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Lithographic results of electron beam photoresists prepared by living free radical polymerization

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Summary

A new family of random copolymers composed of chloromethylstyrene and a silicon based styrenic monomer was prepared using living radical polymerization. The lithographic efficiency of the resulting electron beam resists was examined. A pronounced improvement on the lithographic resolution and image quality of resists with a narrow molecular mass distribution was observed and is described.

Introduction

Photoresists are imageable polymers that must provide several functions including the protection from chemical processes of material under the resist. In some resists, silicon is added to protect the underlying material from etching in oxygen plasma. Any silicon in the resist is converted to a passivating layer of silicon oxide. Imaging performance depends on a number of factors related to polymer solubility including molecular weight and molecular weight distribution as well as chemical composition.

As the development of polymeric materials with controlled architectures is becoming an increasingly important objective for macromolecular engineering, much attention has been devoted to living free radical polymerization (LFRP) (1,2). This new approach may involve the use of a free radical initiator such as benzoyl peroxide (BPO) combined with a free-radical capping agent such as 2,2,6,6-tetramethyl piperidinyl-l-oxy (TEMPO) to regulate the polymer chain growth (3). The architectural control due to such polymerization methods offers possibilities for improved resist performance. This has recently been demonstrated by the work of Barclay and colleagues in the study of base developable resists (4).

Silicon containing copolymers can offer many features desirable for etch resistant, high-resolution resist materials (5), but the preparation of such structures with controlled architectures provides many challenges. Therefore polymers prepared by living polymerization methods are usually modified via polymer analogous chemistry to obtain new polymers having special properties. For example, except for the direct polymerization of poly(dimethylsiloxane), most silicon-containing polymers prepared by living polymerizations methods are modified to obtain new polymers having special properties or else produced from specially prepared monomers. For the studies reported here, a styrenic monomer, trimethylsilyl methyl(4-vinylbenzoate), containing a single silicon atom was prepared.

In order to improve electron beam sensitivity of the resulting resist, a comonomer of chloromethylstyrene was employed. Normally, the radical polymerization of this monomer leads to a crosslinked polymer gel. However, as Georges *et al.* (6) have recently shown, largely linear poly(chloromethylstyrene) can be obtained by living free radical polymerization.

In this study, living radical polymerization was used to synthesize random copolymers of the structure shown in Figure 1, containing chloromethylstyrene and trimethylsilyl methyl-4-vinylbenzoate.

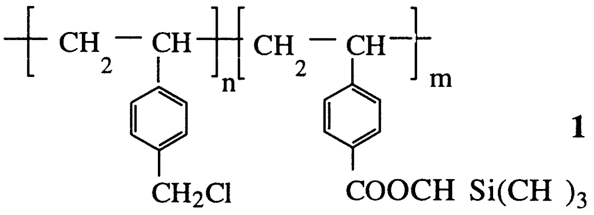

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Fig. 1. Structure of Polymers Studied

In this paper the use of silicon containing copolymers obtained by living radical polymerization as electron beam resist materials will be described. Resist performance is assessed in terms of exposure dose, development conditions and image performance. The goal was to assess the importance of molecular weight distribution and molecular weight on electron beam resist performance.

Experimental

Materials: Benzoyl peroxide (BPO), 2,2,6,6-tetramethylpiperidinyl-l-oxy (TEMPO), 2-fluoro-l-methylpyridinium p-toluene sulfonate (FMPTS) and 4-vinylbenzoic acid were purchased by Aldrich and used as received. 4-Chloromethylstyrene was distilled before use.

(Trimethylsilyl)methyl (4-vinylbenzoate) **(3):** A mixture of 15.0 g (0.101 mol) of 4-vinylbenzoic acid **(2),** 15 ml (0.205 mol) thionyl chloride and 2-3 drops of dry pyridine was stirred at room temperature under dry argon, until a transparent solution was obtained. The vinyl benzoyl chloride was distilled under vacuum (100°C; 0.5 mm Hg) and added dropwise to a solution (prechilled to 2°C) of 9.47 g (0.091 mol) of (trimethylsilyl)methanol and 8.17 ml (0.101 mol) of dry pyridine in 20 ml of CH_2Cl_2. The reaction mixture was stirred at 3-5°C for one hour and at room temperature for 12 hours under dry argon. The reaction mixture was then filtered and the solvent evaporated under vacuum. The product was purified by flash chromatography column with hexane/acetone 9:1 as eluent. Yield: 65%.

^{1}H-NMR ($CDCl_3$): δ = 8.0 (dd, aromatic); 7.5 (dd, aromatic); 6.8-6.7 (m, $H_2C{=}C\underline{H}$-Ph); 5.85 (dd, $H\underline{H}C{=}CH$-Ph); 5.4 (dd, $\underline{H}HC{=}CH$-); 4.0 (s, OCH_2); 0.35 (s, $(CH_3)_3Si$).

Copolymers **1a-c***:* The copolymerizations were conducted in two necked ampoules sealed under reduced pressure. Copolymers **1a-c** were prepared with a mole ratio R between monomers (**3** and **4**) and initiator (BPO) equal to 200. Mole ratios were adjusted slightly to control the silicon content. As a typical example, the synthesis of copolymer **1a** is reported. 6.0 g (25.0 mmol) of (trimethylsilyl)methyl(4-vinylbenzoate) (**3**), 0.76 g (5.0 mmol) of 4-chloromethylstyrene (**4**), 37.0 mg (0.15 mmol) of BPO and 31.5 mg (0.20 mmol) of TEMPO were introduced into the ampoule. The concentration of the accelerant, 2-fluoro-l-methylpyridinium p-toluensulfonate (FMPTS), was 0.017 M in the ampoule. After 2 hours at 135°C, the ampoule was removed from the oil bath and cooled at room temperature. Copolymers **1a-c** were then precipitated into 2-propanol and purified with several precipitations from tetrahydrofuran into 2-propanol. The conversion of both monomers during the copolymerization was ~ 80 % for all samples. Monomer mole ratios and the silicon atom content in random copolymers **1a-c** were determined by ^{1}H-NMR and are collected in Table1.

Tab. 1. Experimental Conditions for Synthesis of Copolymers **1a-c.**

Sample	Feed mole ratio (3):(4)	R [monomers] /[initiator]	Copolymer mole ratio$^{(a)}$ (3):(4)	Silicon monomer content$^{(a)}$ (wt-%)	Si atom content$^{(a)}$ (wt-%)
1a	5:1	200	4.8:1	88.1	10.5
1b	5:1	200	3.7:1	85.7	10.0
1c	5:1	200	4.2:1	86.6	10.2

$^{(a)}$ Determined by ^{1}H-NMR

Physicochemical Characterization: ^{1}H-NMR spectra were recorded on a Varian Gemini 200 spectrometer. The composition of the copolymers was determined from 'H-NMR spectra. Molar mass characteristics were determined by size exclusion chromatography (SEC) in tetrahydrofuran solution using a Waters chromatograph equipped with Waters 420 UV and Waters 410 RI detectors, a set of four Waters Styragel HT 3, 5, 4, 5, 6E columns and a Waters 510 injector. Polystyrene standard samples were used for calibration.

Tab. 2. Molar Mass Characteristics Of Copolymers **1a-c**.

Sample	R [monomers]/[initiator]	M_n	M_w/M_n
1a	200	23,000	1.2
1b	200	25,840	1.4
1c	200	19,500	1.2

Results and Discussion

The requirements of resist materials for submicron lithography include high sensitivity, high resolution and high dry-etching resistance (7): As an example, poly(chloromethylstyrene) shows high sensitivity and excellent etch resistance but these characteristics strongly depend on polymer molecular weight and its distribution (8). Poly (chloromethylstyrene) has been previously synthesized by free radical polymerization of chloromethylstyrene (8), but an alternative approach to obtain very narrow molecular weight polymer, is that based on the chloromethylation of monodisperse polystyrene previously obtained by anionic polymerization (9). However this method involves the use of a known carcinogen, chloromethyl methyl ether. Living radical polymerization has been recently applied to a large number of styrene based monomers and the substituent effect on styrene ring was found to have a very modest effect from a kinetic point of view. The polymerization of poly(chloromethylstyrene) with TEMPO and BPO as catalysts gives a very rapid reaction as reported by Georges (6,10), but the high polymerization rate leads to a reduced control of the molecular weight distribution. Frechet and coworkers have used the $CuCl_2$/bipy system with chloromethylstyrene to form hyperbranced polymers (11). However, when chloromethylstyrene is copolymerized with styrene or other styrene based monomers, copolymers with narrow polidispersity can be obtained.

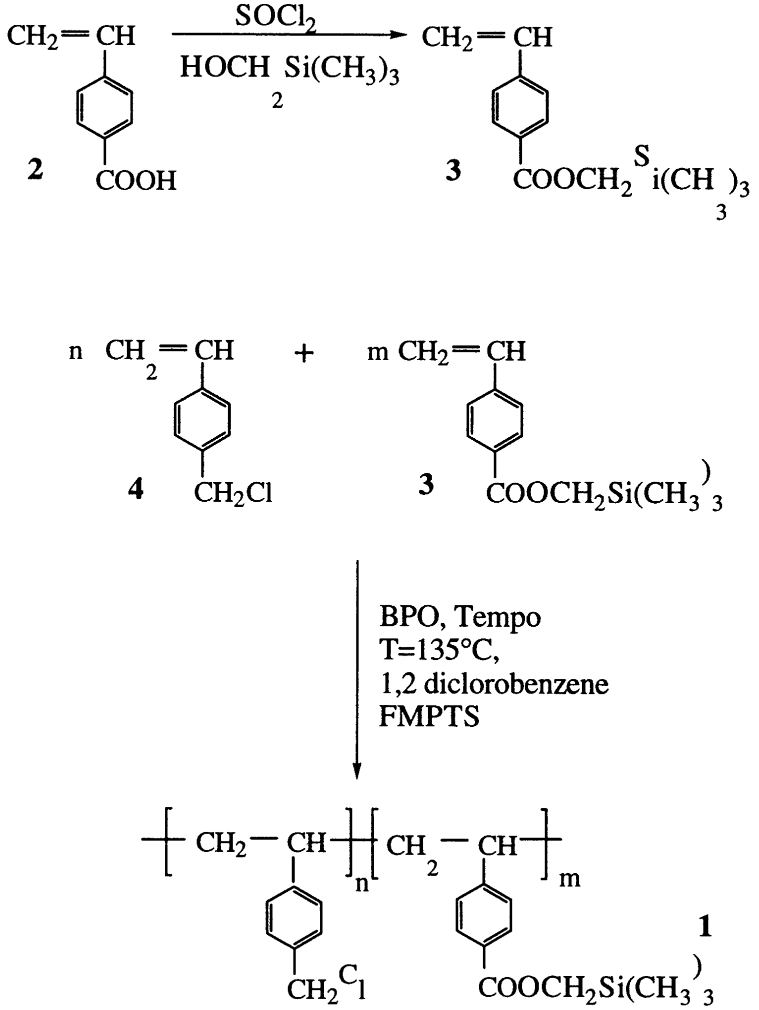


Fig. 2. Synthesis of Si-Containing Monomer and Copolymers

Sample Preparation

Random copolymers **1a-c** were synthesized by one step procedure as illustrated in Figure 2. The copolymerization reaction was carried out at 135 °C under nitrogen using BPO and TEMPO as catalysts. The mole ratio R between monomers (**3**+**4**) and initiator (BPO) was choosen in the feed equal to 200. Molecular mass characteristics of copolymers were determined by SEC: molecular weights and relevant polydispersity indexes are reported in Table 2. In Figure 3, the SEC curves of copolymers **1a-c** are reported. All the samples show a monomodal distribution of their molecular weights even if sample **1b** exhibit a larger molecolar weight dispersion. SEC traces of copolymers **1a-c**, prepared with the same mole ratio R=200 in the feed, are very similar and almost overlapped, thus showing that the new synthetic approach can be useful to prepare materials with reproduceable characteristics.

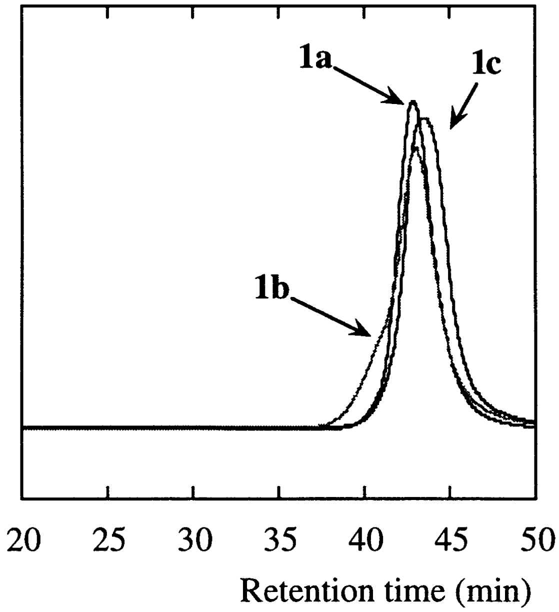


Figure 3. GPC Traces of Copolymers **1a-c**

Identification of casting solvent

Sample preparation consisted of indentifyng a resist casting solvent in which copolymers **1a-c** would readily dissolve, obtaining spin speed curves to spin cast a film thickness of nominally 3000 Å and identifying a compatible solvent for development after electron beam exposure.

To test their solubility, copolymers **1a-c** were dissolved into three potential casting solvents: PropyleneGlycolMethyEthylAcetate (PGMEA), cyclohexanone and Ethyl-Ethoxy-Proprionate (EEP). The nominal concentration was 10% w/v. A quantitiy of 0.5 g of each coploymer was placed into 9 - 25 ml capacity borosilicate glass bottles. 5 ml of each casting solvent was then placed into each bottle. Copolymers **1a-c** took approximately 24 hours to completely dissolve in PGMEA and cyclohexanone. Complete dissolution in EEP was accomplished in a matter of 30 minutes. EEP provided for the most uniform film coating and was selected as the solvent of choice.

Resist spin curves for copolymers **1a-c** were obtained by hand dispensing approximately 2 ml onto 325 µm thick, 3 inch Si wafers. Three separate coatings were carrried out at 1500, 2500 and 2500 rpm respectively on a Headway Resist Spin Coater. Each sample was then submitted to a soft-bake temperature of 90 °C in a box oven. Film thickness measurements were accomplished utilizing a Dektak Model III Stylus Profilometer. A scribe line was applied into the resist film and the relative step height or thickness was measured.

Identification of a developer

The samples were then diced into four pieces respectively to investigate a compatible developer solution. Ethyl alcohol and methyl-ethyl-ketone (MEK) were identified as candidates. Samples of copolymers **1a-c** coated on Si wafers in films approximately

3000A thick were then diced into 4 pieces each. Each copolymer 'slice' was then immersed into a petri dish containing approximately 50 ml of solution and the dissolution time was monitored. An intermediate immersion rinse of methanol and final rinse of H_20 was also used. The volume of both rinse solutions were 50ml each. Samples were then spin dried on a Headway Resist Spin Coater module for 120 seconds.

Tab. 3. Film Thickness Remaining Observed for MEK and Ethyl Alcohol

Time (sec)	MEK *FTR	Ethyl Alcohol *FTR
0	3050	3100
30	2800	3100
60	1625	3100
90	1110	3100
120	0	3100

***FTR – Film Thickness Remaining**

Bulk clearing of the resist film was observed in MEK only. Ethyl alcohol did not dissolve the resist film over any length of time. Table 3 lists the film thickness remaining observed for both solvents over 4 time intervals. Film thickness was measured utilizing a Dektak Model III Stylus Profilometer.

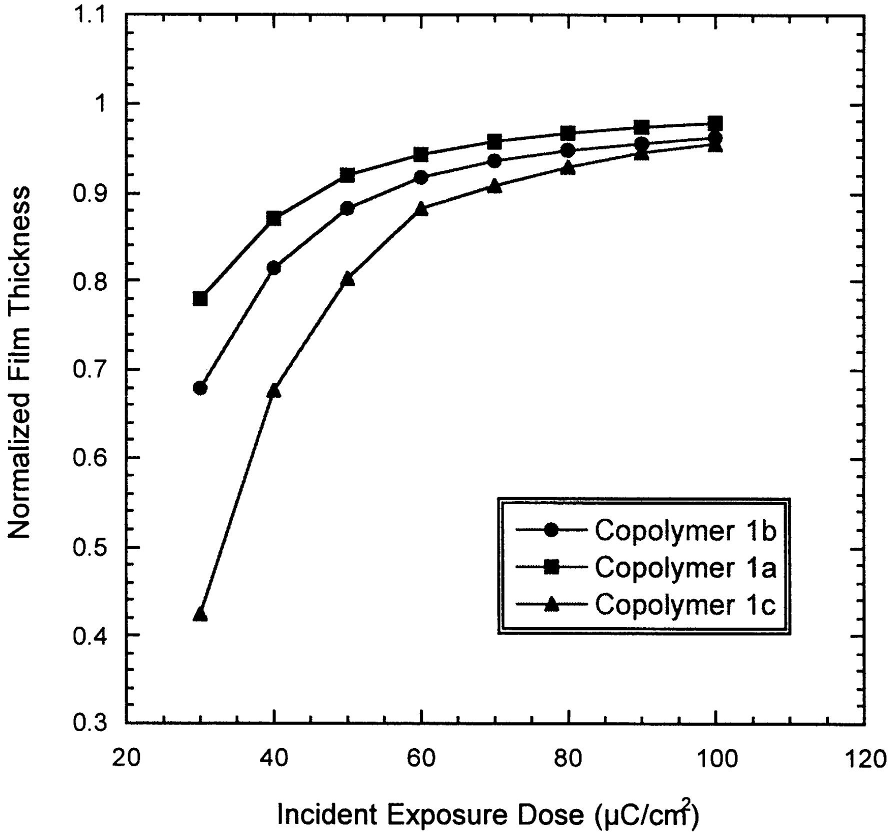
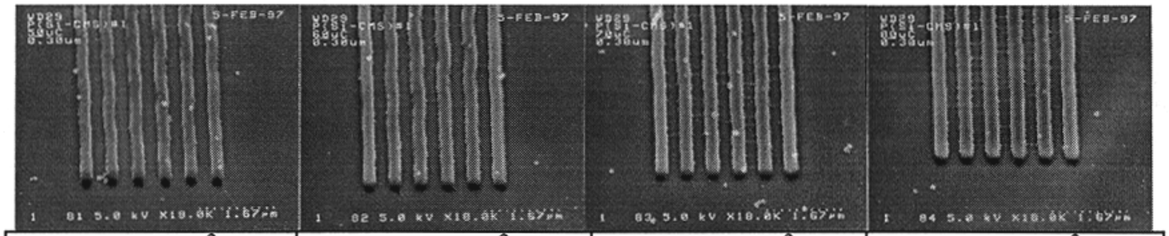


Fig. 4. Plot of Normalized Thickness vs. Incident Dose for the 3 Copolymers Studied.

Lithographic Response

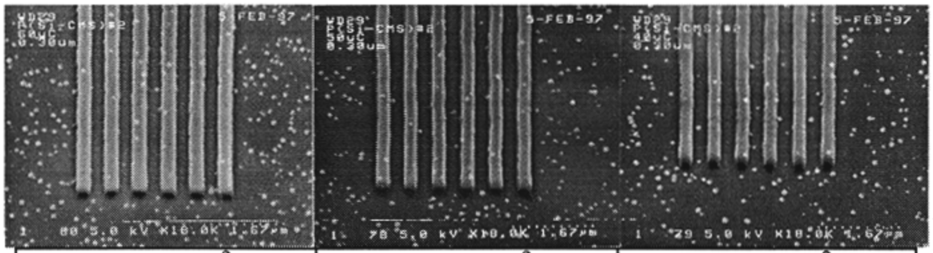
Samples of copolymer **1a-c** were spin cast onto 3 inch Si substrates and soft-baked at 90°C in a box oven for 30 minutes. Exposure response curves were created using a 40 KeV Cambridge Electron-beam Exposure system with a beam address and spot size equal to 0.10 µm.

The electron beam exposure response curve is shown in Figure 4. The exposed pattern consisted of a line/space array as well as large pads to measure film thickness remaining. Resolution was limited in all three materials to 0.30 µm. Development conditions and exposure range were not optimized in this experiment.



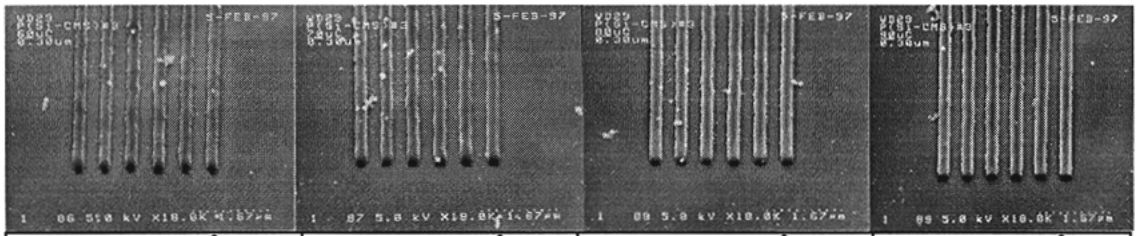
50uC/cm^2	60uC/cm^2	70uC/cm^2	80uC/cm^2

Figure 5a - 0.30 µm Line / Space patterns – Copolymer **1b**



40uC/cm^2	50uC/cm^2	60uC/cm^2

Figure 5b - 0.30 µm Line / Space patterns - Copolymer **1a**



60uC/cm^2	70uC/cm^2	80uC/cm^2	90uC/cm^2

Figure 5c - 0.30 µm Line / Space patterns - Copolymer **1c**

Conclusions

Initial studies of resolution using the unoptimized developer revealed resolved features containing 0.25 - 0.35 µm line/space pairs. Copolymer **1b** had the largest molecular weight distribution (MWD) and subsequently lowest contrast, exhibited the lower level of resolution and image feature quality. For doses investigated, distortion of the features as shown in Figure 5a-c can be seen.

An improvement in resolution and image quality is observed for Copolymer **1a** and Copolymer **1c** where a minimum in pattern distortion is observed. The improved resolution can be in part attributed to the narrower MWD of these materials over Copolymer **1b**. Further optimization of the developer for both copolymers will further enhance their resolution capabilities.

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