# Supporting information

## Effect of molecular weight on the EUV-printability of main chain scission type polymers

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### Section S1. Density and film thickness (FT) data for different Mw PMMA films:

Densities of all the different Mw photoresist solution that was used to spin coat the material were similar and the final FT was also made the same. The density and film thickness data used during the contrast curve and EUV-printability analysis are provided in table S1.

*Table S1: Solution densities of different Mw PMMA used to spin-coat to achieve similar FT for contrast curve and EUV-printability analysis*

| Material | Density of spin coating solution (g/cm$^3$) at 20°C | Final film thickness (FT) |
|---|---|---|
| **15K Mw PMMA** | 0.98 | 19±2 nm |
| **120K Mw PMMA** | 0.99 | 19±2 nm |
| **350K Mw PMMA** | 0.99 | 19±2 nm |
| **600K Mw PMMA** | 0.99 | 19±2 nm |
| **950K Mw PMMA** | 0.99 | 19±2 nm |

### Section S2. Criteria to evaluate EUV-printability of different Mw PMMA and copolymer system:

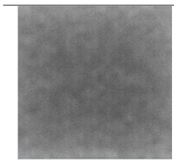
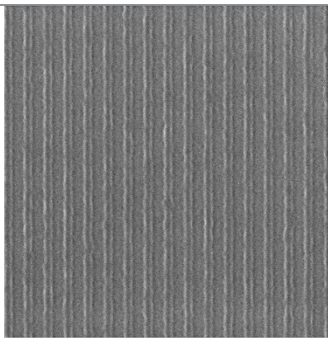
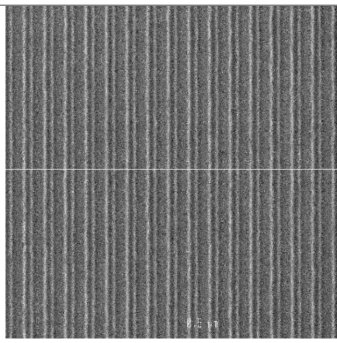
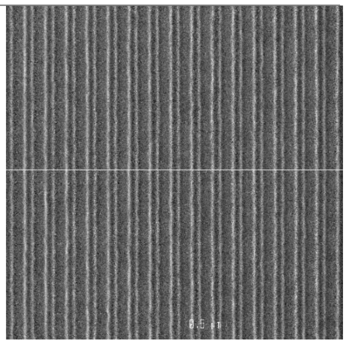
The way we evaluated the printability is by the following process:

1) Focus-Exposure-Matrix (FEM)

In this process, Si wafers were spin-coated with different Mw PMMA and were exposed to a range of different EUV-dose and focus. The printability of the photoresist was checked at different line-spaces (L/S). The EUV-dose and focus range applied were 0-100 mJ/cm$^2$ and -0.8 to 0.8 nm respectively. After patterning, Critical Dimension – Scanning Electron Microscope (CD-SEM) was used to gather images of all the patterns. CD-SEM also provides data such as the CD and roughness values of the images. Of all the different L/S patterns – 50 nm dense L/S patterns were chosen for further analysis.

Based on the CD-SEM data, images whose CD values were in-spec (meaning only 10% variation from the target value, i.e., 50±5 nm), were chosen and their CD and roughness data were averaged to get representative values as provided in table S2.

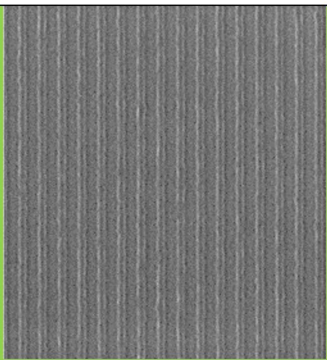
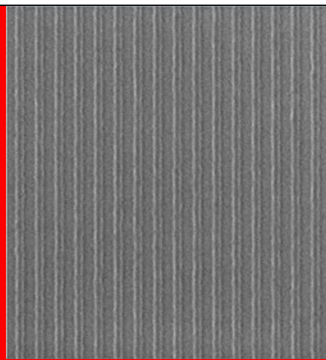
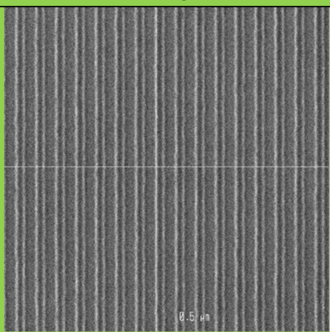
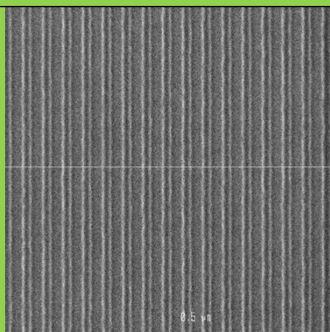
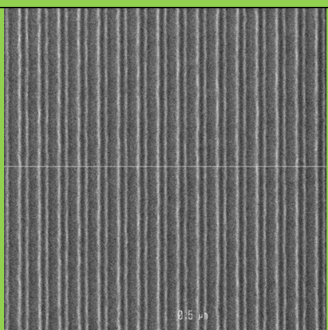
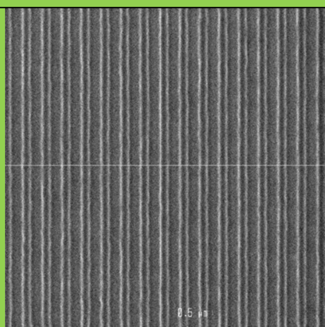
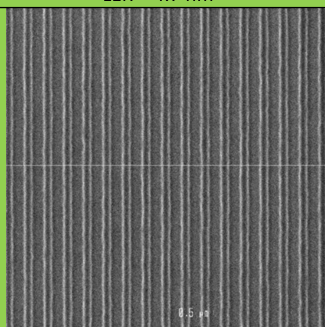
*Table S2: Printability of different Mw PMMA at 50 nm dense L/S*

| **15K Mw PMMA** | **120K Mw PMMA** | **600K Mw PMMA** | **950K Mw PMMA** |
|---|---|---|---|
|  |  |  |  |
| **No resolution** | Dose – 44 mJ/cm$^2$<br>CD – 46.2 nm<br>LER > 5 nm | Dose – 50 mJ/cm$^2$<br>CD – 48.5 nm<br>LER – 4.8 nm | Dose – 52 mJ/cm$^2$<br>CD – 49.9 nm<br>LER – 4.1 nm |

It was clear from SEM-images that the 15k Mw PMMA has no printability at 50 nm L/S. So it was considered a bad photoresist.

Upon comparing 120K, 600K and 950K Mw PMMA at a CD of 50±5 nm range for different EUV-doses, it was identified that the line-edge-roughness (LER) values showed the following tend: 120K > 600K > 950K. This is shown in table S2. Also, the change in LER values w.r.t. EUV-dose for different Mw PMMA is shown in figure S1.

*Table S2: Line-edge-roughness (LER) values for 120K, 600K and 950K Mw PMMA at a CD of 50±5 nm*

| Mw of PMMA | 46 mJ/cm² | 50 mJ/cm² | 54 mJ/cm² |
|---|---|---|---|
| **120K** |  CD – 48.8 nm<br>LER ~ 6.4 |  CD – 46.2 nm<br>LER ~ 6.1 nm |  CD – 43.5<br>LER ~ 5.9 |
| **600K** |  CD – 51.6 nm<br>LER – 4.8 nm |  CD – 48.5 nm<br>LER – 4.8 nm |  CD – 47.3 nm<br>LER – 4.7 nm |
| **950K** |  CD – 52.3 nm<br>LER – 4.1 nm |  CD – 49.9 nm<br>LER – 4.1 nm |  CD – 48.6 nm<br>LER – 4.0 nm |

Colour code: CD in-spec | CD out-of-spec

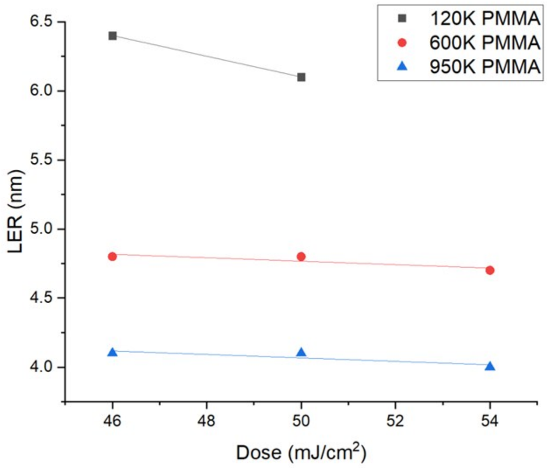


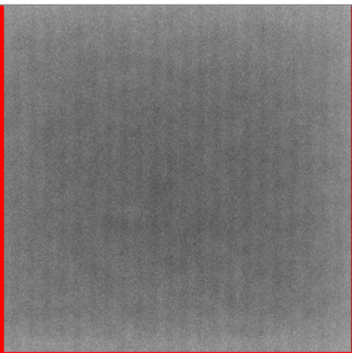
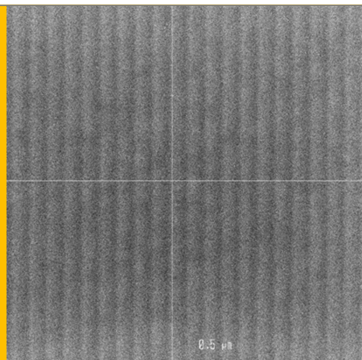

*Figure S1: LER values for different Mw PMMA exposed at a variable EUV-dose*

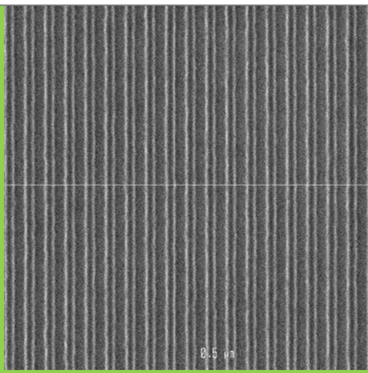
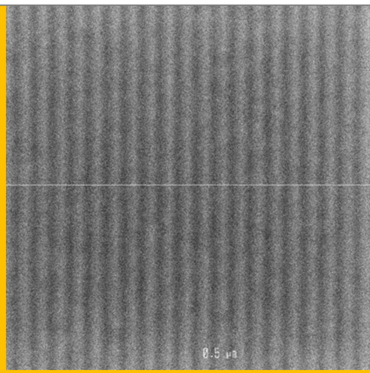
The next criterion used was the resolution check at smaller dense pitches.

<u>2) Resolution check at smaller dense pitches</u>

600K and 950K showed printability at 45nm and signs of resolution at 40nm dense L/S. But 120K has no resolution at 45 nm dense L/S. This is shown in table S3.

*Table S3: Resolution check at 45 and 40 nm dense L/S for 120K, 600K and 950K Mw PMMA*

| PMMA | 45 nm dense L/S | 40 nm dense L/S |
|---|---|---|
| **120K** |  No printability | Did not check |
| **600K** |  Ok printability |  Resolvable |

| | | |
|---|---|---|
| **950K** |  Ok printability |  Resolvable |

**Section S3. Sample preparation for Gel Permeation Chromatography (GPC)**

For each Mw, the photoresist material is coated on four 300-mm wafers to achieve the same FT of 50 nm. The first two wafers are manually stripped with THF. The photoresist-THF solution is allowed to be evaporated overnight, to remove all the solvent. Based on the concentration of the photoresist compound, THF is added again to bring the concentration to 2 mg/mL. This is the reference sample. The next two wafers are flood exposed to EUV-radiation at a particular EUV-dose (30mJ/cm$^2$ in this study), and then the same stripping procedure is repeated to bring the sample concentration to 2 mg/mL. This is the exposed sample. Both, the reference and exposed samples are analyzed with GPC.

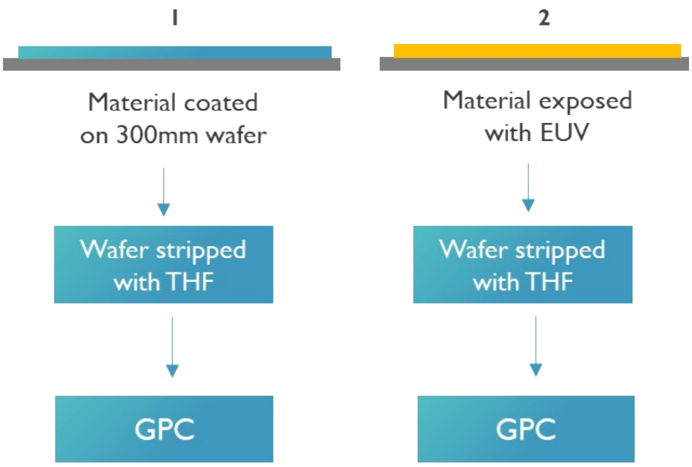



*Figure S2: Sample preparation of photoresist material for GPC analysis*

**Section S4. GPC results: – calibration curve and different Mw PMMA comparison**

The calibration of the GPC column with predefined Mw of PMMA is shown in figure S3. And the GPC results of different Mw PMMA is shown in figure S4.

| Time | Mw |
|---|---|
| 6.271 | 1677000 |
| 6.636 | 679000 |
| 6.976 | 298900 |
| 7.343 | 122300 |
| 7.638 | 62950 |
| 7.961 | 29960 |
| 8.393 | 10900 |
| 8.701 | 4950 |
| 9.016 | 2710 |
| 9.529 | 875 |

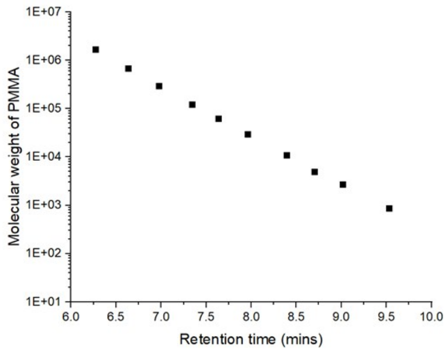



*Figure S3: Calibration curve with predefined Mw of PMMA for the GPC column*

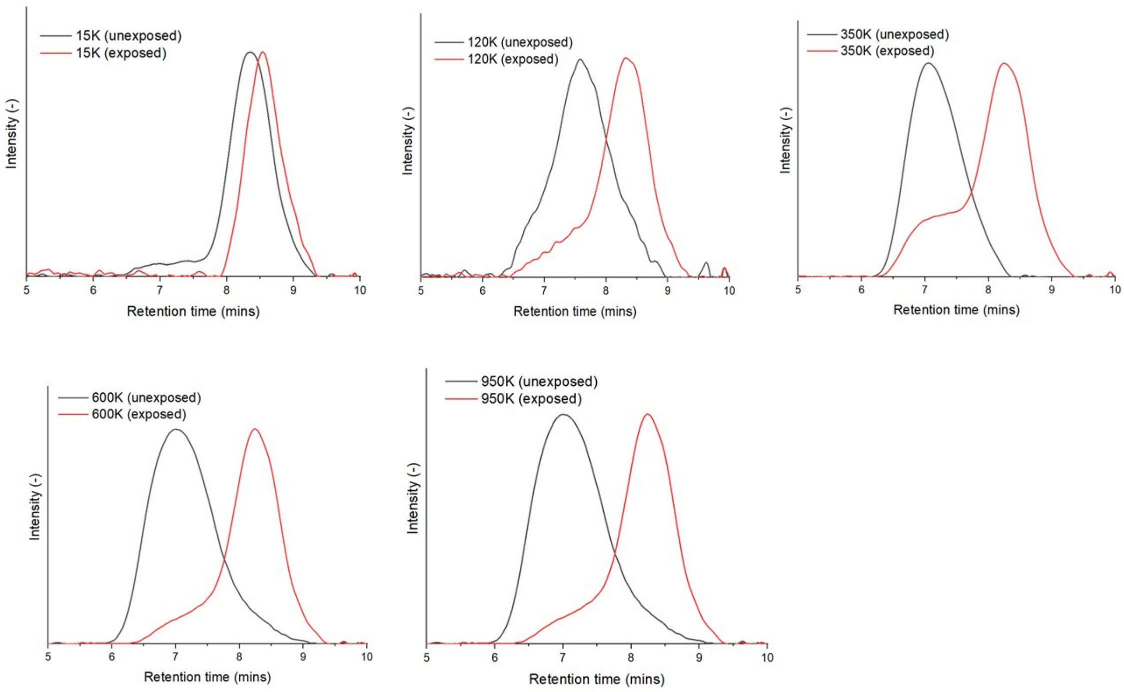



*Figure S4: GPC results of different Mw PMMA*

From the GPC results, Mw of the unexposed and exposed material can be calculated, as shown in table S4. A rough estimation of the amount of MCS in the polymer chains can also be estimated by dividing the unexposed Mw value by the exposed Mw value. This is depicted in figure S5.

*Table S4: GPC data for different Mw PMMA before and after EUV-exposure*

| Photoresist material | Unexposed Mw | Exposed Mw | Amount of MCS in PMMA chains |
|---|---|---|---|
| **15K Mw PMMA** | 9000±300 | 5900±200 | ~ 1 |
| **120K Mw PMMA** | 127000±400 | 28000±350 | ~ 4 |
| **350K Mw PMMA** | 267000±500 | 68000±500 | ~ 4 |
| **600K Mw PMMA** | 457000±300 | 48500±200 | ~ 9 |
| **950K Mw PMMA** | 839000±250 | 44000±20 | ~ 19 |

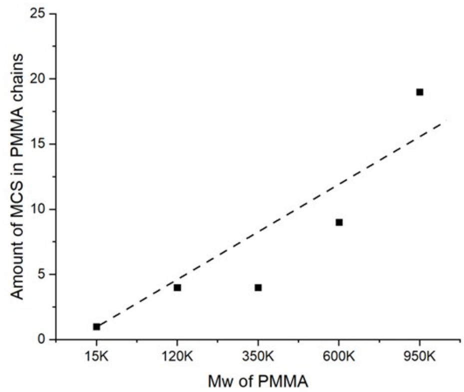


*Figure S5: Amount of MCS in different Mw PMMA based on peak shift in the GPC experiment*

As seen from the figure, higher Mw PMMA show a larger degree of chain fragmentation (which equals a larger difference in the chain solubilities) after EUV-exposure. This results in higher image contrast and better development step during the lithography process.

## Section S5. Litho-parameter: GPC peak shift as a measure of chemical contrast for different Mw PMMA

For MCS-type resist, the GPC peak shift refers to the amount of change in the Mw (signifies the solubility switch for this material). The higher the difference between the unexposed (insoluble) chains compared to the EUV-fragmented (soluble) chains, the higher will be the contrast. Therefore, the higher Mw material with a higher peak shift provides better contrast.

This was also confirmed experimentally for 120K and 950K Mw PMMA by checking the contrast curve, using the same developer solvent. This is shown in figure S3 (updated in the supplementary information file). As seen in the figure, the contrast curve of 950K Mw PMMA shows a step-function with a sharper slope, which means much better contrast, compared to the 120K Mw PMMA.

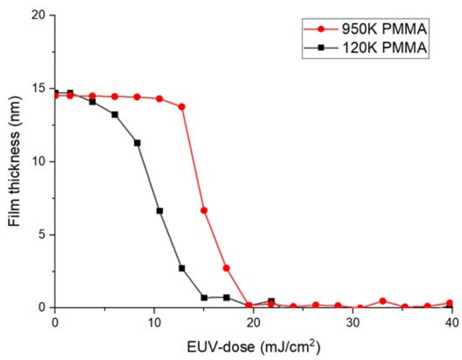


*Figure S6: Chemical contrast curve of 120K and 950K Mw PMMA for MIBK:IPA (1:2) developer solvent*

## Section S6. RGA analysis of 600K Mw

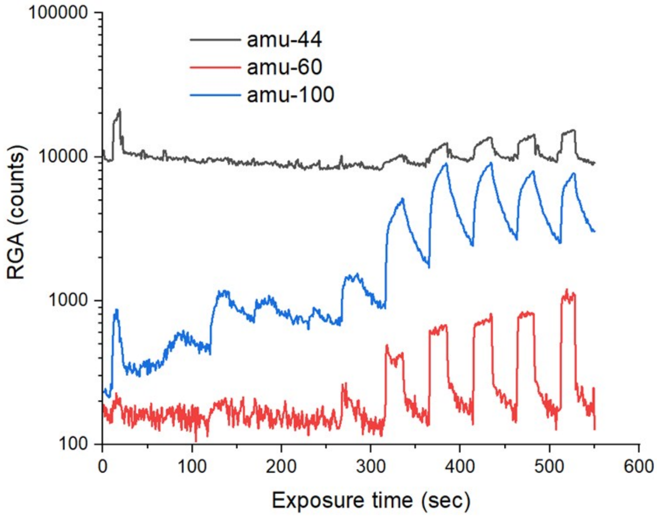



*Figure S7: RGA signal of important desporption species (amu-44, 60 and 100) for LEE-exposed 600K Mw PMMA*

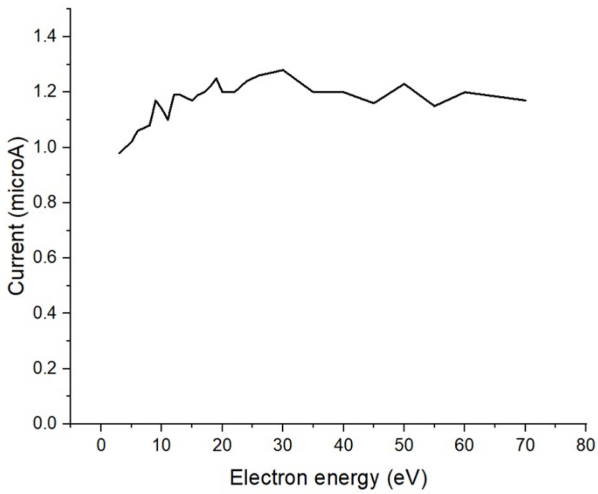



*Figure S8: The current values for different electron energies applied in the RGA experiments*

## Section S7. Chemical stucture of the MCS-type coplolymer system

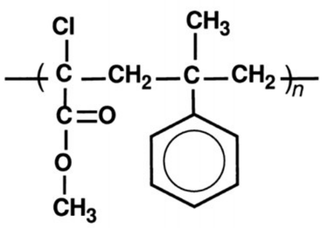



*Figure S9: Chemical structure of the MCS-type copolymer system as obtained from the Zeon corporation – containing monomers chloromethyl acrylate and mehtylstyrene (1:1 ratio)*