Effect of molecular weight distribution on e-beam resist polystyrene

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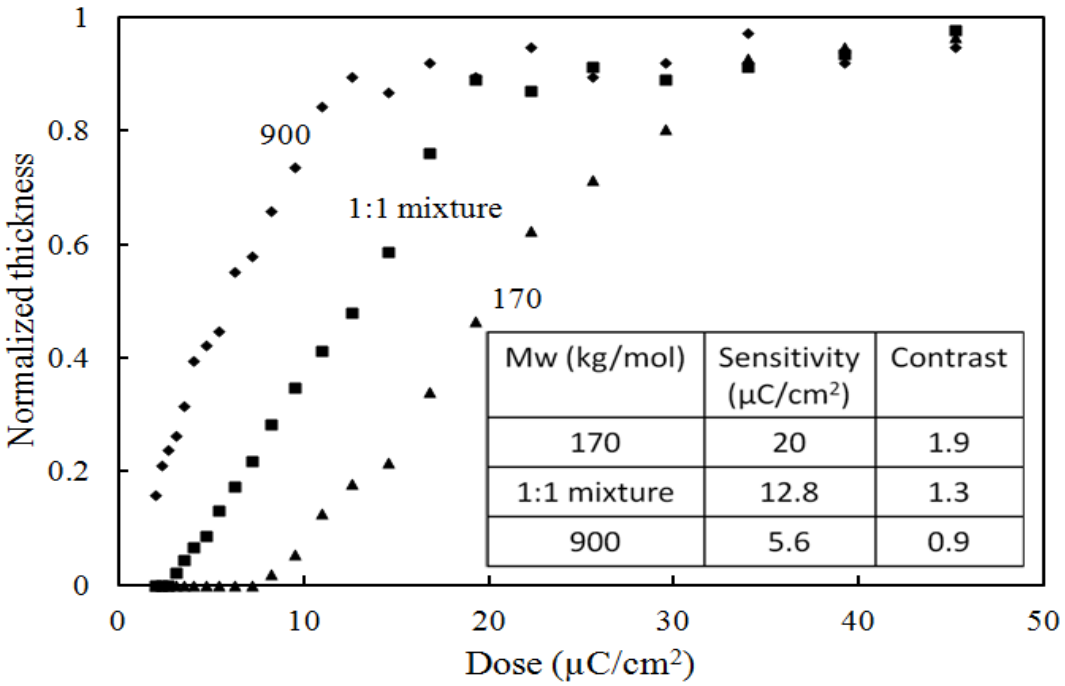
Polystyrene (PS) is a negative electron beam resist whose properties (notably sensitivity and resolution) can be tuned simply by using different molecular weights (Mw). Previously we have demonstrated ultra-high resolution patterning using low Mw of 2 kg/mol [1], and ultra-high sensitivity using high Mw of 900 kg/mol [2]. In both studies, in order to avoid any uncertainties, we have used PS with very narrow Mw distribution with polydispersity of 1.06. Ku et al. also recommended PS with narrow Mw distribution for electron beam lithography (EBL) [3]. In this study we will show that, despite the fact that PS's sensitivity ($\mu C/cm^2$) is inversely proportional to its Mw (kg/mol), no noticeably effect of very broad Mw distribution on achievable resolution is observed. It is thus unnecessary to use PS with very narrow polydispersity whose cost is more than two orders higher than general purpose PS having broad polydispertsity.

Since the polydispersity is unknown for the general purpose PS, we simulated a very high polydispersity PS by mixing at 1:1 ratio two PS samples of Mw of 170 kg/mol and 900 kg/mol, both with very narrow polydispersity of 1.06. For comparison, we also studied the exposure performance of each PS sample. In the experiment, the PS was dissolved in chlorobenzene at 1.2 wt%. The pattern was exposed at 20 kV and 98 pA beam current, and developed by tetrahydrofuran for 3 min. The remaining thickness after development was measured by AFM. The contrast curves for 170 kg/mol, 170:900=1:1 mixture, and 900 kg/mol are shown in Figure 1. As expected, the sensitivity for 900 kg/mol is much higher than that for 170 kg/mol. The contrast curve for the 1:1 mixture resembles that expected for a hypothetical PS with Mw around 400 kg/mol. This also implies that PS of certain Mw can be simulated by a mixture of two PS samples having different Mw. To study the resolution capability of the PS samples, we exposed dense line arrays (whose pattern area was larger than the range of electron backscattering, so similar resolution is expected when patterning over larger areas). As expected and seen in Figure 2a-c, the achievable resolution (half pitch) for the 1:1 mixture is reasonable compared to that of 170 and 900 kg/mol PS samples. In addition, a general purpose PS having Mw of 260 kg/mol (polydispersity unknown) demonstrated similar resolution to the 170 kg/mol PS (polydispersity 1.06) as shown in Figure 2d.

[1] S. Ma, C. Con, M. Yavuz and B. Cui, Nanoscale Res. Lett. 6, 446 (2011).
[2] C. Con, R. Dey, M. Ferguson, J. Zhang, R. Mansour, M. Yavuz and B. Cui, submitted to Microelectronic Engineering.
[3] H. Y. Ku and L. C. Scala, J. Electrochem. Soc.: Solid State Science, 116, 980 (1969).



Mw (kg/mol)	Sensitivity (μC/cm²)	Contrast
170	20	1.9
1:1 mixture	12.8	1.3
900	5.6	0.9

Figure 1. Contrast curves for polystyrene exposed at 20 kV with Mw of 170 kg/mol, a 1:1 mixture of 170 and 900 kg/mol, and 900 kg/mol. The insert shows the sensitivity (dose for 50% remaining thickness) and contrast for each sample.

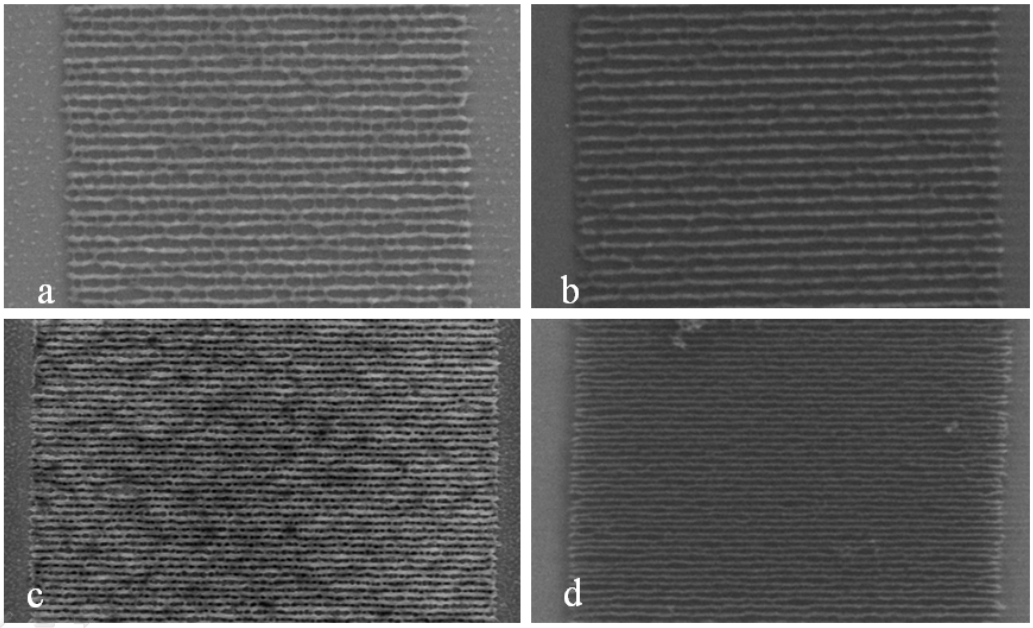


Figure 2. Dense line array exposed at 20 kV in polystyrene with different Mw and its distributions. a) 900 kg/mol, 150 nm period, 0.26 nC/cm line dose; b) 1:1 mixture of 170 and 900 kg/mol, 150 nm period, 0.66 nC/cm; c) 170 kg/mol, 80 nm period, 1.0 nC/cm; d) 260 kg/mol, 80 nm period, 0.91 nC/cm.