower doses the isopropyl alcohol-modified developers improved the edge smoothness of imaged features but did not lead to features with completely smooth edges.

The imperfect development behavior has several possible explanations. One explanation is that the PAG preferentially segregates toward the substrate and that the surface is enriched with a siloxane component. The phenomenon of a PAG phase separating from polymer matrixes was previously described.[29] Uhrich et al. showed that the PAG, triphenylsulfonium hexafluoroarsenate, segregated to the bottom 50 nm of a 800 nm thick film of poly((trimethylsilyl)oxystyrene).[30] Because our PAG is polar and our copolymers are not, it is possible that the PAG segregates from the copolymer matrixes. A siloxane-containing copolymer will form a low energy surface, and therefore the phase-separated PAG is likely to be buried in the bulk of the film and/or the interface between the substrate and resist. Thus in this scenario, the surface layer has a lower solubility in aqueous base than the bulk of the film. The more soluble polymer in the bulk swells and eventually ruptures the insoluble surface layer leading to the ragged appearance of the resolved features. The well-known effect of environmental base contamination could also be a cause for the observed behavior.[24] In this scenario, environmental base reacts with the photogenerated acid in the surface of the resist film, resulting in lower conversion of *tert*-butyl groups in the surface than in the bulk of the film. The surface layer then has a lower solubility than the bulk of the film and the same swelling and eventual rupture of the surface layer occurs as was described above for the PAG segregation siloxane-enriched surface possibility. In both of these scenarios, higher doses minimize the effect because so much acid is generated that even the material at the surface ends up having enough *t*-BMA groups converted for the surface layer to be soluble in aqueous base. When using aqueous base modified with isopropyl alcohol, contrast curves could be obtained (Figure 7). These copolymers have high contrast similar to that reported by other researchers for *t*-BMA-based resists.[4]

3.8. Effect of PAG and Surfactant on Unwanted Cross-Linking of Polymer Films. The purpose of the

(28) McKean, D. R.; Allen, R. D.; Kasai, P. H.; Schaedeli, U. P.; MacDonald, S. A. *Proc. SPIE* **1992**, *1672*, 94.

(29) McKean, D. R.; Schaedeli, U.; Kasai, P. H.; MacDonald, S. A. *Proc. A.C.S. Div. PMSE* **1989**, *61*, 81.

(30) Uhrich, K. E.; Reichmanis, E.; Baiocchi, F. A. *Chem. Mater.* **1994**, *6*, 295.

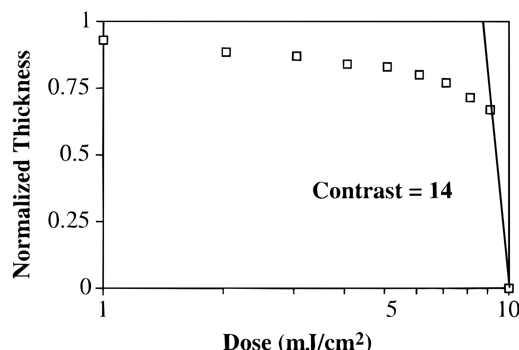

Figure 7. Contrast curve for a block copolymer with 4.1 wt % silicon formulated with 5 wt % PAG. The development was carried out in a mixture of 40% 0.06 N TMAH and 60% isopropyl alcohol for 5 s.

photogenerated acid is to catalyze the cleavage of the *tert*-butyl groups. However, unwanted side reactions are possible. A potential side reaction of concern is the acid catalyzed hydrolysis of ≡Si—O— bonds which would generate ≡Si—OH bonds. Subsequent condensation of the ≡Si—OH groups on two different polymer chains would cause branching of the polymer chains, and if enough condensation between chains occurred, the resist could become cross-linked. If cross-linking was occurring, it could be a contributing cause for the ripping of the resist during some developments described in section 3.7. (It should be noted that P(*t*-BMA) homopolymer developed only slightly better than the copolymers, and therefore the presence of ≡Si—O— bonds cannot alone explain the observed behavior.)

We studied the effect of dose on the solubility of P(SiMA) homopolymer in tetrahydrofuran (THF; 5 wt %, triphenylsulfonium hexafluoroantimonate, both with and without surfactant). After exposure, the wafers were baked at 130 °C for 1 min and then developed in THF for 1 min. The P(SiMA) left a residue on the wafer above a “gel” dose. Both the quality of the spin-coated films and the gel doses depended on whether surfactant was present or not. The quality of the spin-coated films with PAG but no surfactant was poor. However, improvement in the quality of the films [almost to that of the P(SiMA) films spun without PAG] was achieved by adding surfactant. We believe that the surfactant surrounds the phase-separated PAG, with the polar poly(ethylene oxide) part of the surfactant interacting with PAG and the poly(dimethylsiloxane) part interacting with the P(SiMA). With the surfactant, the gel dose was 13 mJ/cm^2, while without the surfactant it was 3 mJ/cm^2. The fact that with the surfactant present the gel dose is higher perhaps is an indication that once the acid is generated it is kept from interacting with the P(SiMA) by the surfactant. This could be caused either by the poly(ethylene oxide) part of the surfactant associating with and effectively neutralizing the photogenerated acid or by the poly(dimethylsiloxane) part of surfactant acting as a barrier and preventing the photogenerated acid from moving into the P(SiMA) matrix.

GPC was used to study the effect of dose on the molecular weight of P(SiMA). Films of P(SiMA) and triphenylsulfonium hexafluoroantimonate, both with and without surfactant, were spun, flood exposed, and PEB at 130 °C. The P(SiMA) films were then dissolved in THF and a portion of the solutions run through a GPC to determine the effect of dose on the molecular weight of the polymer (Table 7). Although at doses higher than the gel dose the film was not completely soluble, the P(SiMA) when spun without surfactant was never completely insoluble, even when exposed to doses as high as 25 mJ/cm^2. Thus, GPC measurements were possible on the soluble fraction of the film even above the gel dose. The GPC results alone lead to the conclusion that no cross-linking is occurring, but this is incorrect as we see a gel left on the wafer above the gel dose. To verify that the gel was not PAG or photogenerated acid that was not dissolved by the THF, we tried to remove the gel with both water and PGMEA, but the gel remained. We believe that the molecular weight of the soluble portion of the P(SiMA) above the gel dose is the same as that of unexposed P(SiMA) for two main reasons. The first is that the PAG is phase separated from the P(SiMA). The second is that the photogenerated acid does not diffuse at an appreciable rate in P(SiMA). Thus, the scenario that we propose is that only the portion of the P(SiMA) next to the phase-separated PAG becomes cross-linked, but the bulk is unaffected by the acid. It is surprising to us that at a dose just below the gel dose, no broadening of the molecular weight distribution or increase in molecular weight is observed, and we seek an explanation for this behavior.

The PAG used also influences the gel dose. When triphenylsulfonium hexafluoroantimonate (5 wt %) was used with a block copolymer with 10 wt % silicon, 1 μm line-space patterns were obtained, and no gel was left even at doses as high as 50 mJ/cm^2. However, when bis(*tert*-butyl phenyl)iodonium triflate (5 wt %) was used, development was not possible. This is an indication that triflic acid is much more active at catalyzing hydrolysis of ≡Si—O— bonds than fluoroantimonic acid. Also, when using surfactant and triphenylsulfonium hexafluoroantimonate, the block copolymer is developable at 2 mJ/cm^2 using isopropyl alcohol enhanced aqueous base. This dose is lower than the gel dose seen with P(SiMA) with surfactant, and it is thought that the unwanted cross-linking reaction does not significantly influence the development behavior of the resist at 2 mJ/cm^2.

3.9. Imaging of Polymers. The 1.0 μm line-space patterns were imaged with the block copolymers containing 4.1 and 10.0 wt % Si using the 248 nm wavelength stepper (Figures 8 and 9). These features were resolved even though the PEB was 55 °C above the T_g of the copolymer with 4.1 wt % silicon and 94 °C above the T_g of the copolymer with 10.0 wt % silicon. Normally, when the PEB is above the T_g of a polymer, diffusion of the PAG is so great that it makes it difficult

Table 7. GPC Analysis of the Soluble Portion of P(SiMA) Films Exposed Both below and above the Gel Dose Shows Little Change in the Molecular Weight and Polydispersity of the Soluble Portion

polymer	surfactant	wt % PAG	exposure dose (mJ/cm^2)	gel dose (mJ/cm^2)	M_n (g/mol)	M_w/M_n	residue on wafer
P(SiMA)I	no	0	0		6460	1.06	no
P(SiMA)I	yes	5	8	13	6380	1.06	no
P(SiMA)I	no	5	1	3	6560	1.05	no
P(SiMA)II	no	0	0		6230	1.03	no
P(SiMA)II	no	5	25	3	6080	1.04	yes

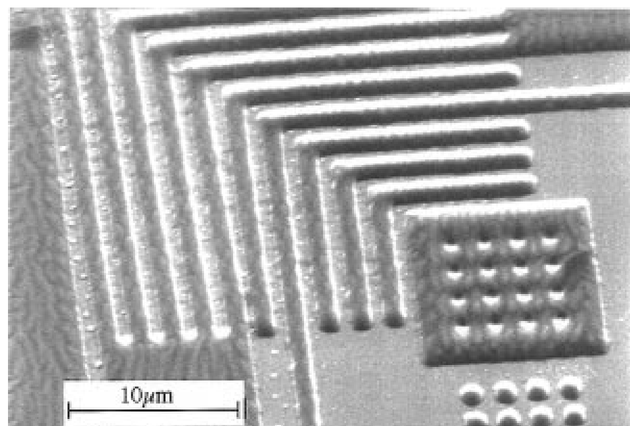

Figure 8. The 1 μm features imaged in a block copolymer with 4.1 wt % silicon, formulated with 5 wt % PAG. An exposure dose of 3 mJ/cm^2 was used, and the resist was developed for 10 s in a mixture of 40% 0.13 N TMAH and 60% IPA.

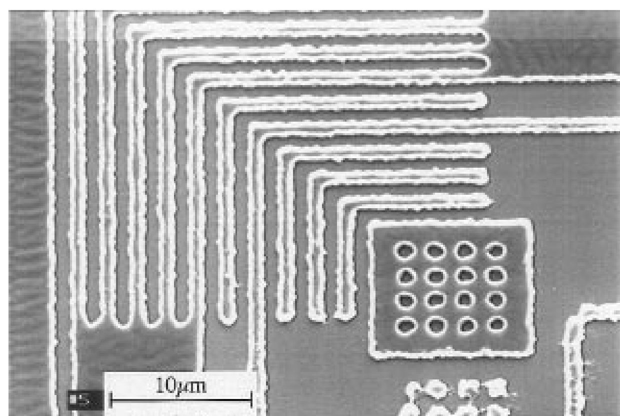

Figure 9. The 1 μm features imaged in a block copolymer with 10.0 wt % silicon, formulated with 5 wt % PAG. An exposure dose of 2 mJ/cm^2 was used, and the resist was developed for 20 s in a mixture of 27% 0.21 N TMAH and 73% IPA.

to image such small features.[8] For example, Schlegel et al. have measured diffusion lengths of photogenerated acid ranging from 2 to 10 μm in 1 min when the PEB was 11 °C above the T_g of the resist.[31] The fact that we are able to resolve 1 μm line-space patterns is an indication that the diffusion of the PAG in these polymeric matrixes is slower than is normal for other chemically amplified resists.

Figure 10 shows a SEM micrograph of features imaged with a random copolymer resist with 9.7 wt % silicon formulated and developed in the same manner as the block copolymer shown in Figure 9 (5 wt % PAG relative to the polymer, developed in a mixture of 27% 0.21 N TMAH and 73% isopropyl alcohol for 20 s). While the exposed regions of the random copolymer (19 mJ/cm^2) were for the most part *not* removed by the developer, pinholes in the exposed regions did form. This behavior was seen over the entire dose range tested (1–49 mJ/cm^2). We believe that the exposed random copolymer itself is not soluble in the developer and that the pinholes result from the developer selectively removing photogenerated acid that is phase separated. The pinholes are approximately 0.3 μm in diameter and

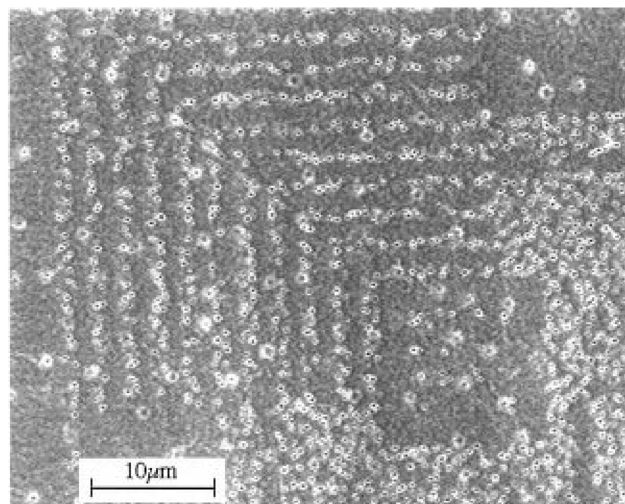

Figure 10. Random copolymer with 9.7 wt % silicon, formulated with 5 wt % PAG, after 1.2 μm features are exposed to 19 mJ/cm^2 and "developed" for 20 s in a mixture of 27% 0.21 N TMAH and 73% IPA. While the random copolymer is insoluble, pinholes do form during "development" and are thought to be from phase-separated acid which is removed by the developer.

are similar in dimension to the spherical phase separated PAG domains observed in other resist systems.[28]

4. Conclusion

Block and random copolymer resists were prepared from *t*-BMA and SiMA. The low absorption at 193 nm wavelength and high oxygen RIE resistance of these copolymers make them attractive candidates for bilevel 193 nm wavelength resists. The block copolymer architecture allows the incorporation of larger amounts of hydrophobic siloxane units into a polymer, compared to a corresponding random copolymer, while still maintaining the ability to develop in aqueous base. However, the development behavior is not ideal. A lower effective concentration of photogenerated acid at the surface of the film compared to the bulk of the film is a probable explanation. One-micron-wide line-space patterns were imaged even though the PEB was as much as 94 °C above T_g. The diffusion of various PAGs in these different polymeric matrices will be the focus of future research.

Acknowledgment. Funding by the SRC Microscience and Technology Program and SRC Lithography Program is gratefully acknowledged. We wish to thank Dr. Roderick Kunz, Dr. Susan Palmateer, Joe Magnant, Deana Downs, Dave Astolfi, and Bill Deady for helping perform various lithographic tests and Mike Chan, Wudbhav Sankar, and Janson Wu for their technical assistance. We also wish to thank Dr. Robert Allen, Dr. George Barclay, Dr. Roger Sinta, and Atsushi Shiota for their helpful discussions. This work was performed in part at the National Nanofabrication Facility, which is supported by the National Science Foundation under Grant ECS-8619049, Cornell University, and industrial affiliates. This work also made use of MRL Central Facilities supported by the National Science Foundation under Award DMR-9121654 as well as the Resist Evaluation Facility at MIT Lincoln Laboratory.

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(31) Schlegel, L.; Ueno, T.; Hayashi, N. *Jpn. J. Appl. Phys.* **1991**, *30(11B)*, 3132.