

Unravelling the effect of fluorinated ligands in hybrid EUV photoresists by X-ray spectroscopy

Lianjia Wu,^a Ivan Bernalov,^a Katharina Witte,^b Olivier Lugier,^a Jarich Haitjema,^a Michaela Vockenhuber,^b Yasin Ekinci,^b Benjamin Watts,^b Albert M. Brouwer,^{ac} and Sonia Castellanos^{*a}

^a Advanced Research Center for Nanolithography, Science Park 106, 1098 XG Amsterdam, the Netherlands. E-mail: s.castellanos@arcnl.nl

^b Paul Scherrer Institute, Forschungstrasse 111, Villigen 5232, Switzerland.

^c van't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands.

Supporting Information

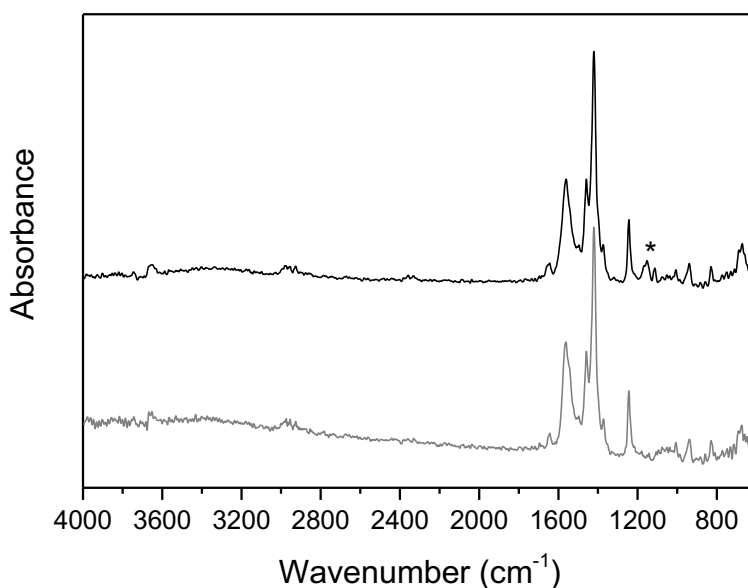


Figure S1 Fourier transform infrared (FTIR) spectra of **ZrMc** (in grey) and **ZrMcF** (in black) thin films, offset for clarity. The absorption band at 1100–1200 cm^{-1} (asterisk) with peaks at 1118, 1149 and 1167 cm^{-1} is assigned to C-F stretching from the trifluoromethacrylate ligand in the molecule.

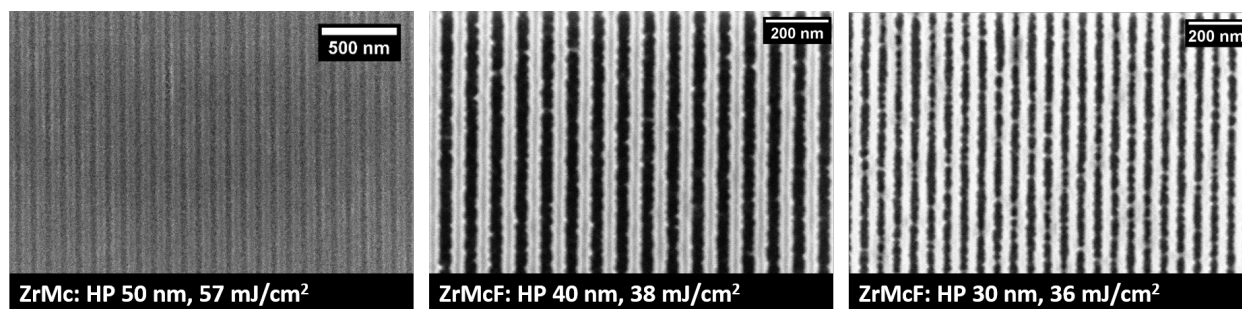


Figure S2 Selected SEM pictures of dense lines patterns printed with EUV interference lithography on **ZrMc** and **ZrMcF** (HP = half-pitch).

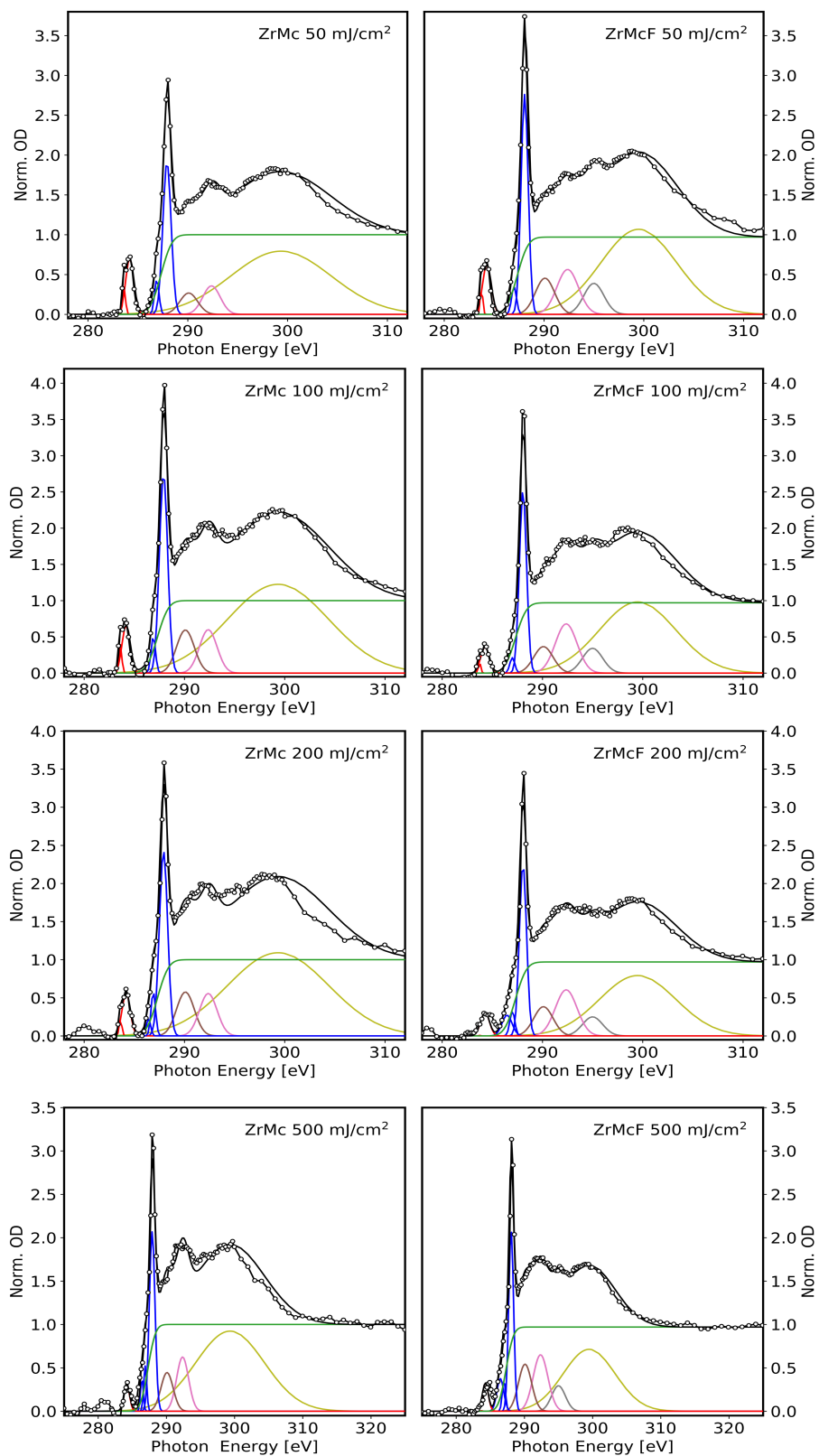


Figure S3 Fitted C K-edge NEXAFS spectra of areas on **ZrMc** and **ZrMcF** exposed to EUV.

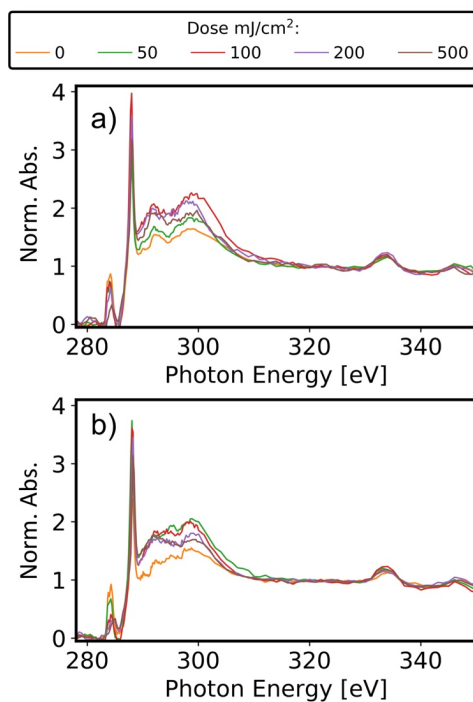


Figure S4 C K-edge NEXAFS spectra of a) **ZrMc** and b) **ZrMcF** before and after exposure normalized to the continuum and extended to photon energies where the peaks of the Zr $M_{2,3}$ -edge (333.8 eV and 346.5 eV) are observed.

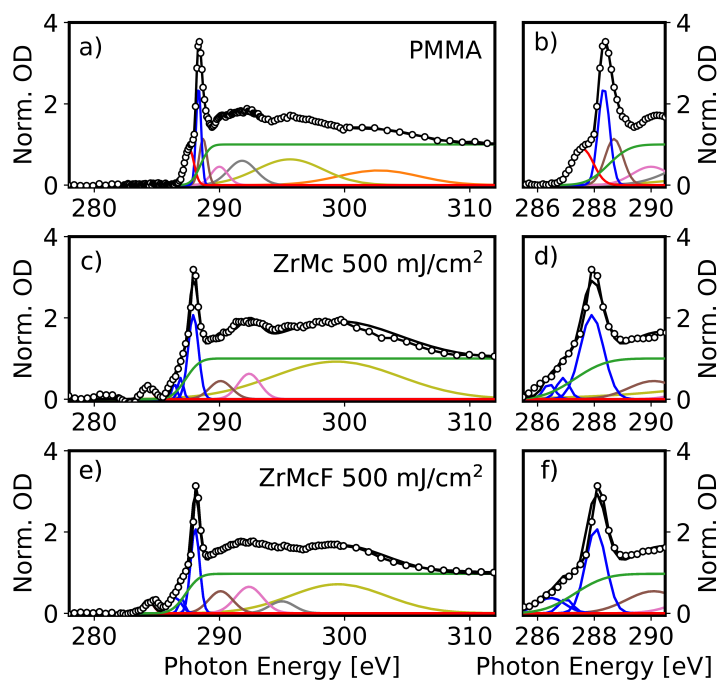


Figure S5 Comparison of the C K-edge spectrum of PMMA with the spectra of **ZrMc** and **ZrMcF** after exposure to the highest EUV dose (500 mJ/cm²).

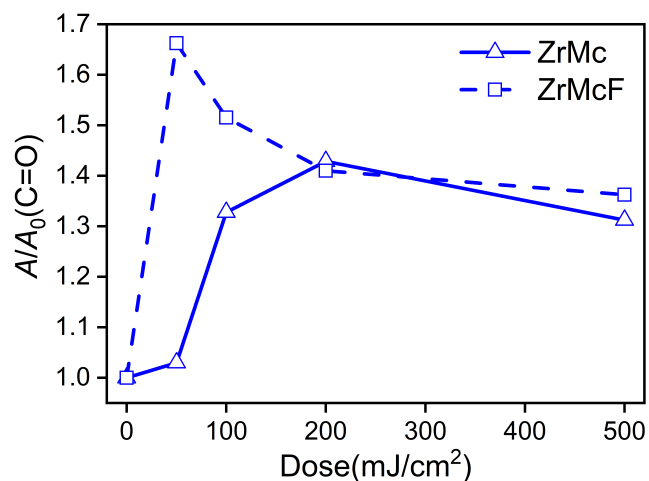


Figure S6 Added absorbance values of the fitted peaks in the normalised spectra associated to C 1s \rightarrow π^* (C=O) electronic transition ($A_{286.9} + A_{287.9}$) relative to the absorbance values in the unexposed sample (A/A_0).

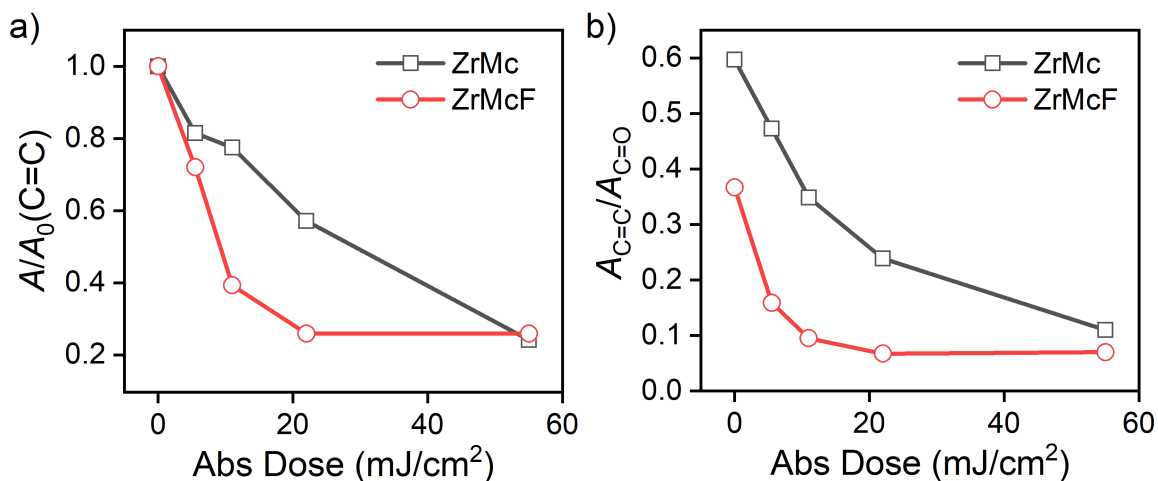


Figure S7 (Replotted from Fig. 4.) Evolution of the absorbance value (A) of some fitted peaks in normalized spectra as a function of estimated absorbed dose, where the absorbed dose = incident dose * (100% - T) and $T = \exp(-\alpha \cdot d)$. **a)** Absorbance of peaks assigned to C 1s \rightarrow π^* (C=C) ($A_{283.6} + A_{284.2}$) relative to initial values (A/A_0); **b)** Absorbance ratio between peaks assigned to C 1s \rightarrow π^* (C=C) ($A_{283.6} + A_{284.2}$) and to C 1s \rightarrow π^* (C=O) ($A_{286.9} + A_{287.9}$).

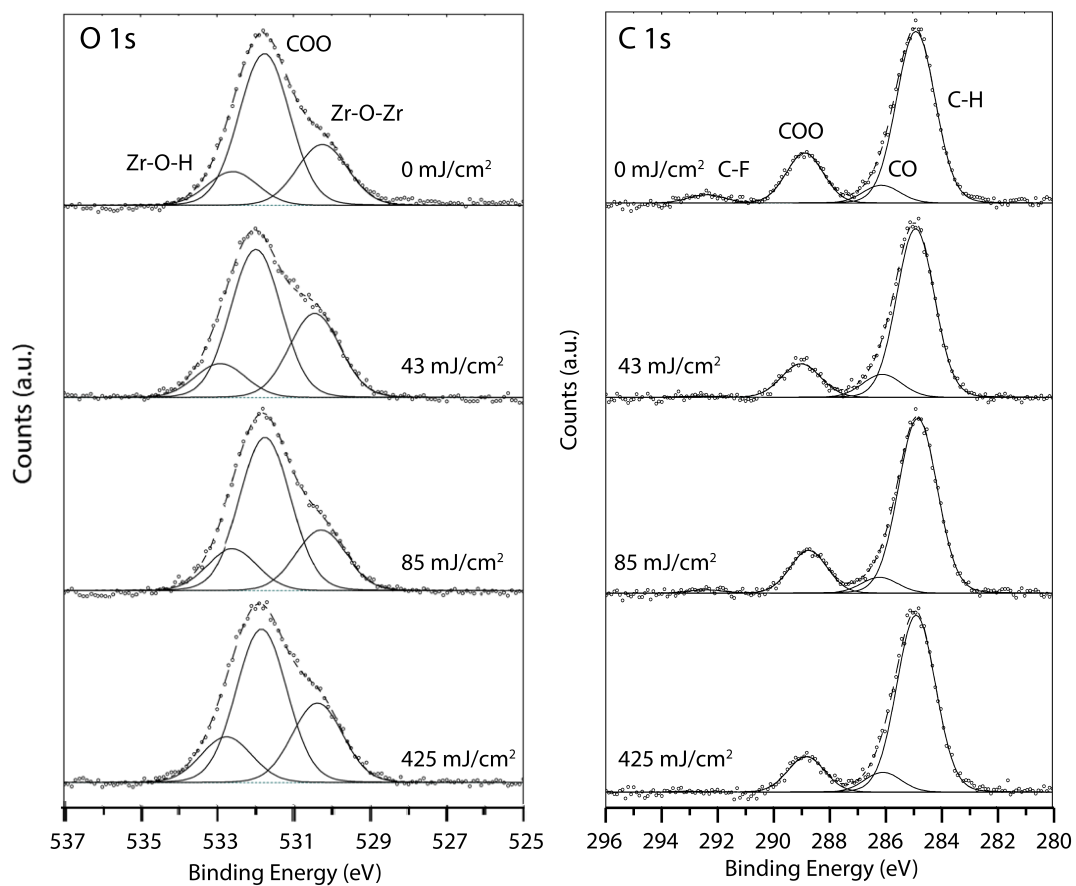


Figure S8 High-resolution XPS spectra of the O 1s and C 1s peaks of the unexposed and the exposed **ZrMcF** resist.

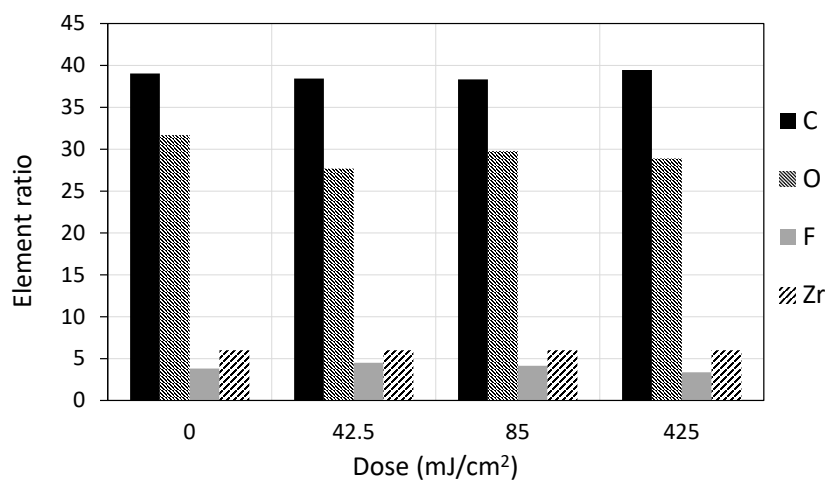


Figure S9 Elemental ratio recorded with XPS of **ZrMcF** thin films before and after exposure to different doses of EUV light.