

Effect of water vapor pressure on positive and negative tone electron-beam patterning of PMMA

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Variable-pressure electron-beam lithography (VP-EBL) employs an ambient gas at sub-atmospheric pressures to reduce charging during electron-beam lithography. Previous work demonstrated that VP-EBL can eliminate distortion and improve resolution when patterning PMMA on insulating substrates.¹ However, it remains unknown how water vapor pressure affects the contrast and clearing dose, nor has anyone studied the effects of water vapor pressure on the negative-tone behavior of PMMA. In addition, water vapor was recently shown to alter the radiation chemistry of the VP-EBL process for Teflon AF, an amorphous fluorinated polymer that can act as a positive or negative resist.² Such changes in radiation chemistry have not been explored for PMMA. In this work, VP-EBL was conducted to study the effect of water vapor pressure on both the positive and negative tone behavior of PMMA.

First, to study the effect of water vapor pressure on positive-tone behavior, rectangular structures were exposed in 175 nm thick PMMA using a dose range of 10-300 μCcm^{-2} . Figure 1 shows the contrast curve of the film exposed at 30 keV under different water vapor pressures. The contrast values ranged from 4.1 – 5.1. At 10 mbar pressure, complete development occurs at a significantly higher exposure dose. This increase in clearing dose is consistent with the increase in electron scattering in water vapor³ but does not suggest a change in radiation chemistry as observed for Teflon AF.

Next, to study the effect of water vapor pressure on negative-tone behavior, sparse dot arrays were exposed with a dose range of 60 fC to 9 pC. Figure 2 shows the cross-linked PMMA thickness vs exposure dose. Below 3 mbar, cross-linking starts around 1.5 pC exposure dose. However, at 10 mbar cross-linking starts around 6 pC, following a similar trend as in positive-tone behavior. Interestingly, the cross-linked PMMA thickness plateaus with increasing dose and decreases with increasing water vapor pressure. This suggests a competition between cross-linking and e-beam induced etching at higher exposure doses.

Thus, water vapor does not appear to strongly alter the radiation chemistry of positive-tone PMMA exposure. However, water vapor does alter the negative tone behavior in a manner consistent with simultaneous cross-linking and etching.

1 Myers, B. D., & Dravid, V. P. (2006). *Nano letters*, 6(5), 963-968.

2 Sultan, M. A., Lami, S. K., Ansary, A., Strachan, D. R., Brill, J. W., & Hastings, J. T. (2019). *Nanotechnology*, 30(30), 305301.

3 Myers, B. D., Pan, Z., & Dravid, V. P. (2008). *Microscopy and Microanalysis*, 14(S2), 1208- 1209.

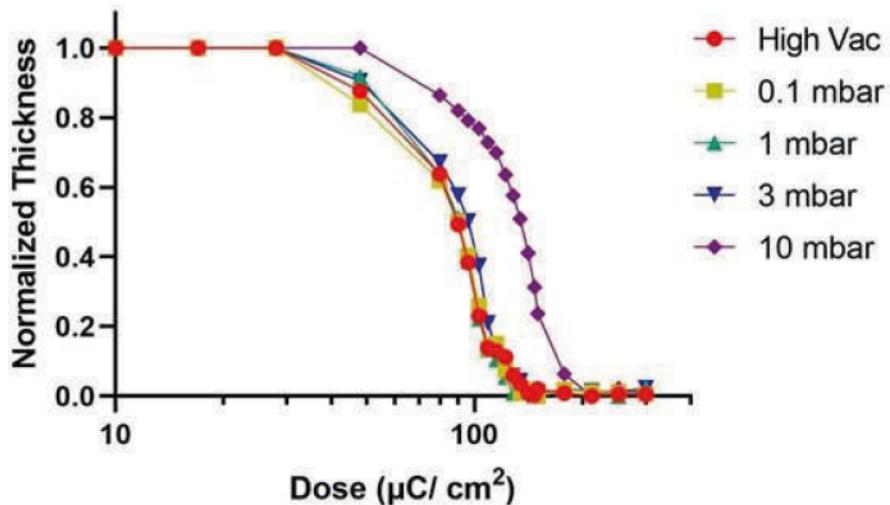


Figure 1: Normalized residual resist thickness vs exposure dose of $20\mu\text{m} \times 100\mu\text{m}$ rectangular structures. 175 nm thick PMMA was exposed at a beam energy of 30 keV with a beam current of 93 pA . PMMA was developed in $1:3\text{ MiBK:IPA}$ for 60 secs at 18°C and rinsed in IPA for 30 secs . The clearing dose increases with increasing water vapor pressure while the contrast remains nearly constant.

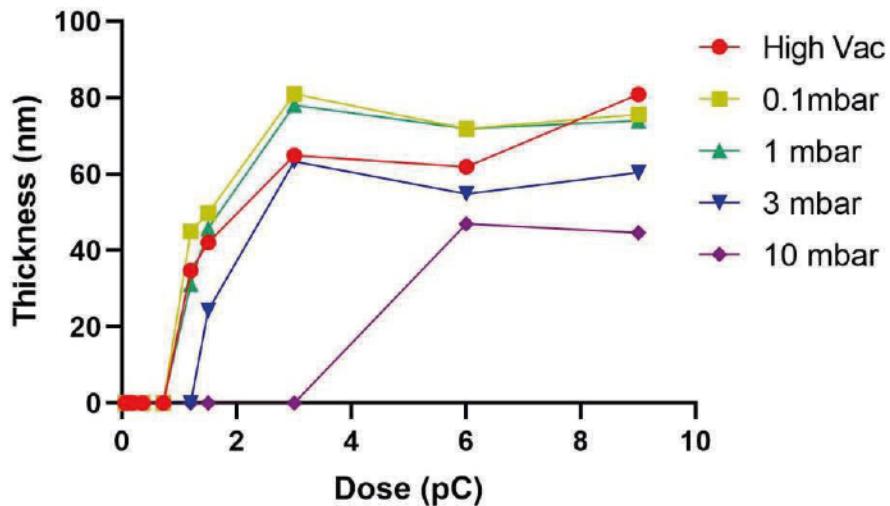


Figure 2: Cross-linked PMMA thickness vs dose. The exposure dose was varied in the range of $60\text{ fC}/\text{dot}$ to $9\text{ pC}/\text{dot}$. 175 nm thick PMMA was exposed at a beam energy of 30 keV with a beam current of $\sim 600\text{ pA}$. PMMA was developed in $1:2\text{ MiBK:IPA}$ for 60 secs at 18°C and rinsed in IPA for 30 secs . The dose required to initiate cross-linking increases with water vapor pressure while the ultimate cross-linked thickness decreases.