Electronic Supplementary Information

Mixed-ligand zinc-oxoclusters: efficient chemistry for high resolution nanolithography

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1. Images of dense line/space features patterned with EUV interference lithography.

AFM images were recorded with a Bruker Dimensions Icon in ScanAsyst-air mode using a silicon tip on nitride lever of SCANASYST-AIR model (Bruker). Processing of the L/S contours profiles were done using NanoScope Analysis version 2.00 software.

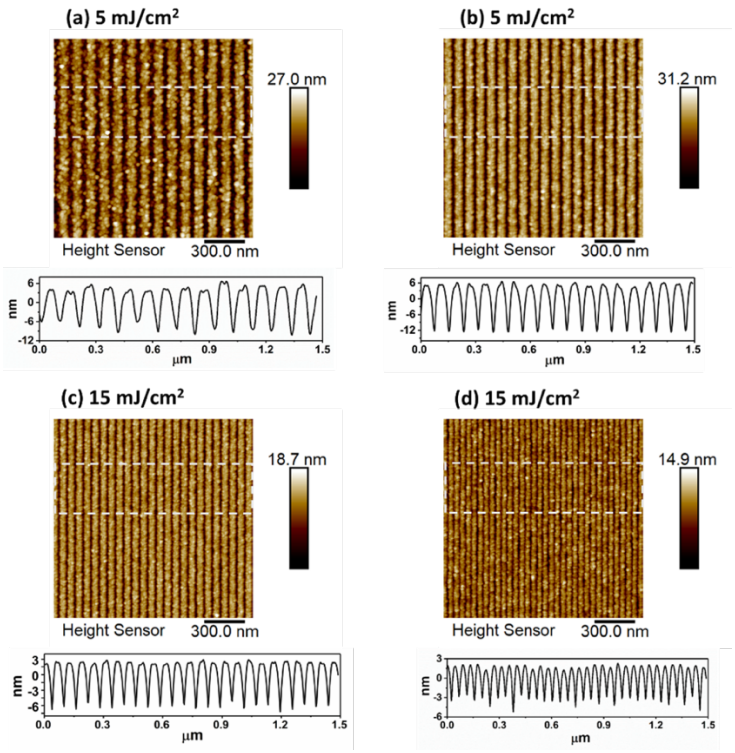

Fig. S1 *Selected AFM images and contour profiles of printed L/S features for HP (a) 50 nm (5 mJ/cm^2); (b) 40 nm (5 mJ/cm^2); (c) 30 nm (15 mJ/cm^2) and (d) 22 nm (15 mJ/cm^2) patterned on Zn(MA)(TFA) using EUV-IL.*

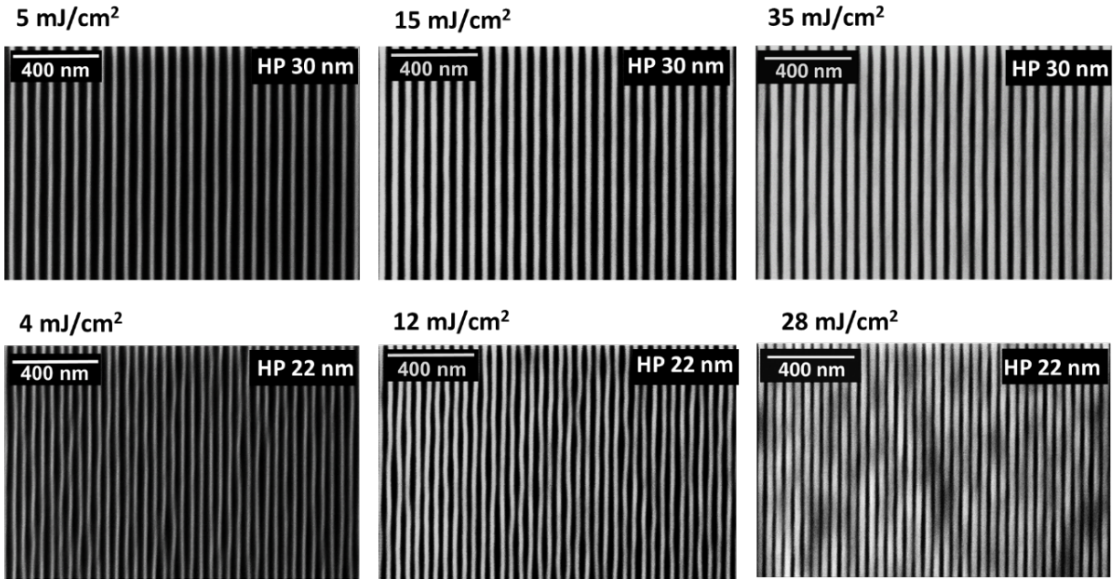

Fig. S2 *Selected SEM (operated at 2 kV) images for HP 30 nm and 22 nm used to calculate the linewidth/ critical dimensions of line/space features over a range of exposure doses.*

2. Control experiments for aging effect.

The effect of aging during the time lapse between exposure in the synchrotron facilities and the spectroscopic analyses in our laboratories was inspected by comparing the FTIR and UV-vis spectra of a freshly spin-coated film. A certain degree of cross-linking and decarboxylation is observed, as previously reported.[1] The effect of aging does not eclipse the changes induced by EUV light, which are clearly distinguished.

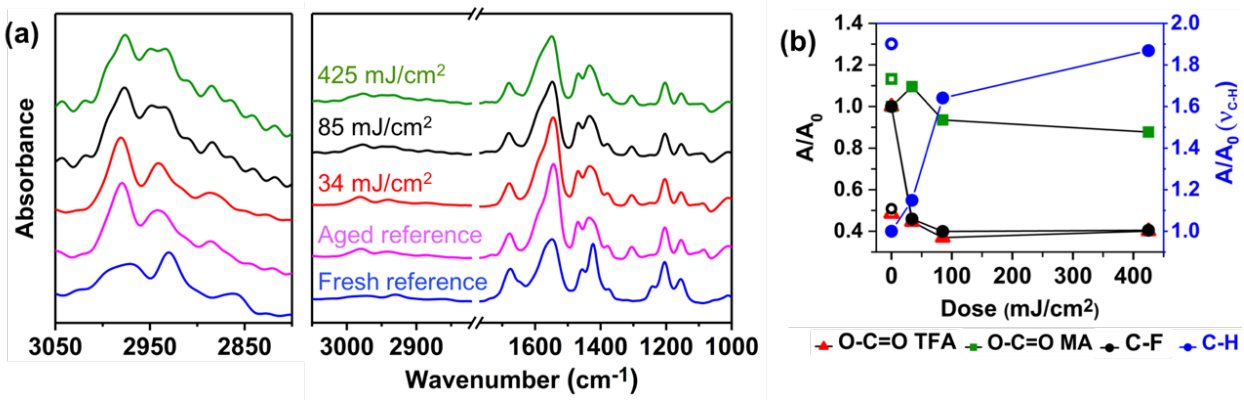

Fig. S3 *(a) FTIR spectra of the exposed (doses given in the graph) and unexposed areas (reference aged) in the sample exposed to EUV and of a freshly spin-coated film (fresh reference) and (b) Peak area ratio of relevant*

peaks relative to the fresh reference for the exposed areas. The peak area ratio of the aged unexposed area relative to the freshly spin-coated sample is given as hollow markers.

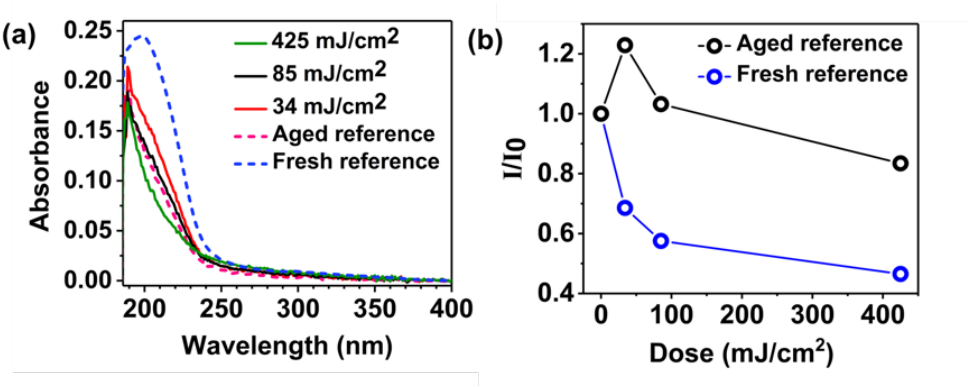

Fig. S4 *(a) UV-vis absorption spectra of the resist film and (b) change in the UV-vis absorbance maximum relative to the aged and fresh sample as a function of EUV dose.*

We conclude that aging has a stronger effect in the MA ligands of the unexposed material than in the exposed one. We speculate that, after EUV exposure, the product consists of a more stable cross linked network.

3. X-ray photoelectron spectroscopy

No significant changes in the Zn 2*p* region are observed upon the formation of Zn-F species. However, the difference in the BE of Zn 2*p* between a Zn^{2+} with only Zn-O bonds and with Zn-F bonds is less than 1 eV, according to the literature.[2] Here, the concentration of the proposed Zn-F species in the overall Zn-content is estimated to be very low (ca. 15%). This might explain why no changes are observed in the Zn 2*p* peaks.

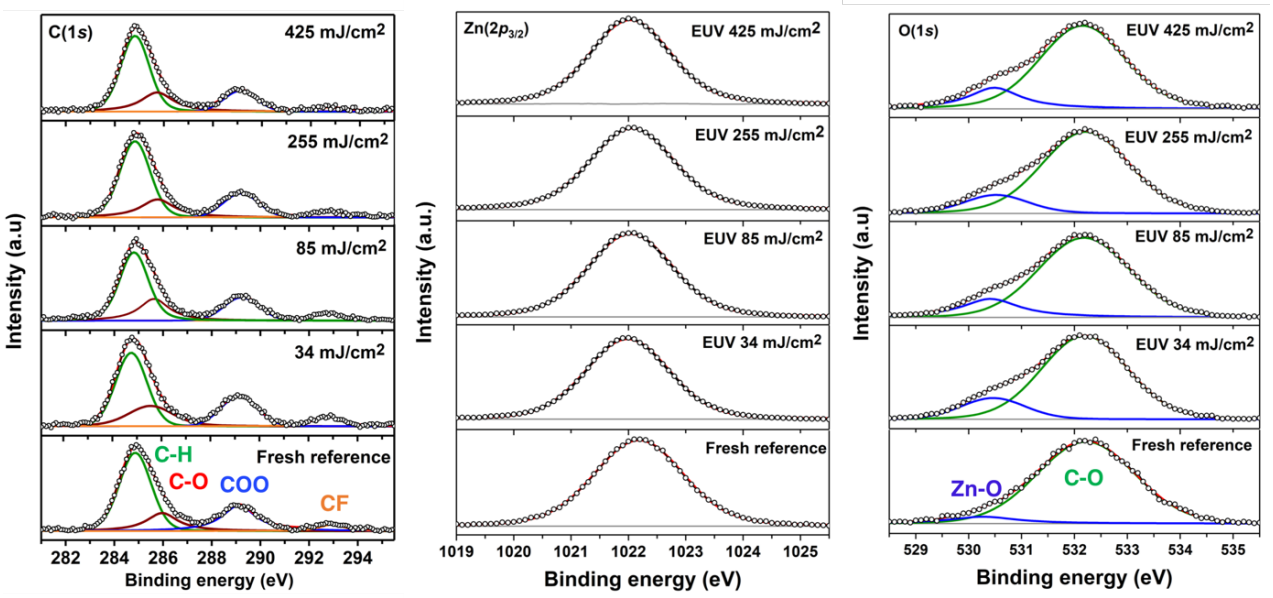

Fig. S5 *High-resolution XPS spectra of C 1s, Zn $2p_{3/2}$, and O 1s*

To obtain the information for zinc metal high resolution spectra for $ZnL_3M_{45}M_{45}$ Auger electron spectra were recorded. The separation between these two peaks for both samples fresh and exposed sample (425 mJ/cm^2) was quite constant, 3.1 ± 0.1 eV.

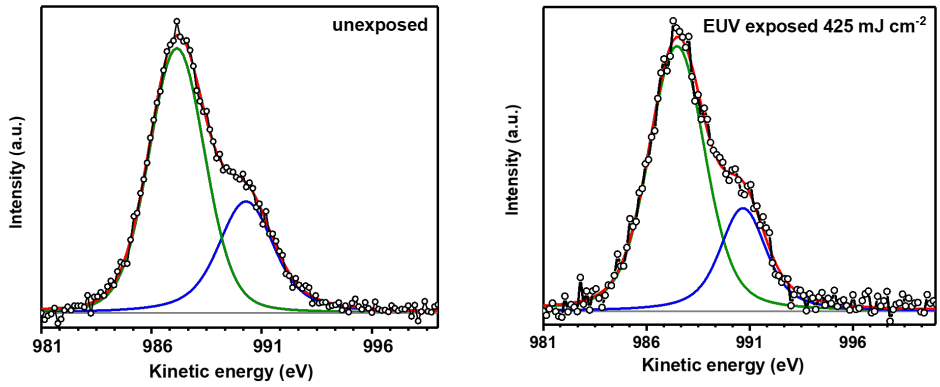

Fig. S6 *High resolution Zn Auger spectra for unexposed and exposed sample at 425 mJ/cm^2. Solid lines without dots represent the fitting results.*

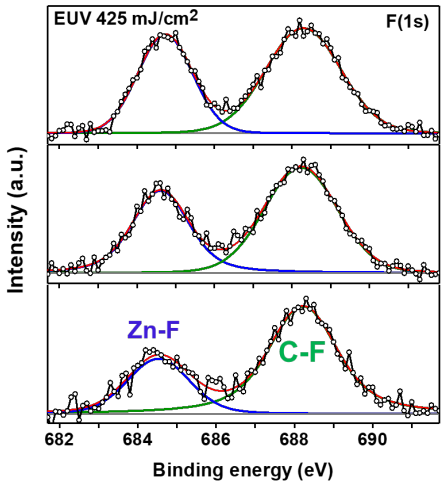

Fig. S7 *From bottom to top, chemical changes induced by X-rays of XPS after consecutive measurements on the same spot on Zn(MA)(TFA) thin film.*

1 N. Thakur, L.-T. Tseng, M. Vockenhuber, Y. Ekinci and S. Castellanos, *J. Micro/Nanolithography, MEMS, MOEMS*, 2019, **18**, 43504.

2 E. Polydorou, A. Zeniou, D. Tsikritzis, A. Soultati, I. Sakellis, S. Gardelis, T. A. Papadopoulos, J. Briscoe, L. C. Palilis and S. Kennou, *J. Mater. Chem. A*, 2016, **4**, 11844–11858.