Electron-Beam Sensitivity and Patterning of an Aqueous-Develop, Epoxy-Based Polynorbornene Dielectric Material

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The lithographic characteristics of electron-beam (e-beam)-induced cross-linking of an epoxy–polynorbornene (PNB) mixture were studied in an effort to explore the feasibility of using this material as a high-contrast, high-sensitivity e-beam-imageable dielectric material. High resolution (for isolated lines) and e-beam sensitivity were obtained for specific mixtures of PNB–epoxy materials. The interaction of an electron beam with the PNB mixture, which includes epoxy cross-linkers, a photoacid generator (PAG), and a sensitizer, was investigated. The contribution of each of the components to the contrast, resolution for isolated lines, and e-beam sensitivity was evaluated. Cross-linking of the irradiated PNB polymer, by itself, was found to occur at relatively high e-beam doses. The primary route to high sensitivity was through epoxy ring-opening and PNB cross-linking by e-beam activation of the PAG. The effects of the post-exposure bake and aqueous-develop conditions on the lithographic characteristics were investigated. Physical structures with critical dimension of 100 nm to 500 nm were fabricated with line edge roughness of 13.5 nm. Contrast values as high as approximately 8 were obtained at doses as low as 0.38 μC/cm^2.

Key words: Electron-beam lithography, epoxy-based PNB, contrast, sensitivity, line edge roughness

INTRODUCTION

Electron-beam lithography (EBL) is an important patterning method for nanosystems and devices, such as molecular electronics,[1,2] high-precision mask making,[3] and mold making for nanoimprint lithography[4] due to its high spatial resolution, and versatile processing.[5] EBL is an established technique for fabrication of small electronic device structures.[6] EBL offers higher spatial resolution than optical photolithography because of the spatial confinement of the electron beam.[7] However, EBL has low throughput due to the sequential nature of the exposure, which can be mitigated to some extent by increasing the sensitivly of the material to be imaged. The most common electron-beam (e-beam) resists, such as ZEP (a copolymer of α-chloromethacrylate and α-methylstyrene),[8] hydrogen silsesquioxane (HSQ),[9,10] and polymethylmethacrylate (PMMA),[5,11] have high spatial resolution but relatively low sensitivity. Excessive exposure time can result in long write times for which beam drift or instability can occur. E-beam-imageable materials with high sensitivity are of special interest.

Epoxy-based polymers have been e-beam cross-linked.[12–15] They possess high sensitivity, but the resolution can be limited by swelling during developing.[16] Recently, chemically amplified, epoxy-based resists have been reported to have high sensitivity for nanoscale EBL.[16–18] The high sensitivity of these materials comes from the chemical amplification mechanism where the e-beam-generated acid catalyzes epoxy cross-linking.[16] Molecular e-beam resists have been shown to somewhat mitigate excess line edge roughness (LER) problems

caused by diffusion of the acid catalyst into unexposed regions.[17,19–21]

Previously, an epoxy cross-linked, aqueous-base-developed, polynorbornene (PNB) dielectric (Avatrel 8000P) was introduced for packaging applications.[22,23] Avatrel 8000P has a simple processing procedure, high mechanical strength, and good thermal stability.[23] The fluorinated alcohol and carboxylic acid groups on the PNB backbone (Fig. 1) provide solubility in aqueous base during developing, and cross-linkable sites for the multifunctional epoxy additives.[15,16] The epoxy-based cross-linking of PNB can be initiated by an acid catalyst. Raeis-Zadeh et al.[23] have shown that addition of a tetra-functional epoxy cross-linker, tetraphenylol ethane tetraglycidyl ether (TPEGE), to this polymer mixture improves the cross-linking and photodefinition. The addition of TPEGE resulted in high contrast, high sensitivity, excellent adhesion, and the ability to make high-aspect-ratio features.

In this investigation, the e-beam-initiated reaction between PNB cross-linking sites and the epoxy cross-linkers was investigated. The e-beam sensitivity and patternability of the PNB dielectric material were evaluated. The relationship between sensitivity and processing conditions was investigated as a function of mixture formulation. The process parameters were optimized for forming lithographic patterns in the 100 nm regime.

EXPERIMENTAL PROCEDURES

The functionalized PNB polymer, Avatrel 8000P, and the photoacid generator (PAG) were provided by Promerus LLC (Brecksville, OH). 4-methylphenyl-[4-(1-methylethyl)phenyl] iodonium tetrakis(penta-fluorophenyl)borate (Rhodorsil PI 2074) was used as a PAG in this study, as described previously.[24–26] The polymer mixture was formulated using propylene glycol monomethyl ether acetate (PGMEA) as the solvent with PNB, Rhodorsil PI 2074, multifunctional epoxy cross-linkers, an ultraviolet radiation sensitizer, and an adhesion promoter. This formulation, with all components present, is denoted as the base formulation (BF) hereinafter. The formulation cont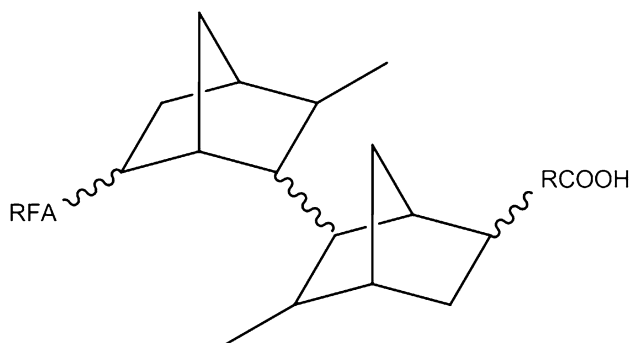aining only PNB and the adhesion promoter in the PGMEA solvent is identified as the base polymer (BP). 1-Chloro-4-propoxy-9H-thioxanthen-9-one (CPTX) was used as a photosensitizer in this mixture.[25,26] PGMEA, CPTX, and epoxy-based cross-linkers were purchased from Aldrich Chemical Co.

The mixtures were diluted with PGMEA to different degrees to produce different thickness films by spin coating. The solutions were each rolled on a ball mill for 72 h. The polymer films were spin-coated on 100-mm-diameter <100> silicon wafers using a CEE 100CB spinner at 2000 rpm for 30 s to produce 200-nm- and 1100-nm-thick films. The polymers were soft-baked and post-exposure baked at 100°C for 2 min on a hotplate. The polymers were e-beam irradiated using a JEOL JBX-9300FS tool with 100 kV acceleration voltage, 50 pA beam current (I), 10 nm beam width, and 50 MHz beam scanning frequency (f). The smallest possible shot pitch (SP) was picked for each exposure dose (D) in the contrast experiments [SP $\geq I/(f{\cdot}D)^{1/2}$]. The exposed films were developed using a Shipley MF-319 [0.26 N-tetramethyl ammonium hydroxide (TMAH)] developer. The film thickness was measured after developing with a Nanospec 3000 film analyzer system. Scanning electron microscopy (SEM) images were obtained using a Zeiss Ultra 60. The polymer films were coated with 60 nm of titanium metal for SEM imaging to prevent charging.

RESULTS AND DISCUSSION

Thin films of PNB and its mixtures are highly soluble in aqueous base (0.26 N TMAH). A 202 nm BF film dissolved in the TMAH developer in less than 10 s after soft-bake to remove the PGMEA casting solvent. This corresponds to the development step of the unexposed Avatrel 8000P film. The addition of 1 wt.% supplementary TPEGE to the BF did not change the dissolution time. This establishes that 10 s immersion in 0.26 N TMAH is an adequate developing time for the formulations used here. Hereafter, all samples in this study were developed for 10 s, unless otherwise stated.

Previously, TPEGE was shown to significantly improve the photopatterning and sensitivity of Avatrel 8000P.[23] To evaluate the impact of TPEGE on the e-beam sensitivity and contrast of Avatrel 8000P, different concentrations of TPEGE were added to the PNB BF. The contrast curves for thin films of BF with varying concentration of TPEGE are compared with PNB (identified as BP) in Fig. 2. This shows that PNB by itself (i.e., BP) is e-beam patternable. E-beam exposure causes random bond breaking and formation, resulting in PNB cross-linking and insolubility in TMAH (10 s develop time) at doses greater than 1000 μC/cm^2. E-50, the dose at which 50% of the resist film is retained after development, for this formulation is 290 μC/cm^2. This dose is comparable to the E-50 values reported for known e-beam resists.[27–31] Hereafter, the contrast sensitivity of the formulations is defined by E-50.

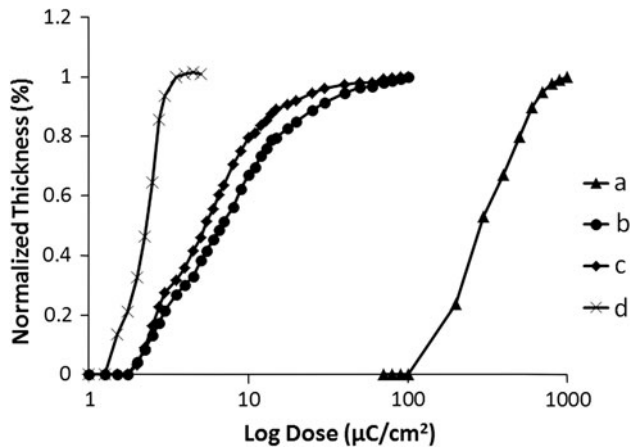Fig. 1. Chemical structure of PNB polymer in Avatrel 8000P.

Fig. 2. Electron-beam contrast curves for PNB formulations: (a) BP with no additives, (b) BF, (c) BF with additional 1 wt.% TPEGE, and (d) BF with additional 3 wt.% TPEGE.

Fig. 3. Effect of PAG on e-beam contrast and sensitivity of the PNB formulations: (a) BP, (b) BP with 0.2X PAG, (c) BP with 0.5X PAG, (d) BP with 1X PAG, (e) BP with epoxy cross-linkers and no PAG, (f) BP with epoxy cross-linkers and 0.2X PAG, (g) BP with epoxy cross-linkers and 0.5X PAG, (h) BP with epoxy cross-linkers and 0.75X PAG, (i) BP with epoxy cross-linkers and 0.9X PAG, (j) BF, and (k) BF with no CPTX and 3.4X PAG.

To investigate the effect of the tetrafunctional epoxy cross-linker and other components in the BF mixture, the contrast for BF and BF with TPEGE is also shown in Fig. 2. The contrast curve for BF in Fig. 2 shows that it has very high sensitivity to e-beam radiation. The E-50 dose for this formulation decreased to 7 $\mu C/cm^2$; that is, addition of the PAG, epoxy-based cross-linkers, and the sensitizer to the PNB polymer (BF) significantly improved the e-beam activation and cross-linking of the PNB polymer. The contribution of each of the components in the BF to the e-beam activation process is discussed below.

The contrast value for each of the films in Fig. 2 was calculated from the slope of the line in the contrast curve where there is a transition from full development (film removal) to 50% normalized film thickness.[17] A similar slope was observed for BF and BP, resulting in similar contrast values for the two formulations. As shown in Fig. 2, E-50 decreased to 5.4 $\mu C/cm^2$ with addition of 1 wt.% TPEGE to BF, and the contrast increased from 0.8 to 1.1. Addition of 3 wt.% TPEGE to BF increased the sensitivity and further improved the contrast of BF. The contrast increased to 2.1 for BF with 3 wt.% TPEGE, and E-50 decreased to 2.3 $\mu C/cm^2$. These results show that addition of TPEGE to BF decreased its solubility in aqueous base after e-beam exposure as a result of polymer cross-linking and interconnectivity. TPEGE has also been used in other negative-tone systems to improve the cross-link density of the polymer.[15,17]

The formulated PNB mixture, BF, was significantly more sensitive than the PNB base polymer (BP, i.e., without epoxy, PAG, or sensitizer), as shown in Fig. 2. The effect of CPTX on the sensitivity of the PNB material was examined first. As CPTX is used in optical photoresists to increase the absorption coefficient in the ultraviolet regions of the spectrum, it was not expected that its inclusion in the formulated PNB mixture would have any effect on the mixture's sensitivity. Two new formulations
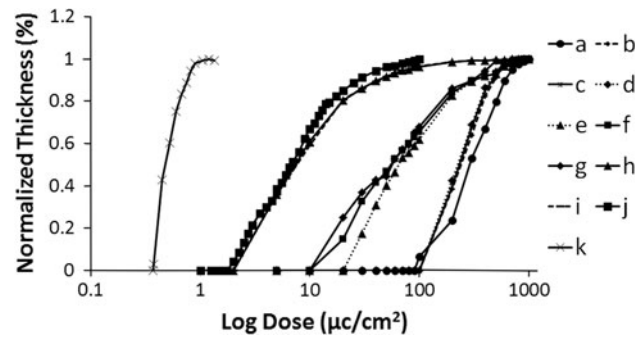
of BP were made with different concentrations of the sensitizer. An amount equal to half the concentration of that contained in BF and an amount equal to the concentration of that contained in BF were added to BP. Contrast experiments were performed, and as expected, the addition of sensitizer to the base polymer had no effect on the e-beam activation of the cross-linking reactions.

The enhanced sensitivity of the formulations containing epoxy cross-linkers, shown in Fig. 2, is due to a higher degree of epoxy ring-opening and cross-linking. Ring-opening of the epoxide structures can occur through thermal treatment, acid activation, or direct e-beam irradiation. Thermal activation is unlikely here since the samples did not experience high temperature. Thus, it is important to understand the contribution of direct electron bombardment and ring-opening versus PAG activation by e-beam exposure and subsequent acid generation, followed by epoxide ring-opening. The activated epoxy quickly leads to cross-linking between PNB molecules or between epoxy molecules themselves. In either case, the higher-molecular-weight products inhibit the rate of dissolution in aqueous base.

To study the effect of PAG, new formulations were made with different amounts of PAG and/or epoxy. Figure 3 shows the contrast curves for 200-nm-thick films. The contrast and sensitivity of the base polymer (BP) were compared with those of BP with 0.2X, 0.5X and 1X PAG, where X is the concentration of PAG in BF (i.e., $X = 1$ in the case of BF). As shown in Fig. 3, base polymer formulations with different PAG concentrations (0.2X, 0.5X, and 1X PAG) resulted in the same contrast and sensitivity as BP; that is, PAG had no effect on the sensitivity or contrast of the base polymer. This result shows that cross-linking of PNB by itself, as occurred in Fig. 2, is not acid activated. The creation of an acid by e-beam activation of PAG did not result in cross-linking.

When epoxy was added to the base polymer with different amounts of PAG, the sensitivity of the mixture to e-beam irradiation increased. Mixtures of base polymer, BP, with epoxy cross-linkers and no PAG showed higher sensitivity and similar contrast compared with BP with no epoxy. An E-50 value of 67 $\mu C/cm^2$ was obtained for BP in the presence of the epoxy cross-linkers compared with 290 $\mu C/cm^2$ for BP with no epoxy. This result shows that the epoxy cross-linkers are activated by e-beam exposure and result in polymer network formation even in the absence of PAG. Adding a small amount of PAG to the base polymer with epoxy (0.2X total PAG) slightly increased the sensitivity. The E-50 value decreased from 67 $\mu C/cm^2$ for BP with epoxy and no PAG to 55 $\mu C/cm^2$ for BP with epoxy and 0.2X PAG. Further additions of PAG (i.e., 0.75X, 0.9X, and 1X) substantially increased the sensitivity, and the E-50 value decreased to the low dose of 7 $\mu C/cm^2$. Increase of the PAG concentration from 0.75X to 0.9X or 1X did not affect the contrast.

These results show that a certain amount of PAG is effective in initiating epoxy cross-linking within the polymer; that is, the irradiated PAG affects the e-beam activation and the rate of epoxy ring-opening within the polymer mixture but does not affect the random PNB cross-linking (epoxy-free cross-linking). A higher concentration of PAG results in a higher degree of cross-linking. However, there is an optimum range of PAG concentration which can initiate the cross-linking reactions and provide the required degree of epoxy activation to obtain adequate cross-linking.

To investigate the effect of even higher concentrations of PAG on the cross-linking and sensitivity of the polymer, an additional mixture was made with higher (3.4X) PAG concentration (i.e., the PAG concentration was 3.4 times that in BF). The sensitizer was not added to the polymer mixture since it was shown to have no e-beam activation. BF with PAG showed significantly higher contrast and sensitivity (Fig. 3). The contrast was 4.4, which is high compared with known e-beam resists. This high-sensitivity formulation was used to pattern 50 μm^2 patterns at the low E-50 dose of 0.48 $\mu C/cm^2$. Higher concentrations of PAG result in greater quantities of acid generation and epoxy ring-opening, increasing the polymer cross-linking.

The experiments presented thus far were performed on thin films, 200 nm to 300 nm thick. To evaluate the effect of film thickness on the imaging characteristics of the polymer, the e-beam contrast experiments were replicated on thicker samples, 1025 nm thick. The contrast curves for 200-nm- and 1025-nm-thick films of the BF are shown in Fig. 4. Thin-film and thick-film samples were developed in TMAH developer for 10 s and 12 s, respectively, to create a 50 μm^2 pattern. No residue was observed in the developed images. As shown in Fig. 4, the thicker film resulted in higher contrast ($\gamma = 1.9$) compared with the thin-film sample, whose contrast
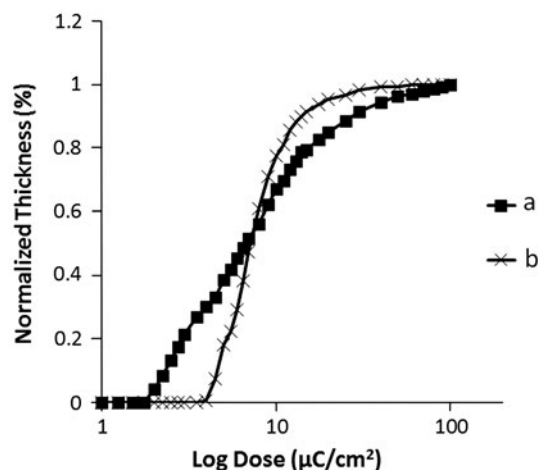

Fig. 4. Electron-beam contrast curves for Avatrel 8000P with two different film thicknesses: (a) 200 nm, and (b) 1025 nm.

was 0.8. However, the minimum dose required to induce (50 μm^2) patterning of the thicker film increased from 2 $\mu C/cm^2$ for the 200-nm-thick sample to 4 $\mu C/cm^2$ for the 1025-nm-thick sample.

The effect of developing time on the sensitivity and contrast of 1025-nm-thick BF was investigated. BF samples, 1025 nm thick, were developed in 0.26 N TMAH, yielding features with sharp corners and edges with no residue. Figure 5 shows the contrast curves for three developing processes. First, a sample was developed in 0.26 N TMAH for 12 s. A 50 μm^2 pattern was observed at doses as low as 4 $\mu C/cm^2$, and E-50 of 7 $\mu C/cm^2$ was obtained. The second sample was developed in TMAH developer for 7 s, rinsed with deionized (DI) water for 30 s, and immersed in the developer for an additional 5 s. The DI rinse allowed time for dissolution of the soluble products which had been neutralized by base. A 50 μm^2 pattern was observed at a dose of 1 $\mu C/cm^2$, and an E-50 value of 1.1 $\mu C/cm^2$ was obtained. The contrast increased from 1.9, for the first sample, to 3.7 for the second sample. TMAH which penetrates into the film results in neutralization of the acidic protons, and the development process becomes dissolution limited, creating an opportunity for enhanced development in DI water without degradation in base during the water soak. The dissolution-limited aspect (after penetration of base) was further demonstrated by developing a film in diluted (2:1 by weight with DI water) TMAH developer for 19 s. As shown in Fig. 5, the sample had the same contrast and sensitivity as the second sample (with DI soak), confirming that the developing process is limited by the dissolution of the neutralized PNB and not by the penetration of the TMAH.

The effect of the developer concentration was also evaluated on thin-film BF samples with (1 wt.% and 3 wt.% TPEGE) and without additional TPEGE. Films (300 nm thick) were developed in diluted (2:1 by weight with DI water) TMAH developer for 15 s
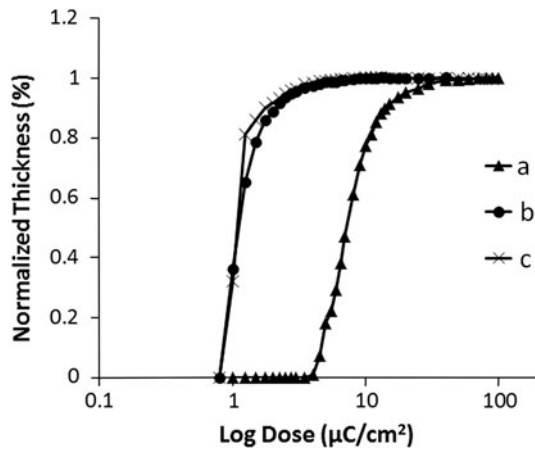
Fig. 5. Effect of developing on e-beam contrast and sensitivity of Avatrel 8000P: (a) developed in TMAH for 12 s, (b) developed in TMAH for 7 s, rinsed with DI water for 30 s, and immersed in TMAH for an additional 5 s, (c) developed in diluted (2:1 by weight with DI water) TMAH for 19 s.

Fig. 6. Electron-beam contrast curves for Avatrel 8000P at three different 100°C PEB times: (a) 2 min, (b) 4 min, and (c) 6 min.

and compared with those developed in 0.26 N TMAH for 10 s. The samples developed in the diluted developer resulted in poorer LER at low doses. The longer developing time, which was required to fully remove polymer residue in the unexposed regions, degraded the sharpness of the exposed edges. Thus, in next experiments the contrast and sensitivity of thick-film samples were compared with those of thin-film samples developed in 0.26 N TMAH developer for 10 s.

The film thickness and the developing time affected the sensitivity and the pattern quality of the developed polymer. The effects of thickness and developing time on BF with additional TPEGE were also evaluated (1 wt.% and 3 wt.% additional TPEGE). The contrast and sensitivity of thick-film (1100 nm) samples, were compared with values obtained for 300-nm-thick samples. The thin-film BF sample with 1 wt.% TPEGE developed in 0.26 N TMAH for 10 s had contrast of 1 and E-50 of 5.4 $\mu C/cm^2$ (results not shown here). The thick-film sample developed in TMAH developer for 16 s showed improved contrast and sensitivity compared with the thin-film sample. The contrast was 2.5 and the E-50 was 1.27 $\mu C/cm^2$. Developing a 1100-nm-thick BF film containing an additional 1 wt.% TPEGE in diluted (2:1 by weight with DI water) TMAH for 25 s resulted in similar contrast and sensitivity to the film developed in TMAH developer for 16 s. The addition of the tetrafunctional epoxy allowed the developing time to be extended to longer values because the film had enhanced film-to-substrate adhesion. The longer develop time resulted in higher contrast and sensitivity. It has been shown previously that enhanced adhesion of TPEGE is due to epoxy ring-opening and polymer cross-linking.[23]

The contrast and sensitivity of BF with 3 wt.% TPEGE were investigated as functions of thickness and developing conditions. Nearly the same contrast
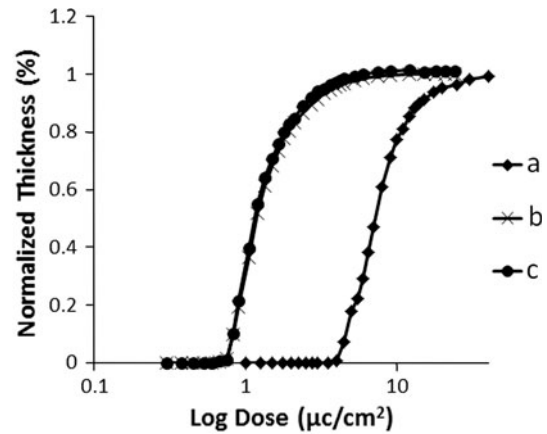
($\gamma = 2.1$) and sensitively (E-50 of 2.3 $\mu C/cm^2$) could be obtained by changing the developer concentration and time over a limited range of values. The thick-film sample was developed in 0.26 N TMAH developer for 16 s. Developing the thick-film sample in diluted (2:1 with DI water) TMAH developer for 30 s showed no significant change in the sensitivity and contrast. The longer developing time could be used in these experiments because the films had greater adhesion from the inclusion of 3 wt.% TPEGE.

In the results discussed above, it is shown that the develop time affected the sensitivity of thick-film BF samples. Post-exposure bake (PEB) is another important processing step which can affect the polymer cross-linking and pattern quality. Three different PEB times (100°C) were used to investigate the impact of PEB on the sensitivity and contrast of thick-film samples. Figure 6 shows the e-beam contrast curves for BF samples post-exposure baked for 2 min, 4 min, and 6 min. All samples were developed in 0.26 N TMAH developer for 12 s, and the developed features had sharp edges and no residue. The sample with shorter PEB time had lower sensitivity than but similar contrast to the samples with longer PEB. The longer PEB time resulted in a higher degree of epoxy reaction (higher cross-linking), improved substrate adhesion, and lower residual solvent in the film.

The impact of PEB time on the minimum exposure dose of the most sensitive formulation, i.e., BF with 3.4X PAG and no CPTX, was investigated. Two PEB times (100°C) were investigated on 950-nm-thick films. As shown in Fig. 7, the longer PEB time did not affect the sensitivity of the polymer, and the contrast was slightly improved. The sample post-exposure baked for 6 min yielded contrast of 7.9.

Based on the results presented above, the exposure process was optimized for the BF samples. Lines 100 nm to 500 nm in width were fabricated using e-beam dose from 5 $\mu C/cm^2$ to 50 $\mu C/cm^2$. The resolution and LER of the 200-nm-thick lines were compared. The optimum dose needed to resolve the 200-nm-, 300-nm-, 400-nm-, and 500-nm-wide lines
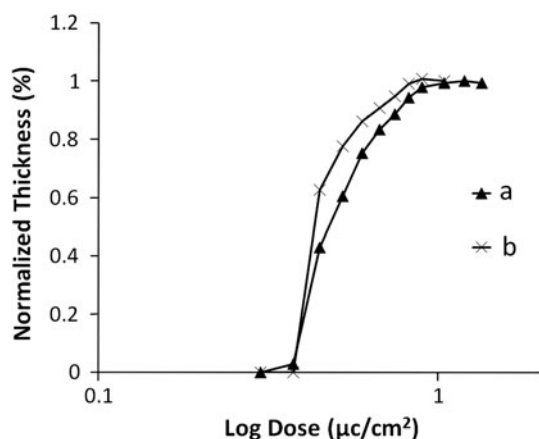
Fig. 7. Electron-beam contrast curves for BF with 3.4*X* PAG and no CPTX at two different 100°C PEB times: (a) 2 min, and (b) 4 min.
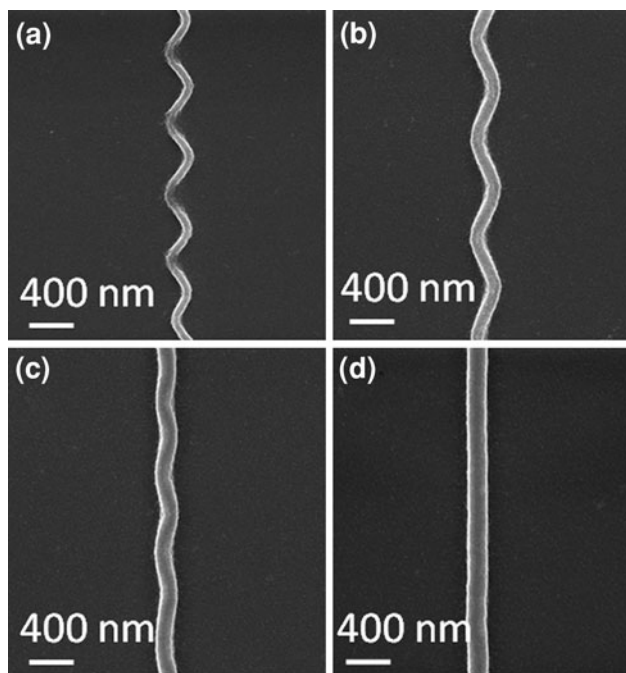

Fig. 9. SEM images of Avatrel 8000P with 1 wt.% TPEGE demonstrating 100 nm resolution at different exposure doses: (a) 10 μC/cm^2, (b) 20 μC/cm^2, (c) 35 μC/cm^2, and (d) 45 μC/cm^2.

Fig. 8. SEM images of Avatrel 8000P demonstrating 200 nm resolution at different exposure doses: (a) 5 μC/cm^2, (b) 10 μC/cm^2, (c) 25 μC/cm^2, and (d) 40 μC/cm^2.

was 40 μC/cm^2, 20 μC/cm^2, 15 μC/cm^2, and 10 μC/cm^2, respectively. Patterns produced at lower exposure dose suffered an unacceptable degree of swelling resulting in excessive LER. Figure 8 shows four of the exposure doses for the 200-nm-wide lines: 5 μC/cm^2, 10 μC/cm^2, 25 μC/cm^2, and 40 μC/cm^2. The lines exposed at low doses were distorted (not straight) due to a high degree of swelling along with inadequate surface adhesion caused by low cross-link density in the films. The highest resolution was obtained at doses greater than 40 μC/cm^2. The 100-nm lines were not printed without excessive distortion.

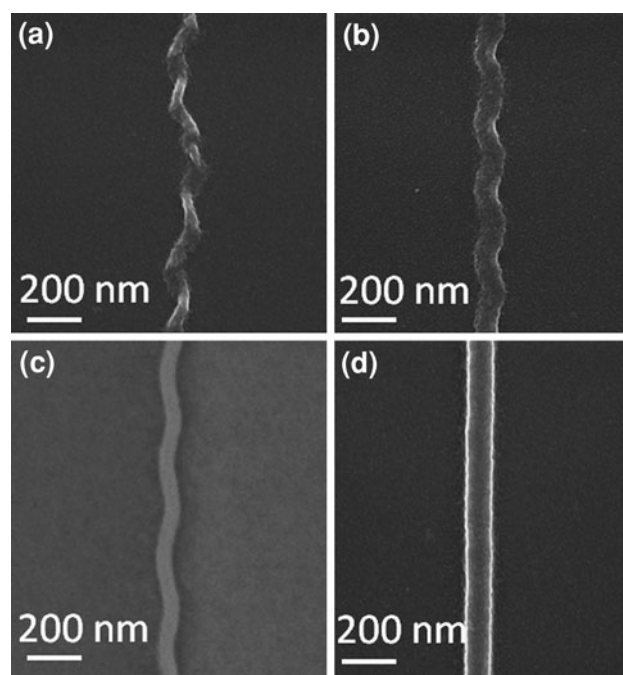Addition of TPEGE to the BF improved the cross-link density of the polymer and substrate adhesion. The exposure process was optimized for BF samples with 1 wt.% TPEGE to investigate the effect of the additional cross-linker on the resolution and pattern quality of the patterns. Films (200 nm thick) were exposed to doses from 5 μC/cm^2 to 50 μC/cm^2. A similar trend to the BF samples was observed, and the minimum exposure dose decreased with the line width. However, a lower dose was required to pattern the 200-nm- (35 μC/cm^2) and 300-nm-wide (15 μC/cm^2) lines compared with the BF samples. In addition, it was possible to pattern 100-nm-wide lines when TPEGE was added to BF, whereas these lines could not be resolved without TPEGE. The optimum dose for the 100-nm-wide lines was 45 μC/cm^2. As shown in Fig. 9, the 100-nm-wide lines at doses below 45 μC/cm^2 suffered from poor adhesion and curling. They showed a high degree of swelling, especially at doses below 20 μC/cm^2. It can be concluded that addition of the tetrafunctional epoxy cross-linker improved the polymer cross-linking density and substrate adhesion as measured during the develop cycle.

In addition to improved resolution, the LER also improved by adding the tetrafunctional cross-linker to the polymer mixture. The LER values were calculated by the method described by Leunissen et al.[32] using an inspection length of 500 nm and magnification of 300 k. The LER (3σ) was 17.9 nm for 200-nm BF lines and 13.5 nm for 100-nm BF lines with 1 wt.% additional TPEGE. Formulations with higher concentrations of TPEGE (3 wt.% and

Table I. List of processing conditions, contrast, and sensitivity of PNB formulations

Formulation	Film Thickness (nm)	PEB (min)	Developing Time (s)	Developer	Contrast (γ)	Sensitivity, E-50 ($\mu C/cm^2$)
BF	200	2	10	TMAH	0.8	7
BF	1025	2	12	TMAH	1.9	7
BF	1025	4	12	TMAH	1.9	1.2
BF	1025	6	12	TMAH	1.9	1.2
BF	1025	2	7/DI rinse/5	TMAH	3.7	1.1
BF	1025	2	19	Diluted TMAH	3.7	1.1
BF with 1 wt.% TPEGE	300	2	10	TMAH	1.1	5.4
BF with 1 wt.% TPEGE	1100	2	16	TMAH	2.5	1.27
BF with 1 wt.% TPEGE	1100	2	25	Diluted TMAH	2.5	1.27
BF with 3 wt.% TPEGE	300	2	10	TMAH	2.1	2.3
BF with 3 wt.% TPEGE	1025	2	16	TMAH	2.1	2.3
BF with 3 wt.% TPEGE	1025	2	30	Diluted TMAH	2.1	2
BP (no additives)	200	2	10	TMAH	0.8	290
BP with 0.2X PAG	200	2	10	TMAH	0.8	230
BP with 0.5X PAG	200	2	10	TMAH	0.8	230
BP with 1X PAG	200	2	10	TMAH	0.8	230
BP with epoxy and no PAG	200	2	10	TMAH	0.8	67
BP with epoxy and 0.2X PAG	200	2	10	TMAH	0.7	55
BP with epoxy and 0.5X PAG	200	2	10	TMAH	0.7	55
BP with epoxy and 0.75X PAG	200	2	10	TMAH	0.8	7
BP with epoxy and 0.9X PAG	200	2	10	TMAH	0.8	7
BF	200	2	10	TMAH	0.8	7
BF with 3.4X PAG (no CPTX)	200	2	10	TMAH	4.4	0.48
BF with 3.4X PAG (no CPTX)	950	2	12	TMAH	4.4	0.48
BF with 3.4X PAG (no CPTX)	950	6	12	TMAH	7.9	0.43

5 wt.% TPEGE) resulted in larger LER for the 100-nm lines, which could be the result of higher cross-linking within the polymer. At high TPEGE concentrations, the mole ratio of TPEGE to PNB increased, resulting in greater interconnectivity and cross-linking, increasing the LER.

Overall, the PNB formulations with the epoxy and PAG showed extremely high sensitivity compared with known e-beam resists.[27–31] The contrast, sensitivity, and processing conditions of the PNB formulations are summarized in Table I. Previously described chemically amplified e-beam resists have also been shown to have high e-beam sensitivity.[33,34] PNB formulations with PAG and epoxy have higher sensitivity than and comparable contrast to other e-beam-sensitive materials.[9,35] The minimum resolution for isolated lines found for PNB formulations was 100 nm with LER of 13.5 nm. Molecular e-beam resists have been shown to have high resolution and lower LER values due to the lower average molecular weight of the cross-linked materials.[5,14,17,36] The PNB used in this study was significantly higher in molecular weight than the molecular resists used in the past. Improvements in minimum feature size and LER may be expected with lower-molecular-weight PNB formulations. The optimum cross-linking to produce the highest resolution and lowest LER was not investigated here and may be a subject of future reports.

CONCLUSIONS

Avatrel 8000P, a negative-tone epoxy-based PNB dielectric, has been shown to have very high e-beam sensitivity and acceptable resolution for 100-nm-size features. The e-beam interaction with the components in the polymer formulation was studied. It was shown that addition of a PAG to the polymer–epoxy mixture enhanced the contrast and sensitivity. Formulations with the additional tetrafunctional cross-linker, TPEGE, showed improved contrast, sensitivity, and substrate adhesion. 200-nm-wide lines of PNB formulations had LER of 17.9 nm, and 100-nm-wide structures fabricated using PNB formulations with additional tetrafunctional cross-linker had LER of 13.5 nm. The influence of developing time, developer concentration, PEB, and film thickness on the contrast and sensitivity was studied. Structures with contrast values as high as approximately 8 were fabricated at doses as low as 0.38 $\mu C/cm^2$.

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