

High aspect ratio features in poly(methylglutarimide) using electron beam lithography and solvent developers

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The properties of poly(methylglutarimide) (PMGI) when used as an electron beam resist are investigated. The results show that PMGI, when developed with a weak developer, xylenes, shows contrast higher than 12, which is comparable to the contrast achieved in cold developed poly(methylmethacrylate), and approximately twice as high as the recently achieved PMGI contrast using other developers. Using this high contrast polymer, sub 20 nm features with aspect ratios greater than 30:1 can be readily achieved. In addition to the superior positive tone behavior, this polymer behaves as a negative tone resist at higher exposure doses. Negative resist features as small as 20 nm can be fabricated when methyl isobutyl ketone is used to develop negative tone PMGI. © 2012 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4750217>]

I. INTRODUCTION

Electron beam lithography (EBL), which mainly uses poly(methylmethacrylate) (PMMA) and Nippon Zeon (ZEP) as electron sensitive polymers, has been a standard method for nano-fabrication. Different techniques, including the use of isopropyl alcohol (IPA); deionized (DI) water as the developer,^{1,2} cold developing,³ replacing the bulk substrate with a thin membrane,² the use of higher electron beam acceleration voltages,² or ultrasonic agitation while developing^{1,4} have been used to enhance the ultimate contrast and resolution of these polymers. Features with aspect ratios of approximately 14:1 have been fabricated by developing PMMA in a mixture of IPA and DI water with ultrasonic agitation.¹ Using the same mixture in a different ratio, a 20:1 aspect ratio was achieved when the bulk substrate was replaced by a thin membrane.²

Poly(methylglutarimide) (PMGI) is an alkaline soluble polymer derived from PMMA.^{5,6} It has been widely used in photo and electron beam lithography for lift off processes where an undercut is required to form a discontinuous metal layer.^{7,8} Alkaline developers containing tetramethylammonium hydroxide (TMAH), sodium hydroxide, or potassium hydroxide are used to develop even unexposed PMGI.⁶ PMGI was found to be highly sensitive to electron beam when developed in developers containing TMAH.⁸ Having poor contrast despite high sensitivity, PMGI developed by alkaline solutions is not widely used for nanofabrication. Recently, it was discovered that PMGI has a contrast close to that of PMMA, yet approximately four times less sensitive, when developed with common PMMA developers.⁹ However, we have shown that using a weak solvent, xylenes, which is a common developer for ZEP, the contrast of PMGI can be higher than 12. This high contrast enables the formation of narrow trenches in a thick layer of the resist; sub 20 nm features with aspect ratios of approximately 30:1 are readily achievable as shown in Fig. 1.

While PMMA is known to behave as a negative tone resist when exposed at high doses,^{10,11} this behavior has not been investigated for PMGI. Using methyl isobutyl ketone (MIBK), we investigated the negative tone behavior of this polymer.

The lower sensitivity of PMGI relative to PMMA when developed in solvent developers can be attributed to the difficulty of the developer to penetrate into PMGI.¹² It is important to mention that despite this lower sensitivity, PMGI is more resistant to dry etch, and produces thermally stable images up to approximately 180 °C, with the glass transition temperature of 189 °C versus 105 °C for PMMA. Chemical degradation of PMMA starts at 200 °C, while PMGI is chemically stable up to 350 °C.^{5,13,14} Moreover, there is no intermixing of resists when conventional or deep ultraviolet (DUV) photoresists are spun over PMGI due to its insolubility in the solvents used in these resists.^{5,13}

II. EXPERIMENTAL RESULTS AND DISCUSSION

A. Positive tone PMGI process

The contrast curve of PMGI was plotted based on the data collected from the following set of experiments. Prior to applying PMGI SF9 from MicroChem Corporation, the 2 × 2 cm² silicon substrates were dipped in acetone, methanol, and isopropanol with ultrasonic agitation for 5 min each. To evaporate any residual solvent, the samples were baked at 200 °C for 10 min subsequent to blow drying with nitrogen. After dispensing the resist, the samples were spun for 45 s at 9000 rpm, and immediately transferred to a hot plate at 180 °C. The bake time was varied to investigate its effect on the sensitivity and contrast of PMGI. Following the exposure, the samples were developed in xylenes for 2 min and rinsed in IPA for 20 s. One sample was developed for 1 min with ultrasonic agitation to investigate its effect on sensitivity and contrast. After developing, the remaining thickness of the resist was measured using a KLA Tencor P6 profiler. The contrast of PMGI was measured at three different acceleration voltages: 50, 75, and 100 kV. Exposures were done with a Vistec 5200 EBL tool at 50 and 100 kV and with an

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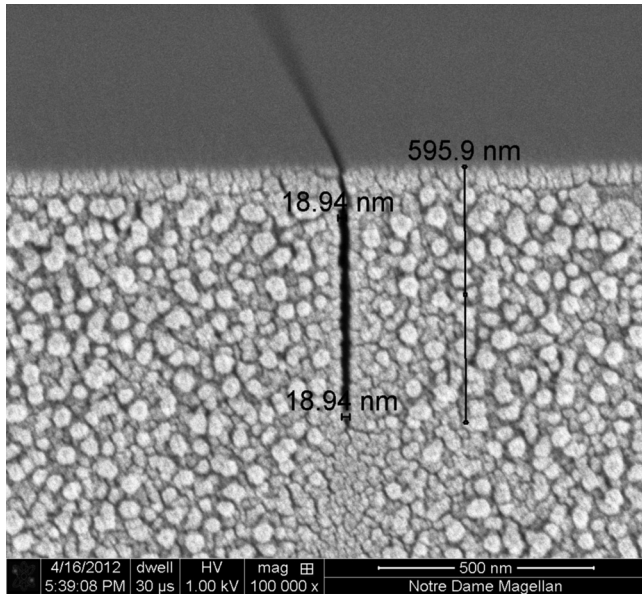


Fig. 1. 19 nm wide trench with a 31:1 aspect ratio fabricated in PMGI SF9. The PMGI was baked for 5 min at 180 °C, exposed at 100 keV with a dose of 15 mC/cm², and developed for 7 min in xylenes with ultrasonic agitation.

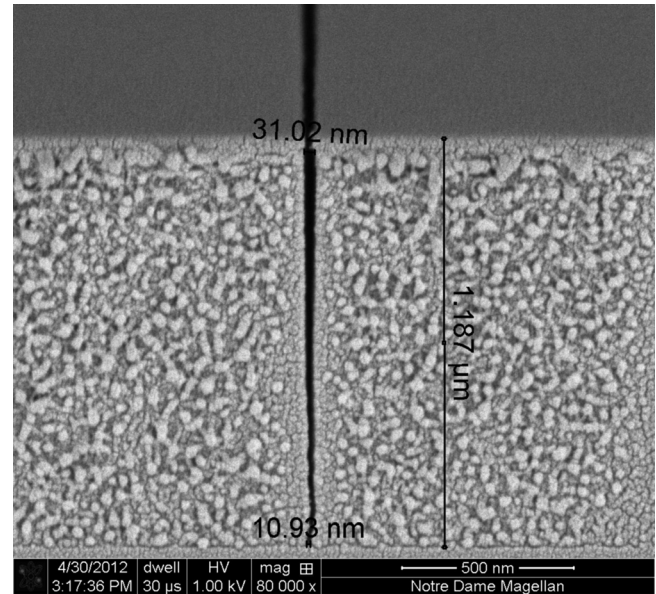


Fig. 3. Trench with a 38:1 aspect ratio in 1.2 μm of PMGI SF9. The exposure dose was 18 mC/cm² at 100 keV. The sample was baked for 5 min at 180 °C prior to exposure and developed in xylenes for 15 min with ultrasonic agitation.

Elionix ELS-7700 system at 75 kV. All the processes were carried out at room temperature using xylenes as the developer. Figure 2 shows the contrast curve for PMGI under different acceleration voltages and bake times. The contrast was calculated using $\gamma = [\log(D_{100}/D_0)]^{-1}$, where γ is the contrast, D_{100} is the extrapolated dose for full thickness removal, and D_0 is the extrapolated dose for full thickness remaining. Based on our observations, longer bake times increase the sensitivity of PMGI, while lowering its contrast; PMGI baked for 5 min had a contrast of 12, while 30 min baked PMGI showed a contrast of 3.68. We also found that ultrasonic agitation while developing increased the sensitivity as well as the contrast of the 30 min baked PMGI, from 3.68 to 5.6.

In order to compare the contrast and ultimate aspect ratio of features in PMMA and PMGI, films of 1 μm of each resist

were exposed by electron beam. The exposure dose was 18 mC/cm² for PMGI and 2 mC/cm² for PMMA. Following the exposure, samples were developed with ultrasonic agitation. PMMA films were dipped for 10 min in a mixture of IPA:DI water in 3:1 ratio, while xylenes were used to develop the PMGI films for 15 min. Figures 3 and 4 show the cross section of the two profiles using scanning electron microscopy (SEM). All SEM images were captured with a Magellan 400 SEM, using a 1 kV acceleration voltage. Prior to imaging, 3 nm of iridium was sputtered on the samples to mitigate charging and increase the image contrast. In PMMA, the bottom of the trench is wider than the top due to the spread of forward scattered electrons as they penetrate deeper into the resist.^{1,2} However, this undercut profile is not seen in the PMGI film. The 1.2 μm deep trench in PMGI is 31 nm wide at the top and narrows to 11 nm at the bottom,

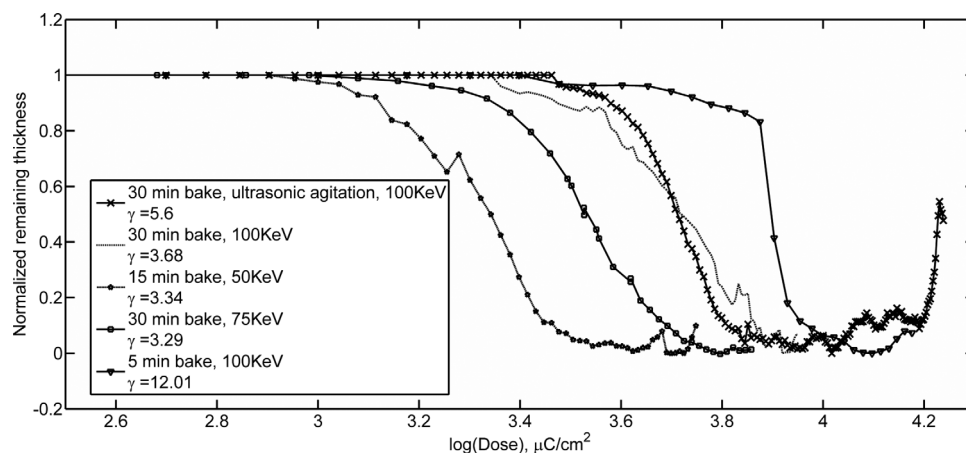


Fig. 2. Contrast curves of PMGI at 50, 75, and 100 keV electron beam acceleration energies and different bake times. The effect of ultrasonic agitation is also illustrated.

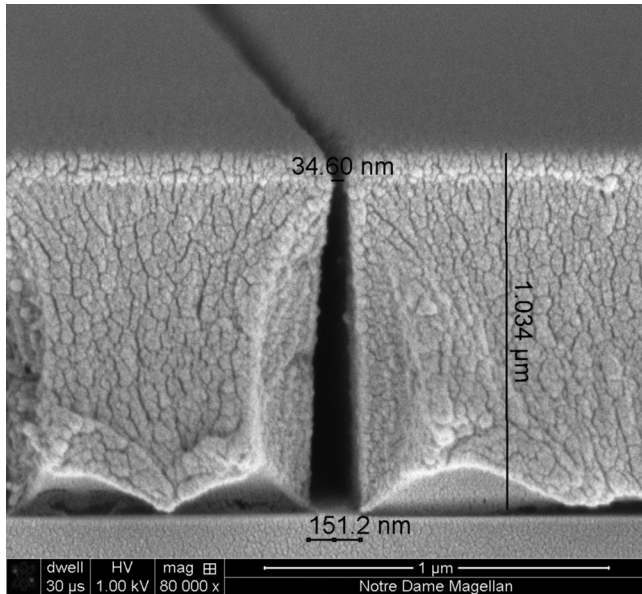


Fig. 4. Profile of a $1\ \mu\text{m}$ deep trench in PMMA 950K C7. The sample was baked for 60 min at 180°C prior to exposure, and developed in IPA:DI water in 3:1 ratio for 10 min after being exposed with a dose of $2\ \text{mC}/\text{cm}^2$ at 100 keV.

giving an aspect ratio of 38:1. The slow rate of solvent diffusion into PMGI while developing and a higher contrast of this polymer can account for this difference.⁸

A possible application for these high aspect ratio features is the fabrication of *T*-gates for high speed transistors. Here, a high aspect ratio trunk is desirable to provide a short gate length while placing the gate head high above the surface to reduce the parasitic gate-source and gate-drain capacitance. A single step electron beam exposure and developing can produce the required profile in a three-layer resist stack. PMGI is used as the bottom layer where the stem of the *T*-gate is formed. The intermediate P(MMA-MAA) layer, a copolymer of methyl methacrylate and methacrylic acid, forms an undercut and facilitates the lift off process, and the dimension of the gate head is determined by the opening in the ZEP 520 A top layer. Prior to spinning the top ZEP, the P(MMA-MAA) layer is exposed with DUV (220 nm) to increase its dissolution rate when developed in xylenes. PMGI, unlike ZEP, shows no sensitivity to DUV exposure when developed in xylenes. Therefore, the size of the undercut can be controlled without affecting the dimension of the gate foot. A line dose of $20\ \text{nC}/\text{cm}$ at 75 kV was used for the electron beam lithography. The resist stack was developed for 100 s in xylenes. Figure 5 is the SEM image taken after cleaving the sample that shows the cross section of this resist stack. We believe that the closure at the bottom of the trench is an artifact of the cleaving. Contraction of the resists when exposed to an electron beam results in a slight change of the dimensions of the trenches during imaging.

B. Negative tone PMGI process

When PMGI, like other electron sensitive polymers, is exposed to an electron beam, two competing phenomena take

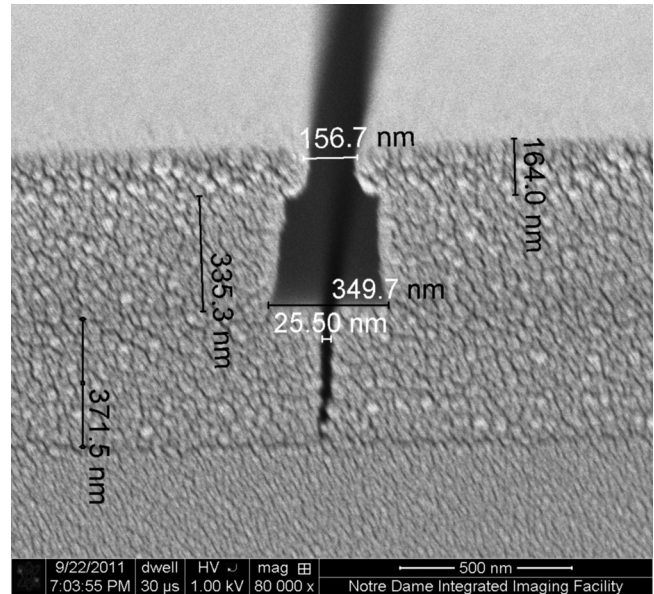


Fig. 5. Resist profile proposed for *T*-gate fabrication. $25.5\ \text{nm}$ wide stem is formed in the $370\ \text{nm}$ thick PMGI bottom layer. The P(MMA-MAA) mid-layer provides the undercut to facilitate lift off, and the dimension of the gate head is defined by the opening in ZEP top layer.

place inside the polymer: scission, in which the linear chain polymer breaks into shorter chains with lower molecular weights, and cross-linking which fuses the linear polymer chains to produce high molecular weight branched polymers.^{3,15} The former increases the dissolution rate as the exposure dose increases, while the latter has the effect of decreasing the dissolution rate, turning the polymer into a negative tone resist. It is important to note that in PMMA and PMGI, cross-linking of polymer chains is more prominent at higher doses, while scission is the dominant process when the

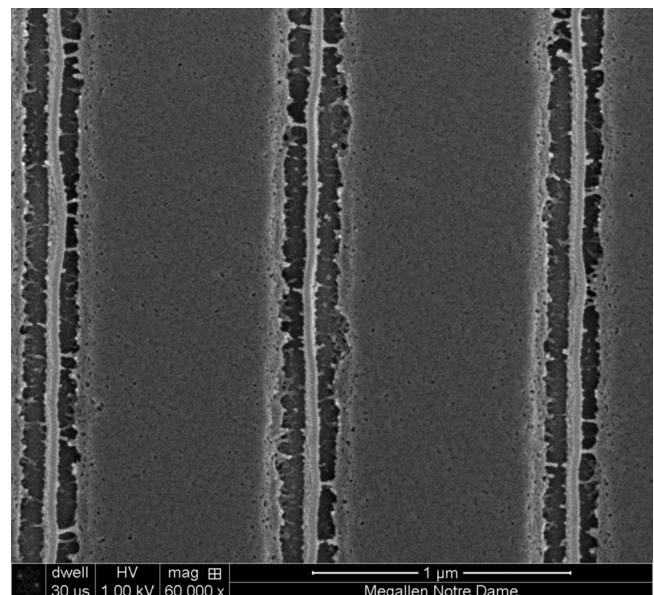


Fig. 6. Deformed negative tone features and residue including filaments that appear to pull on the features. The sample was baked for 30 min at 200°C prior to exposure, and developed in MIBK for 30 min after being exposed with a dose of $250\ \text{mC}/\text{cm}^2$ at 100 keV.

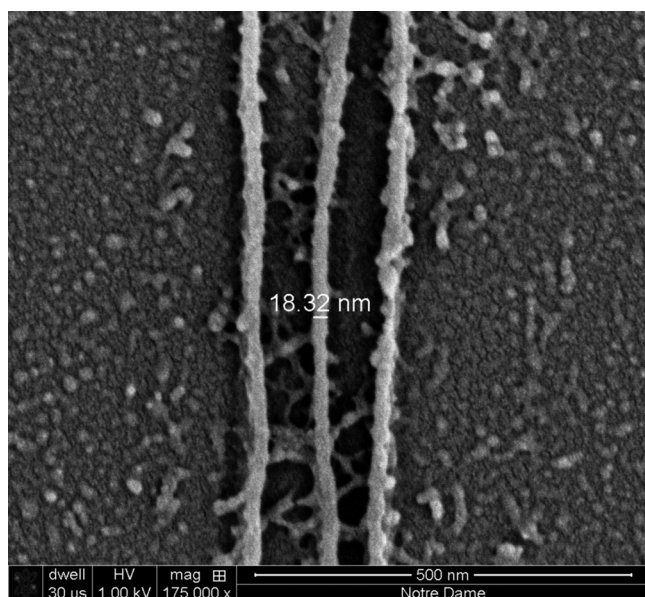


Fig. 7. 18 nm wide negative tone features with 100 nm pitch. The sample was baked for 30 min at 200 °C prior to exposure, and developed in MIBK for 30 min after being exposed at 100 keV, with a dose of 20 mC/cm² in 10 nm wide areas, where the features are formed, and 14 mC/cm² in a 400 nm wide area around the features .

exposure dose is relatively low. The negative tone effect is well known in PMMA, but, to our knowledge, has not been investigated in PMGI.

To investigate the negative tone behavior in PMGI, PMGI SF5 was spun on a silicon substrate at 9000 rpm for 45 s to give a 100 nm thick film. In PMMA, the onset of the negative tone behavior is at the doses approximately 20–30 times higher than that for positive tone behavior, while negative tone behavior of PMGI begins at doses about three times higher than positive tone dose. This relatively small dose difference results in removal of a narrower area around negative tone features. Moreover, the strong tendency of PMGI chains to cross-link results in incomplete removal of the PMGI film near these features, leaving residue and often forming filaments attached to the features. Based on a number of samples, these cross-linked filaments appear to pull against the features and may deform them. Figure 6 illustrates the effect of cross-linked filaments on deformation of the negative tone features. A possible solution to alleviate the deformation of these features is to expose a wide area around them with a dose in the positive-tone range to clear away a larger area in the vicinity of them. Figure 7 shows

three 18 nm wide lines with 100 nm pitch. The area dose for developing the wide area was 14 mC/cm² and the dose for negative tone features was 20 mC/cm². Our experiments show that ultrasonic agitation decreases the sensitivity of PMGI in the negative tone regime unlike longer bake times that increase the sensitivity of this polymer in negative tone.

III. CONCLUSION

The goal of this work was to characterize PMGI as an electron beam sensitive polymer when xylenes or MIBK are used to develop this resist. Results show that using xylenes in the positive tone regime, sub 20 nm wide trenches with aspect ratios greater than 30:1 can be readily fabricated. These high aspect ratio trenches can be used to form a “T” shaped gate with a short gate length and a tall stem. Moreover, negative resist features as small as 20 nm are achievable in PMGI when it is exposed at high doses and is developed in MIBK.

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