Extreme ultraviolet induced chemical reactions in photoresists and model systems

S. Castellanos

Advanced Research Center for Nanolithography

2017 EUVL workshop, June 12-15

ARCNL

ADVANCED RESEARCH CENTER FOR NANOLITHOGRAPHY

Partners

ASML

Universiteit van Amsterdam

Gemeente Amsterdam

NWO

VU Vrije Universiteit Amsterdam

Provincie Noord-Holland

List of contributors

ARCNL:

EUV Photoresists group:

L. Wu
O. Lugier

Nanophotochemistry group:

Prof. Dr. F. Brouwer
Ing. van Leeuwen
J. Haitjema
Y. Zhang
Dr. A. Thete

EUV Photoemission group:

N. Ottosson
X. Liu

Paul Scherrer Institut:

D. Kazazis
M. Vockenhuber
R. Fallica

Uppsala University:

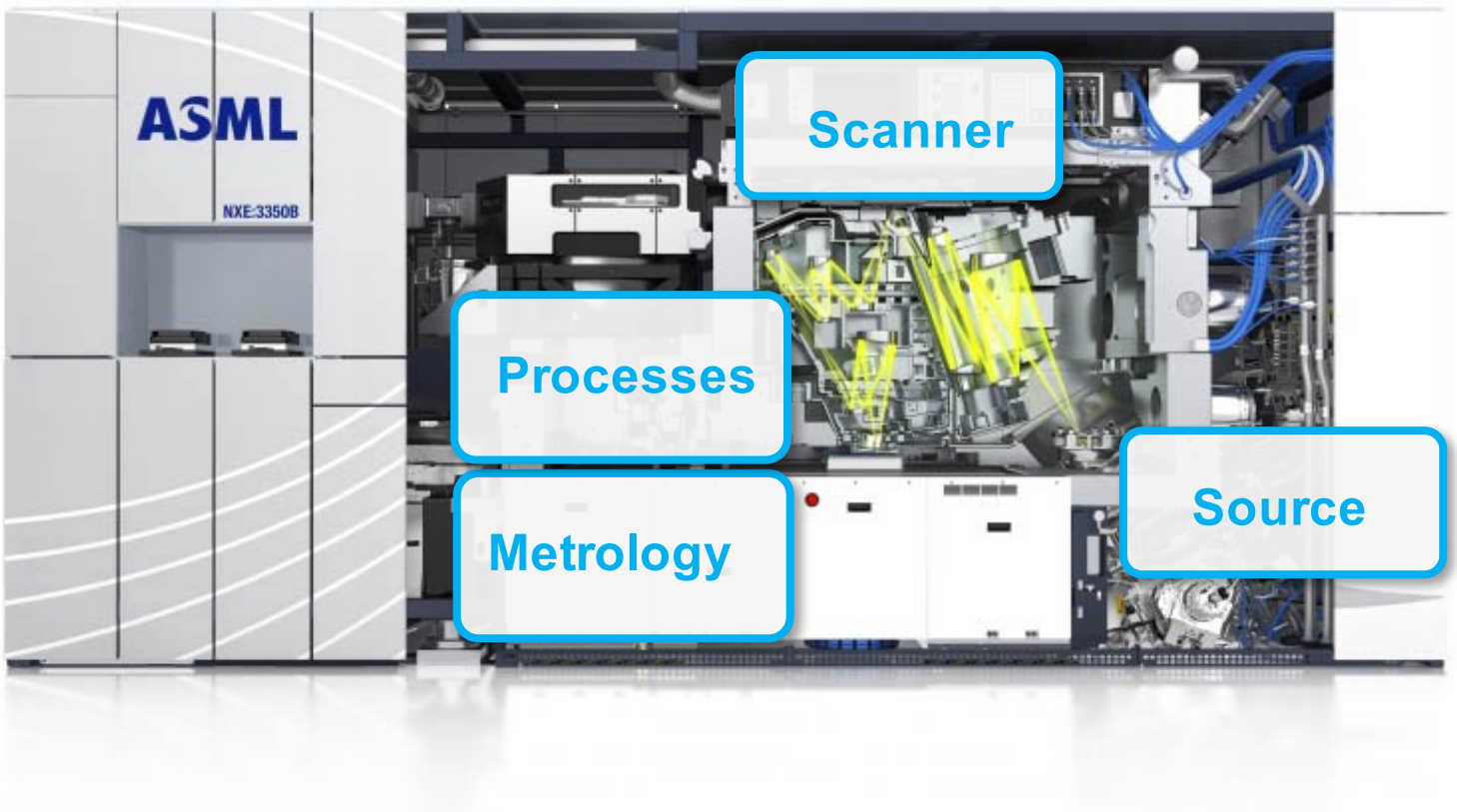
F. Johansson
A. Lindblad

Leiden University:

D. Geelen
S.J. van der Molen
R.M. Tromp

Advanced Research Center for Nanolithography

Fundamental research with a mission



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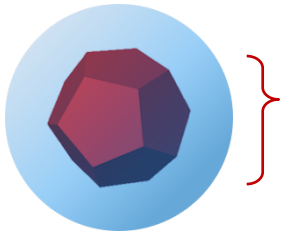
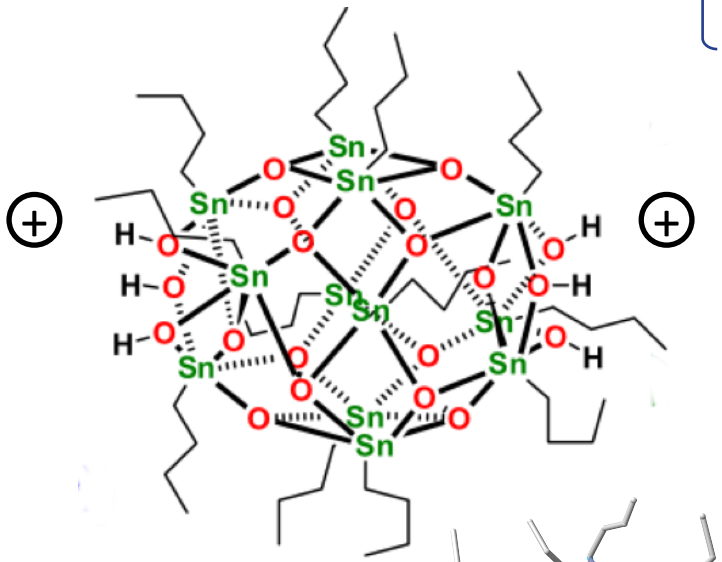
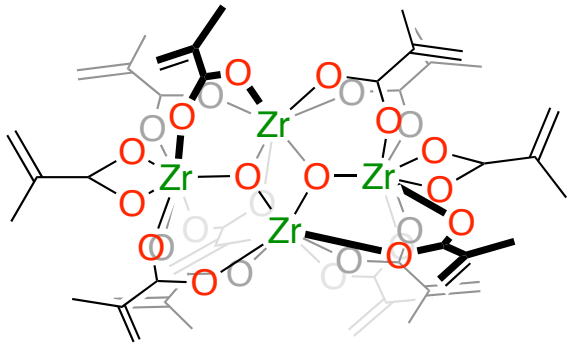
Hybrid materials as EUV photoresists

organic shell (C, H, N)
- Solubility contrast

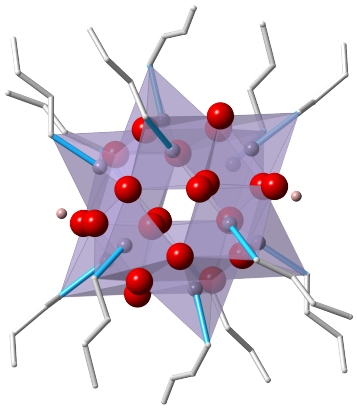


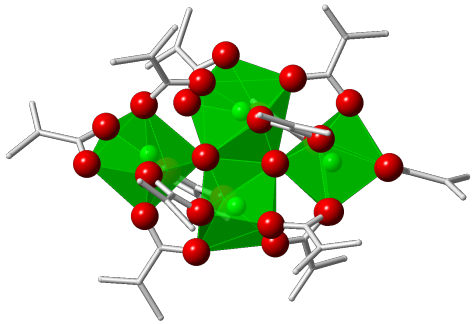
inorganic core (metallic elements, O)
- high EUV cross section
- Mechanical stability of patterns





Sn oxocages[1]
Sn-O/Sn-C





Metal oxoclusters[2]
Zr-O, Hf-O

[1] C. Eychenne-Baron, F. Ribot, C. J. Sanchez *Organomet. Chem.* **1998**, *567*, 137; B. Cardineau, et al. *Microelectron. Eng.* **2014**, *127*, 44
[2] Kickelbick, G.; Schubert, U. *Chem. Ber.* **1997**, *130*, 473

EUV interference lithography

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Swiss Light Source. X-ray Interference Lithography (SLS-XIL)

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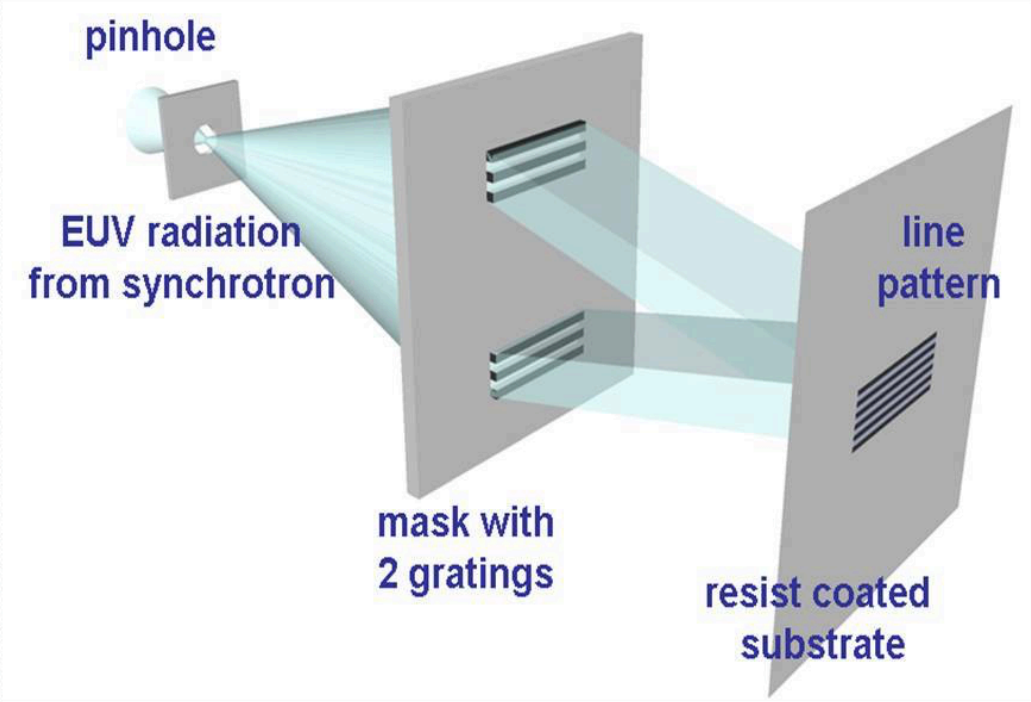
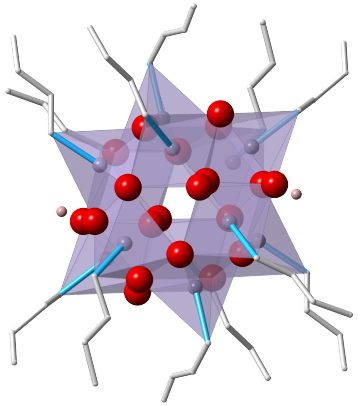
nffa.eu nanoscience foundries & fine analysis



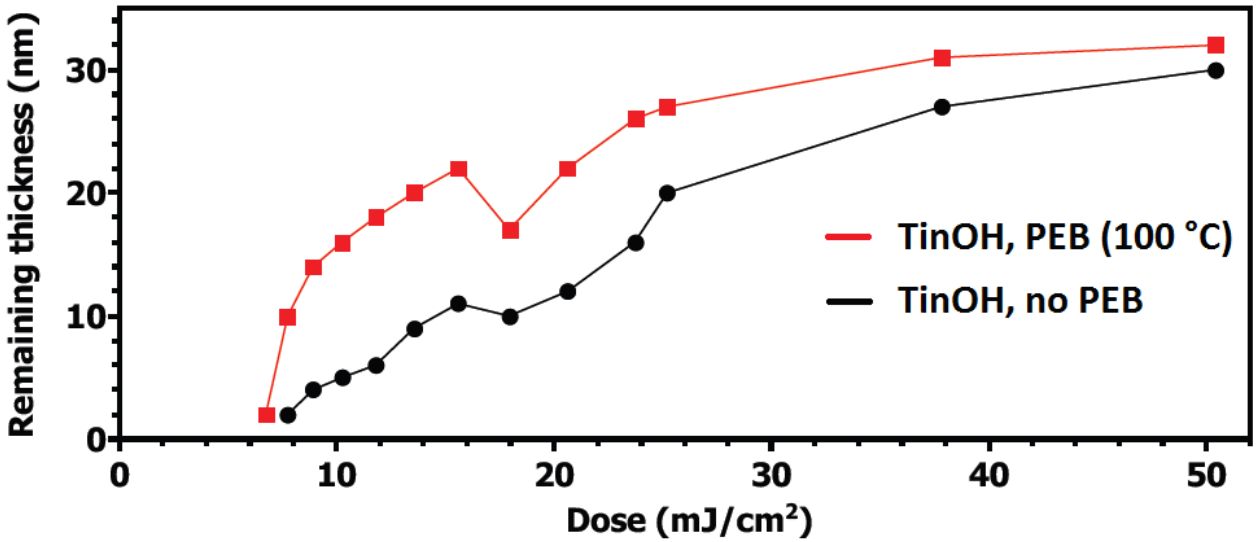
Y. Ekinci
D. Kazazis
M. Vockenhuber
R. Fallica

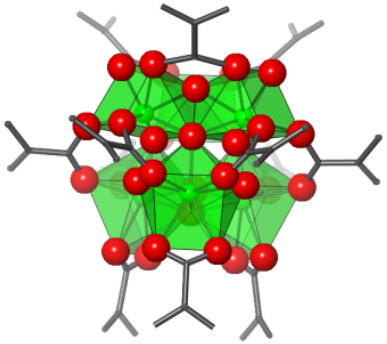
E. Buitrago, R. Fallica, D. Fan, W. Karim, M. Vockenhuber, J. van Bokhoven, Y. Ekinci, *SPIE Newsroom* **2016**, 10.1117/2.1201609.006687

Contrast curve

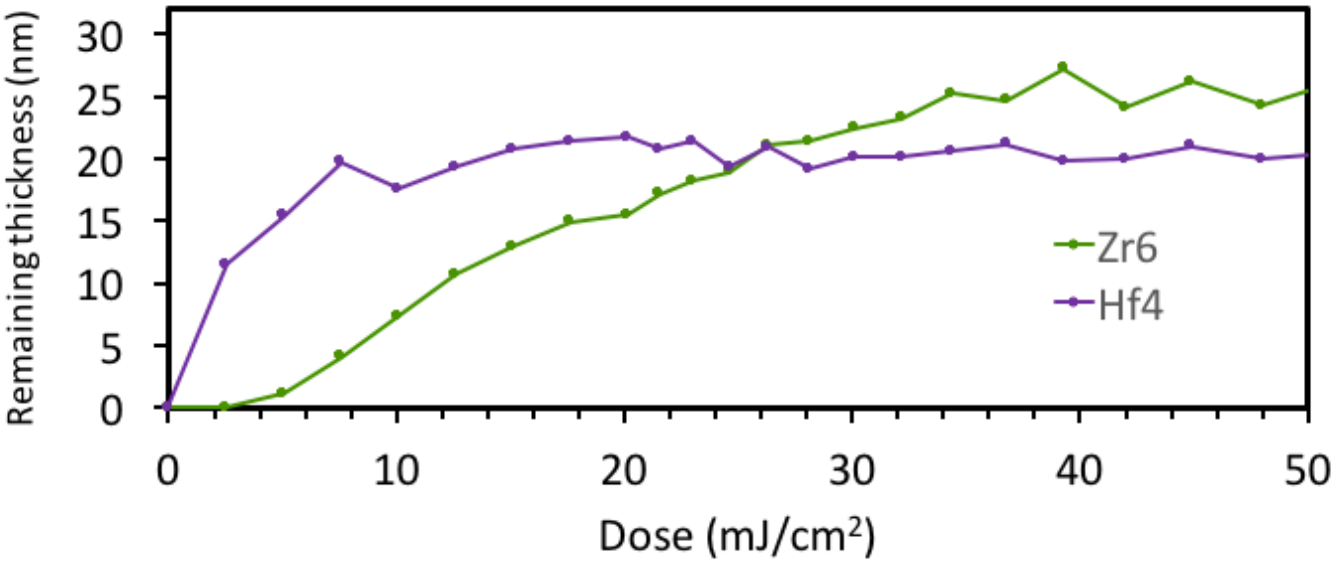


Sn-based



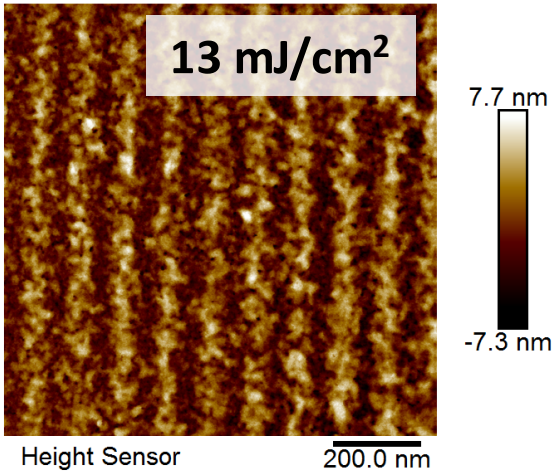


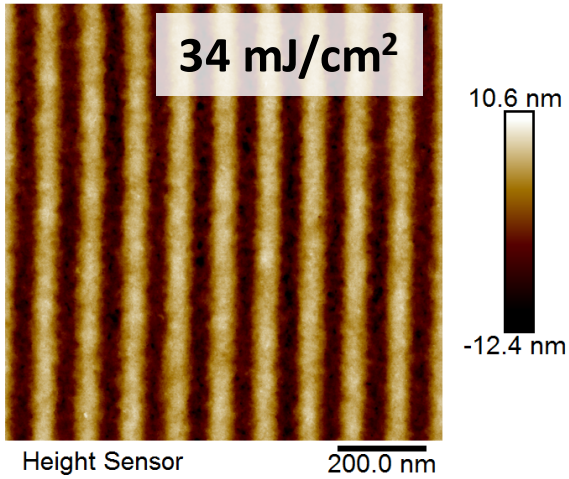
Zr-/ Hf-based

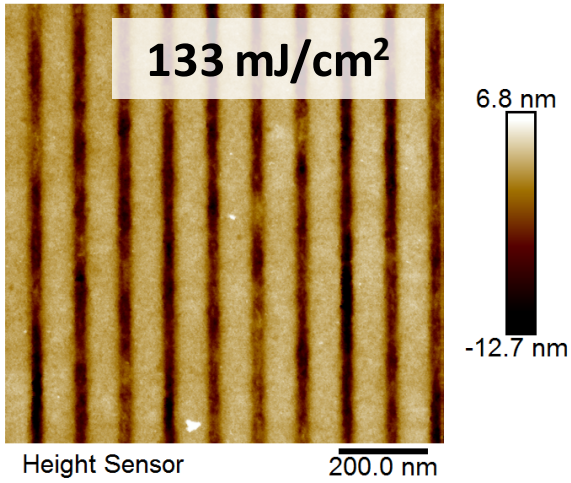


J. Haitjema, Y. Zhang, M. Vockenhuber, D. Kazazis, Y. Ekinci, A. M. Brouwer, Proc. SPIE Vol *10143*, 1014325

Contrast curve

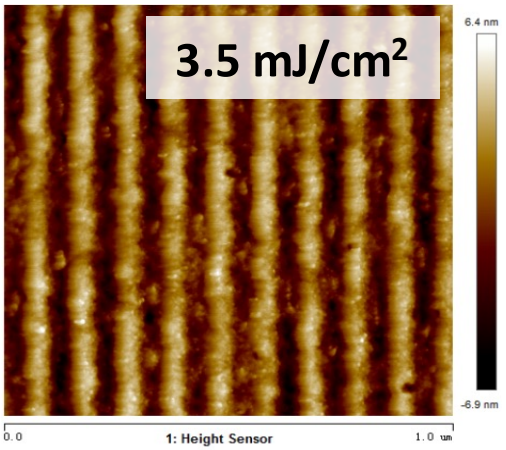




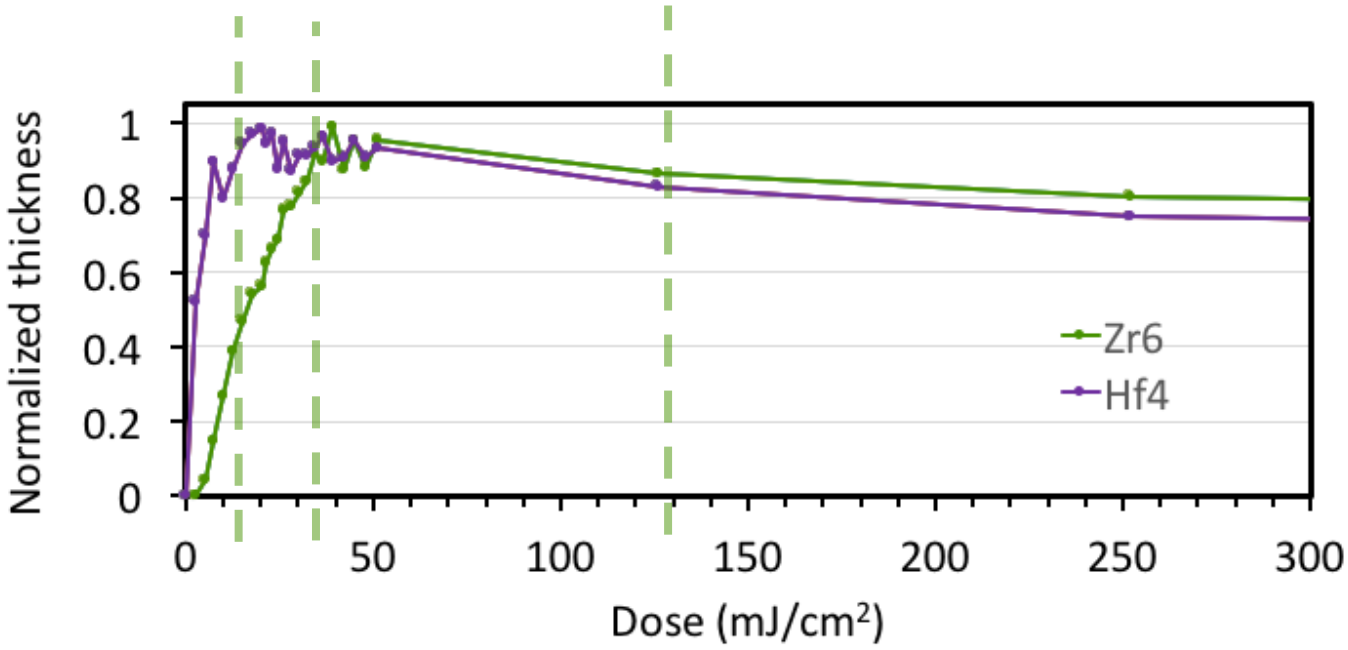


Zr-based

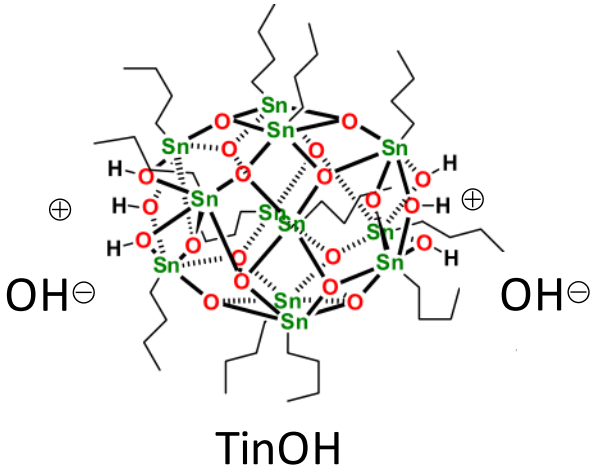
AFM 100 nm pitch

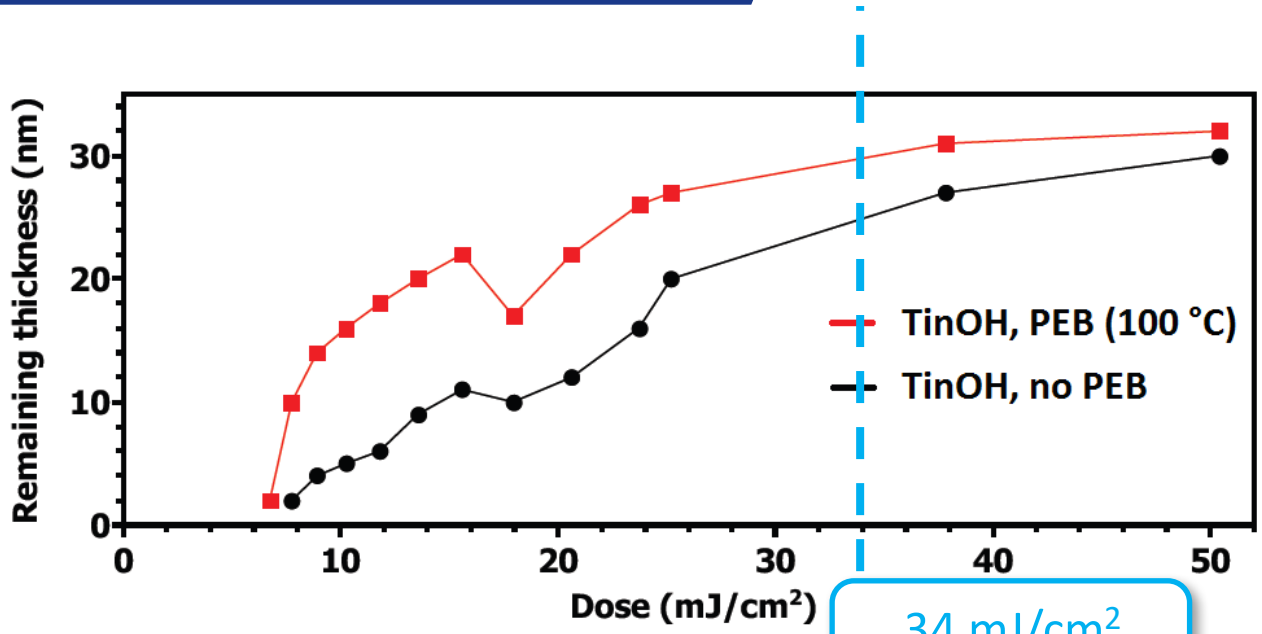


Hf-based



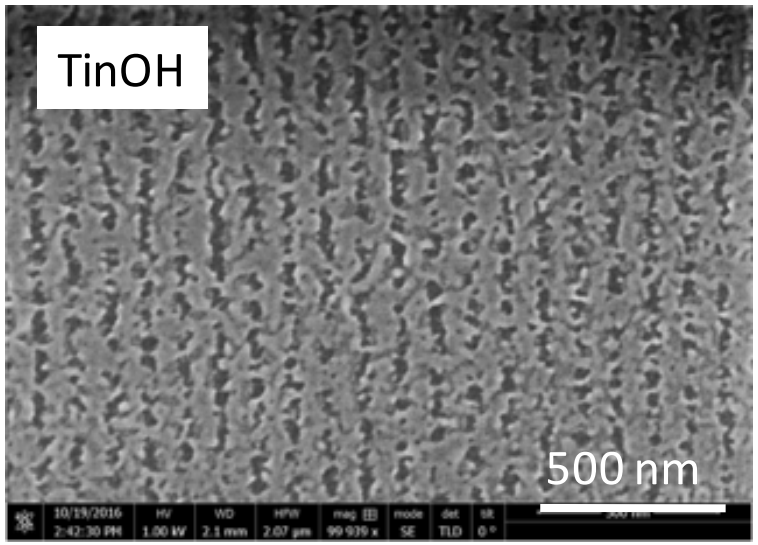
Contrast curve

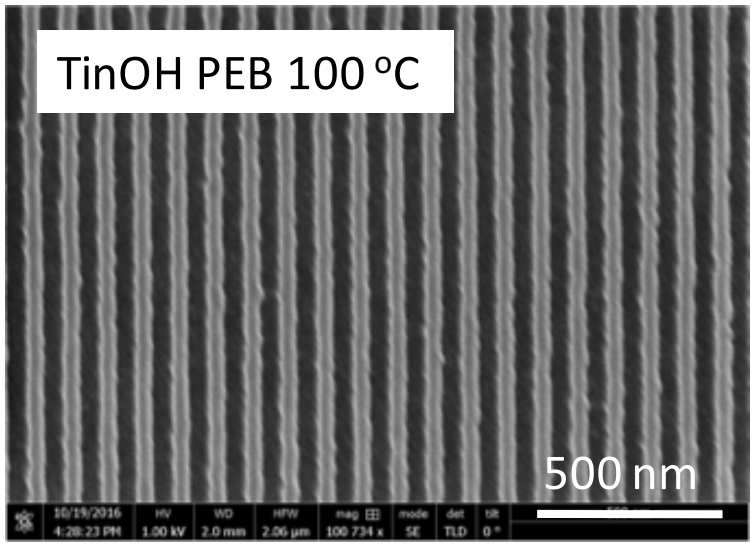




SEM 100 nm pitch

34 mJ/cm^2

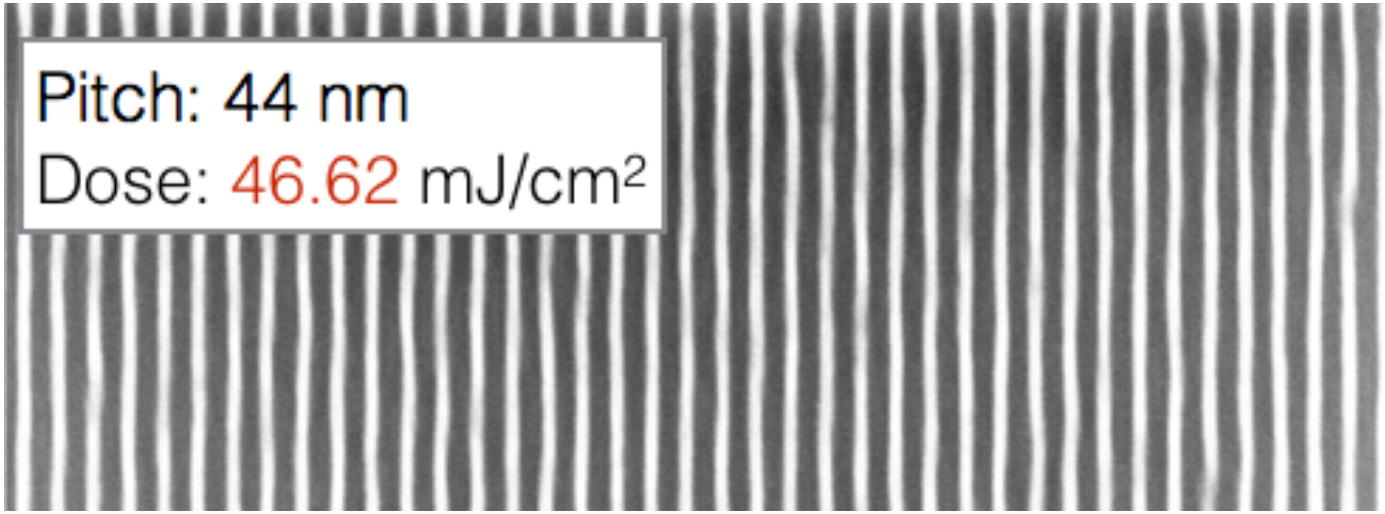




J. Haitjema, Y. Zhang, M. Vockenhuber, D. Kazazis, Y. Ekinci, A. M. Brouwer, Proc. SPIE Vol *10143*, 1014325

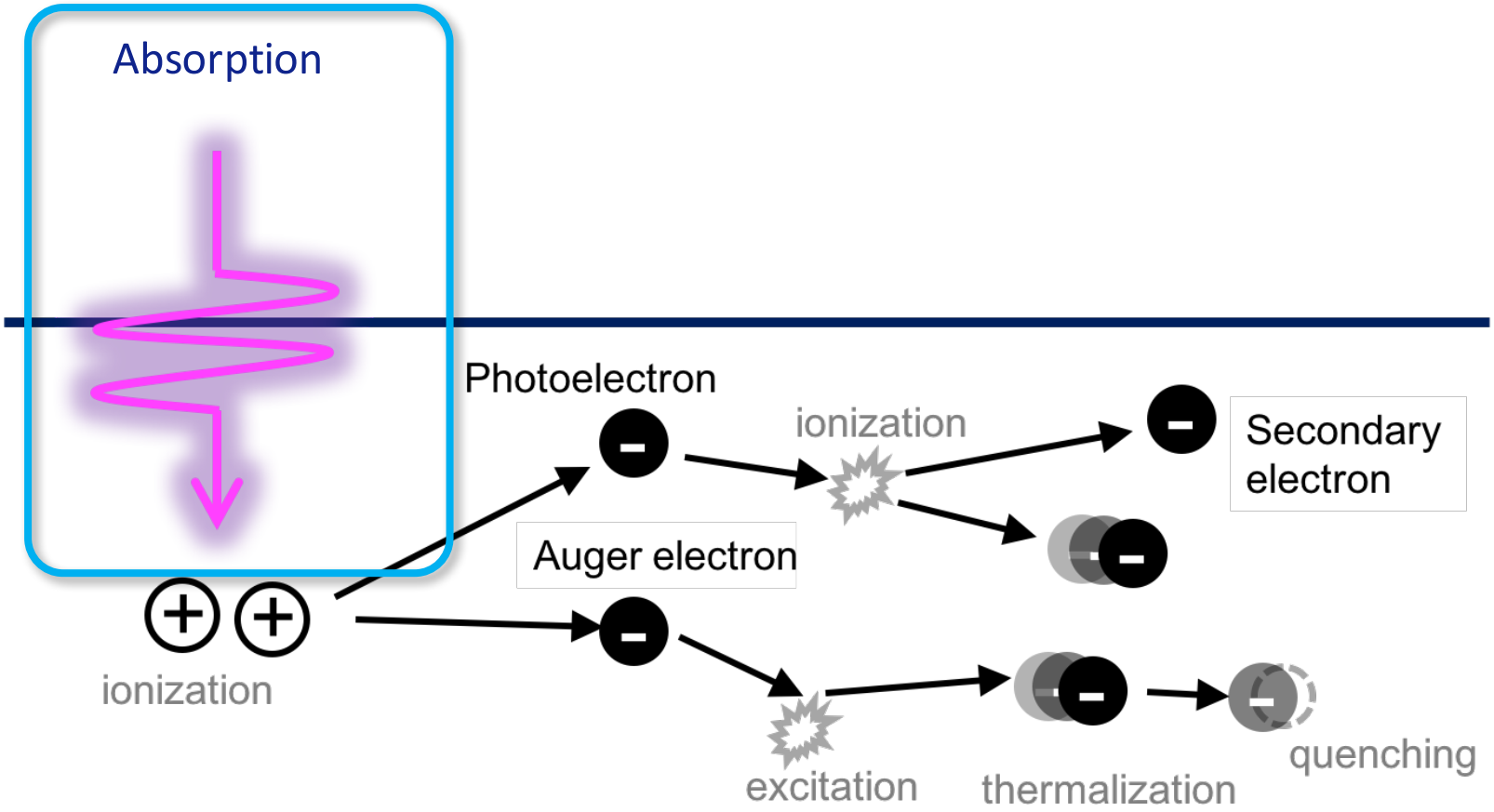
After optimisation…

SEM of patterned Sn-based PR



- What are exactly the chemical processes occurring in every step?
- Which parts of the molecular structure have a major contribution to them?

Where are the differences coming from?



Absorptivity vs structure

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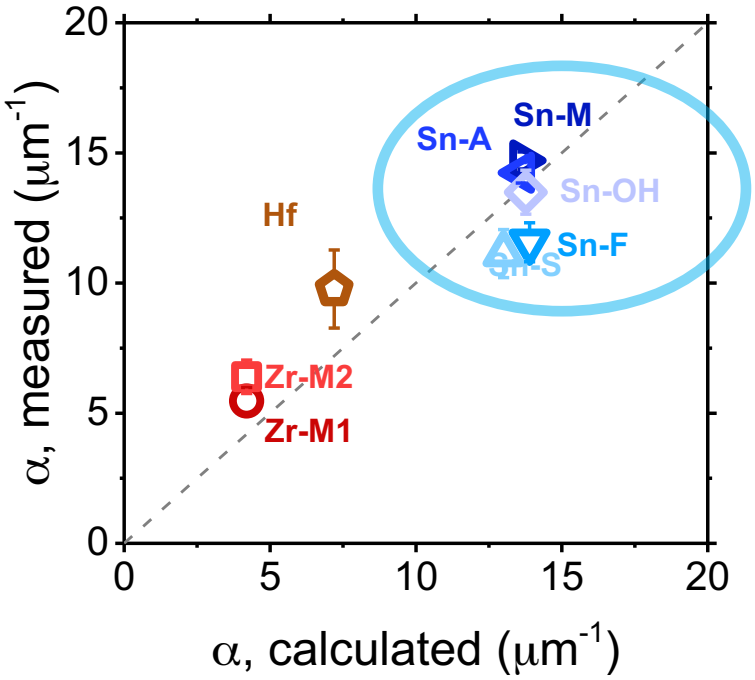
Methodology

XIL BEAMLINE

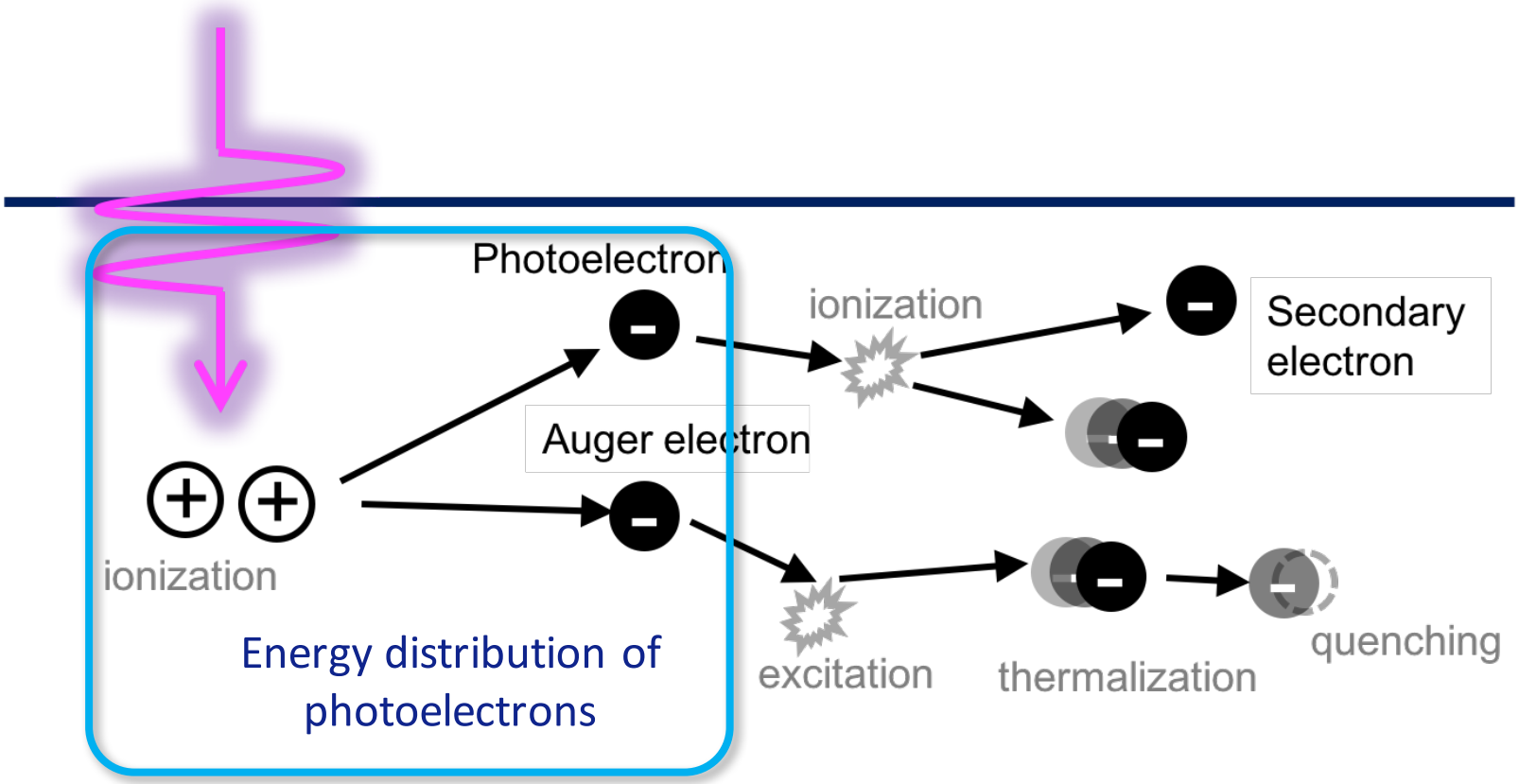


Similar values as for SnO_x-based EUV photoresists.

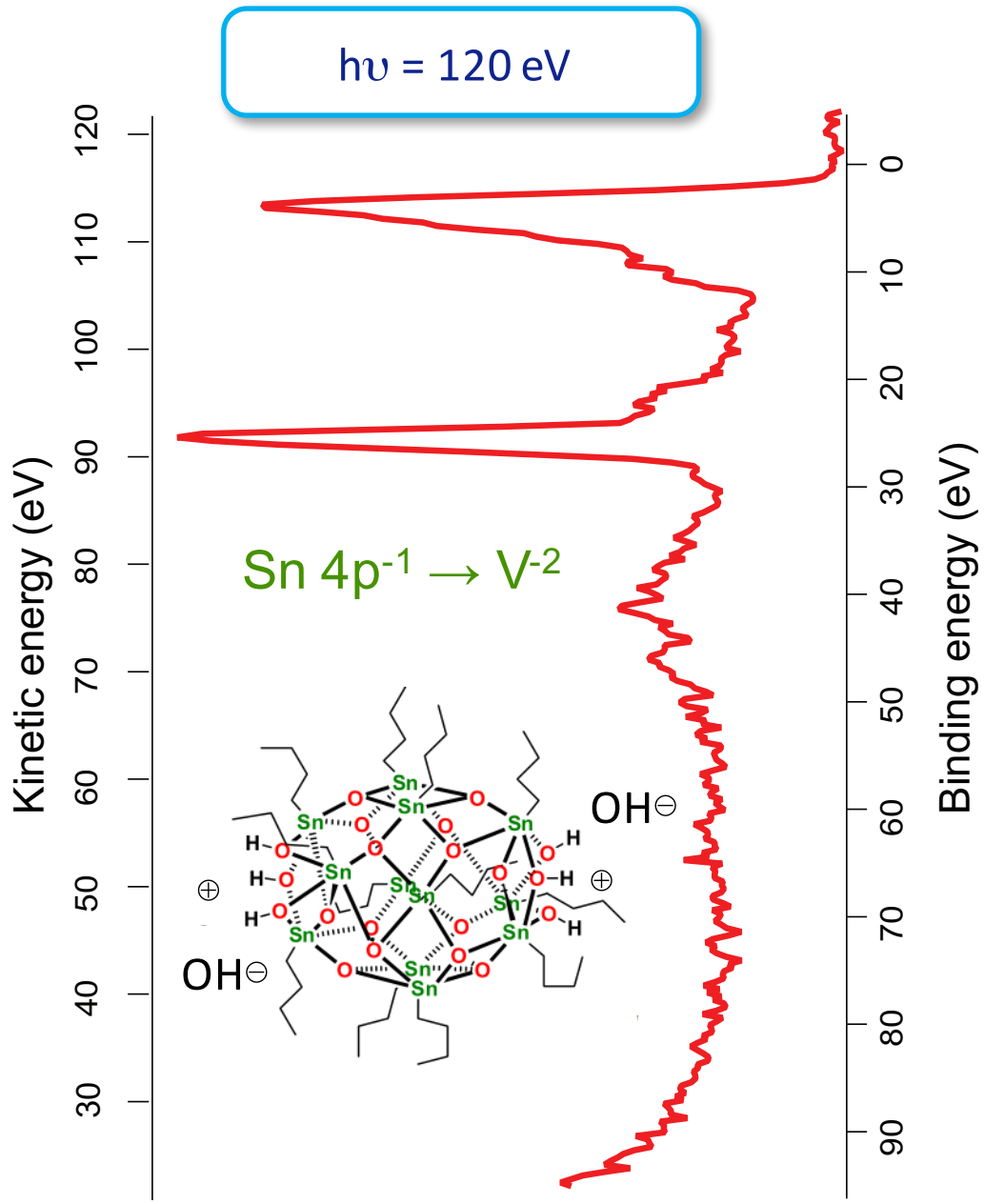
R. Fallica , JK. Stowers, A. Grenville, A. Frommhold, AG. Robinson, Y. Ekinci, *J. Micro/Nanolith. MEMS MOEMS.* **2016**, 15(3):033506, doi:10.1117/1.JMM.15.3.033506.

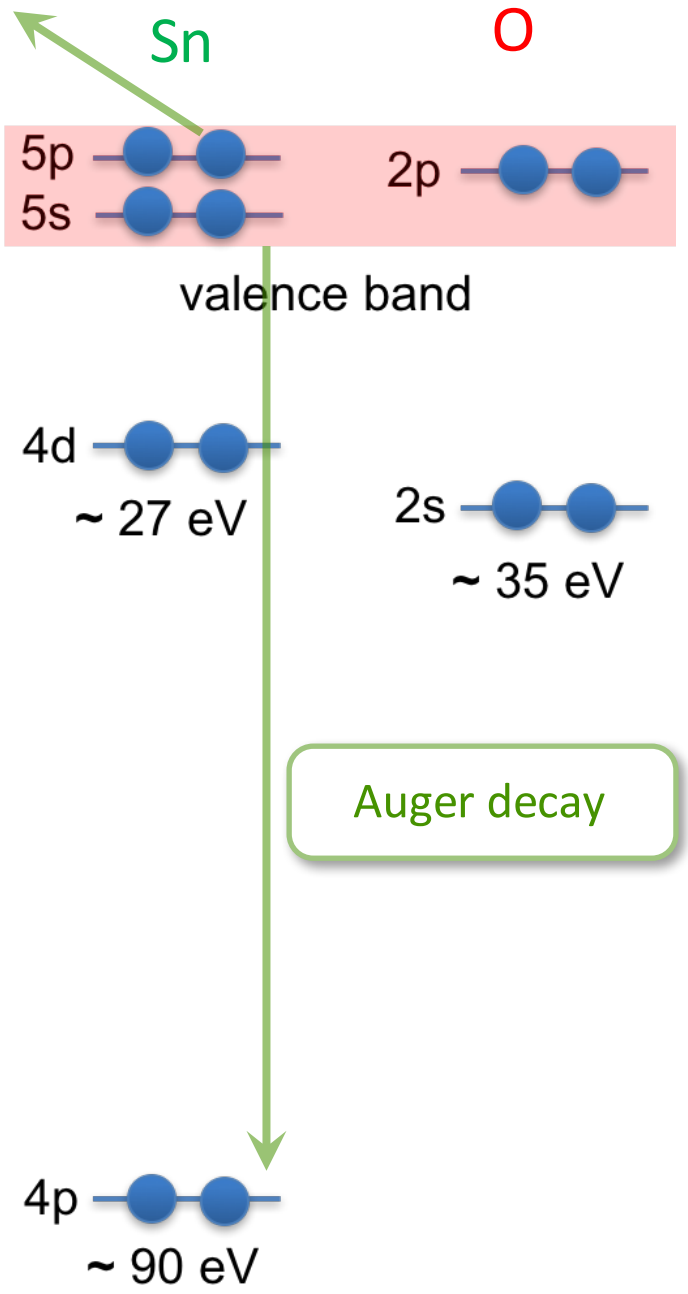
R. Fallica, J. Haitjema, L. Wu, S. Castellanos, A. M. Brouwer, Y. Ekinci, *Proc. SPIE Vol. 10143* , 101430A

Where are the differences coming from?



Kinetic energy distribution Sn-based photoresists





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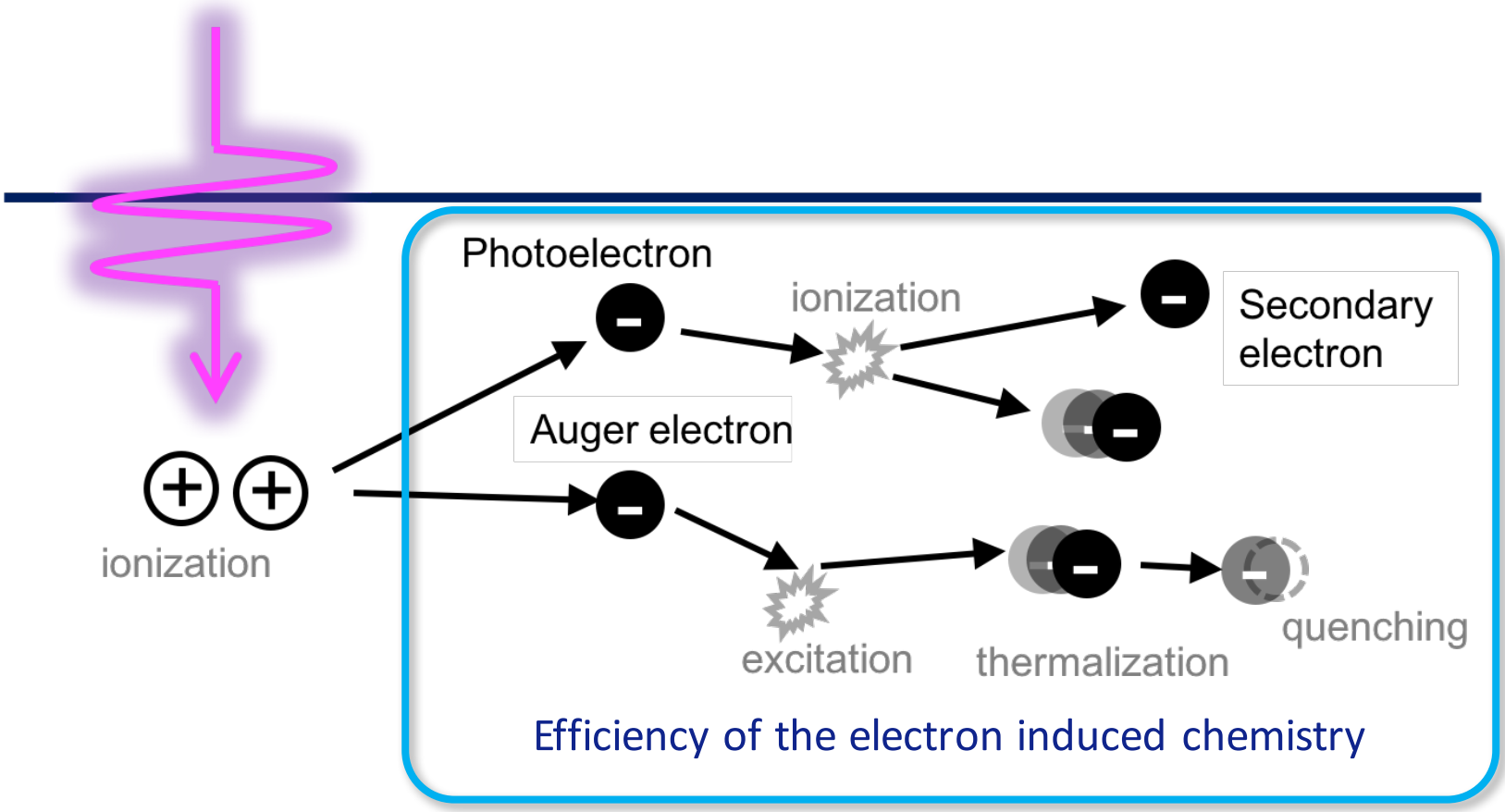
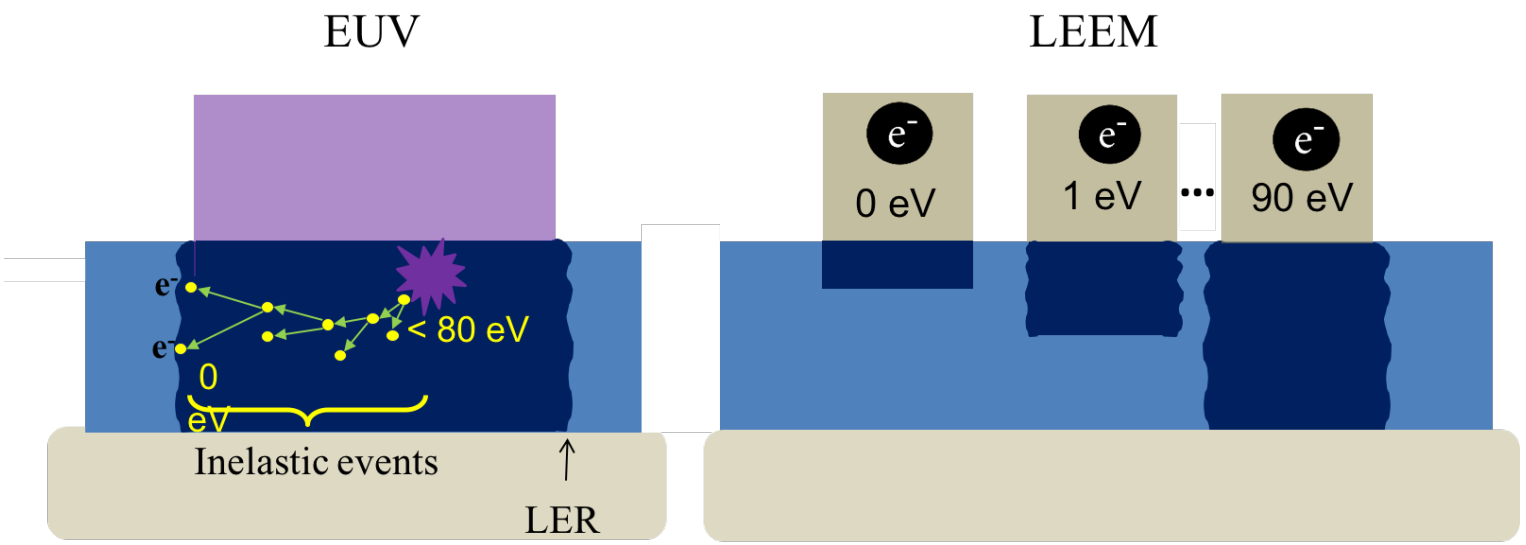
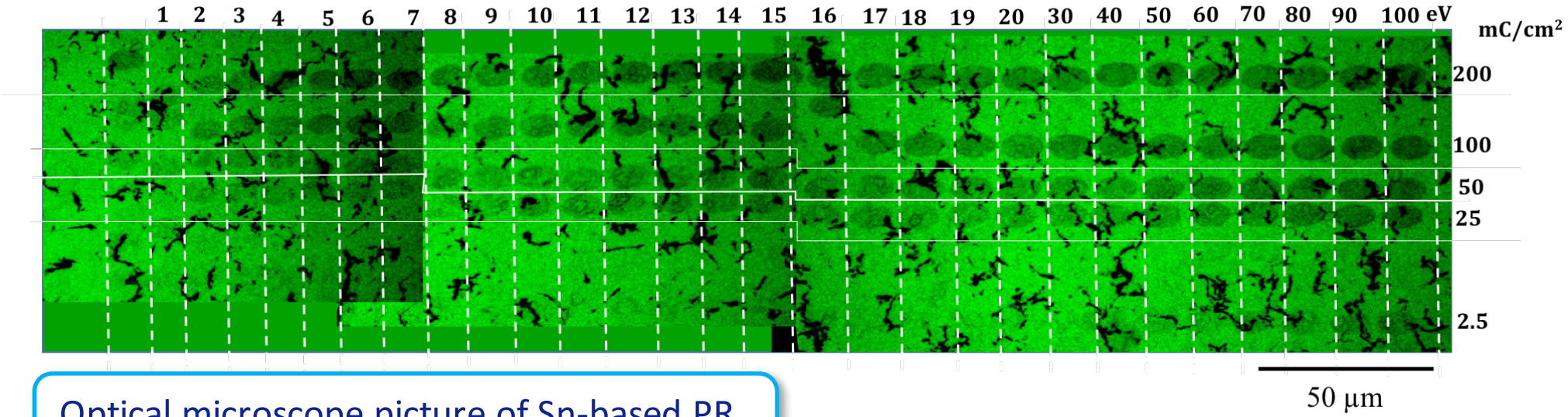


Low energy electrons





Optical microscope picture of Sn-based PR

A.Thete, D. Geelen, S.J. van der Molen, R.M. Tromp, *Phys. Rev. Lett. Submitted.*

Monitoring photochemistry of thin films

DUV, Hard X-ray, EUV

photoresist

- Au/Cr/glass
- Si
- quartz

➔ High Kinetic Energy PES (chemical composition)
➔ FT infrared spectroscopy (chemical bonding)
➔ UV-vis spectroscopy (structure)

Monitoring photochemistry with HIKE

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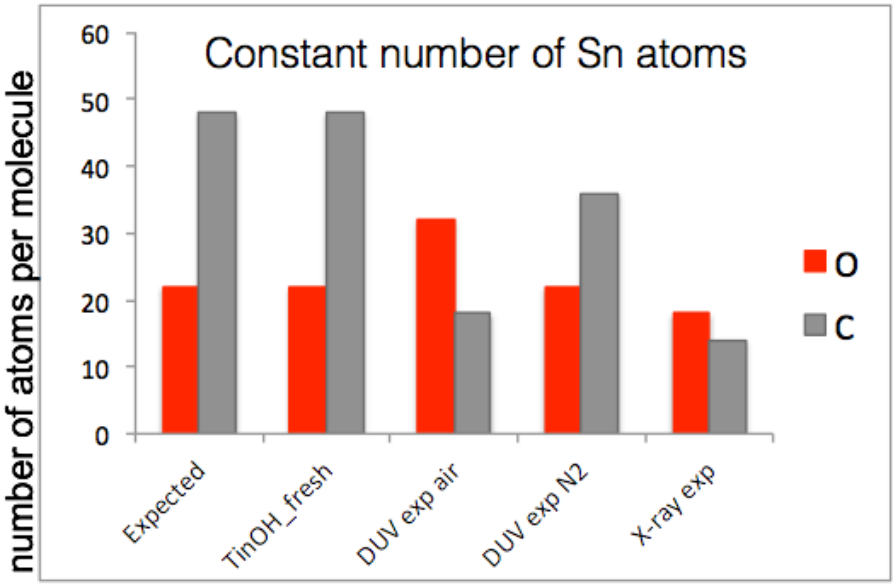
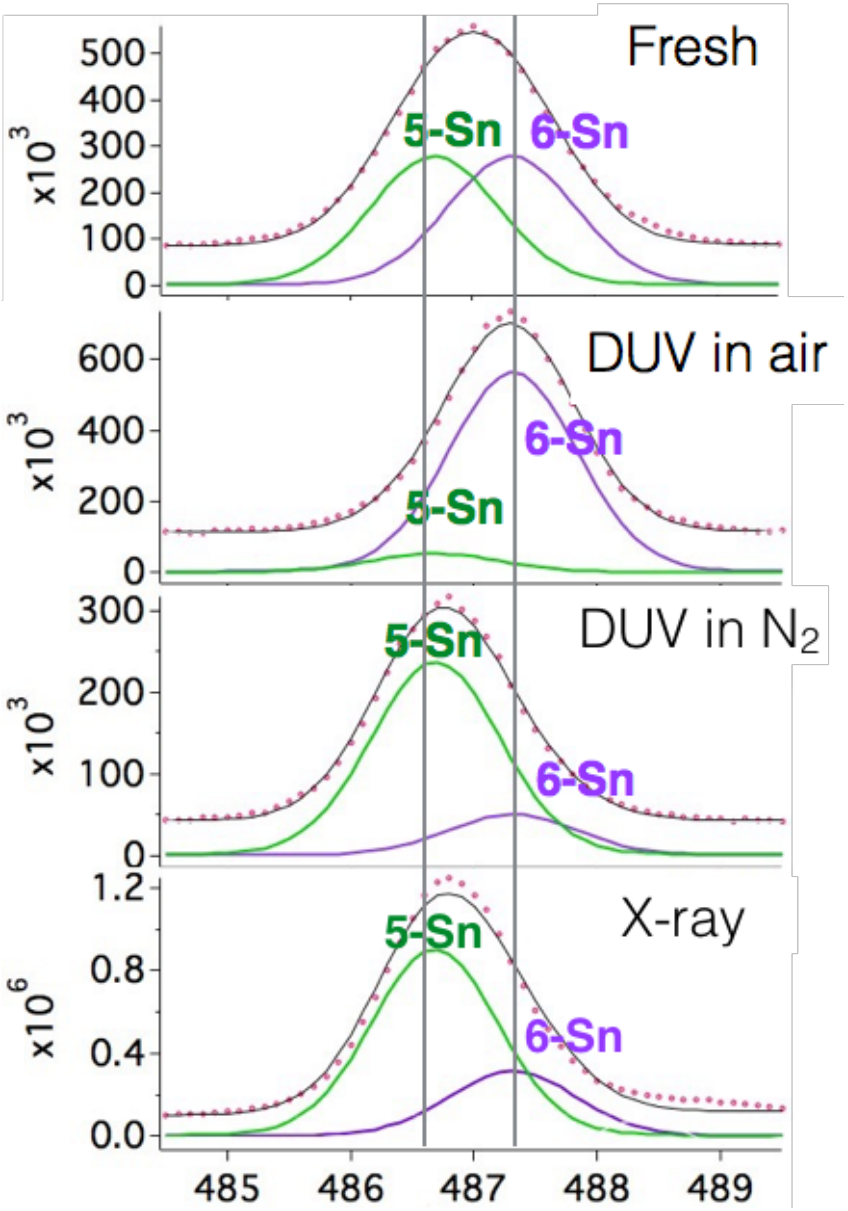
HZB Helmholtz Zentrum Berlin

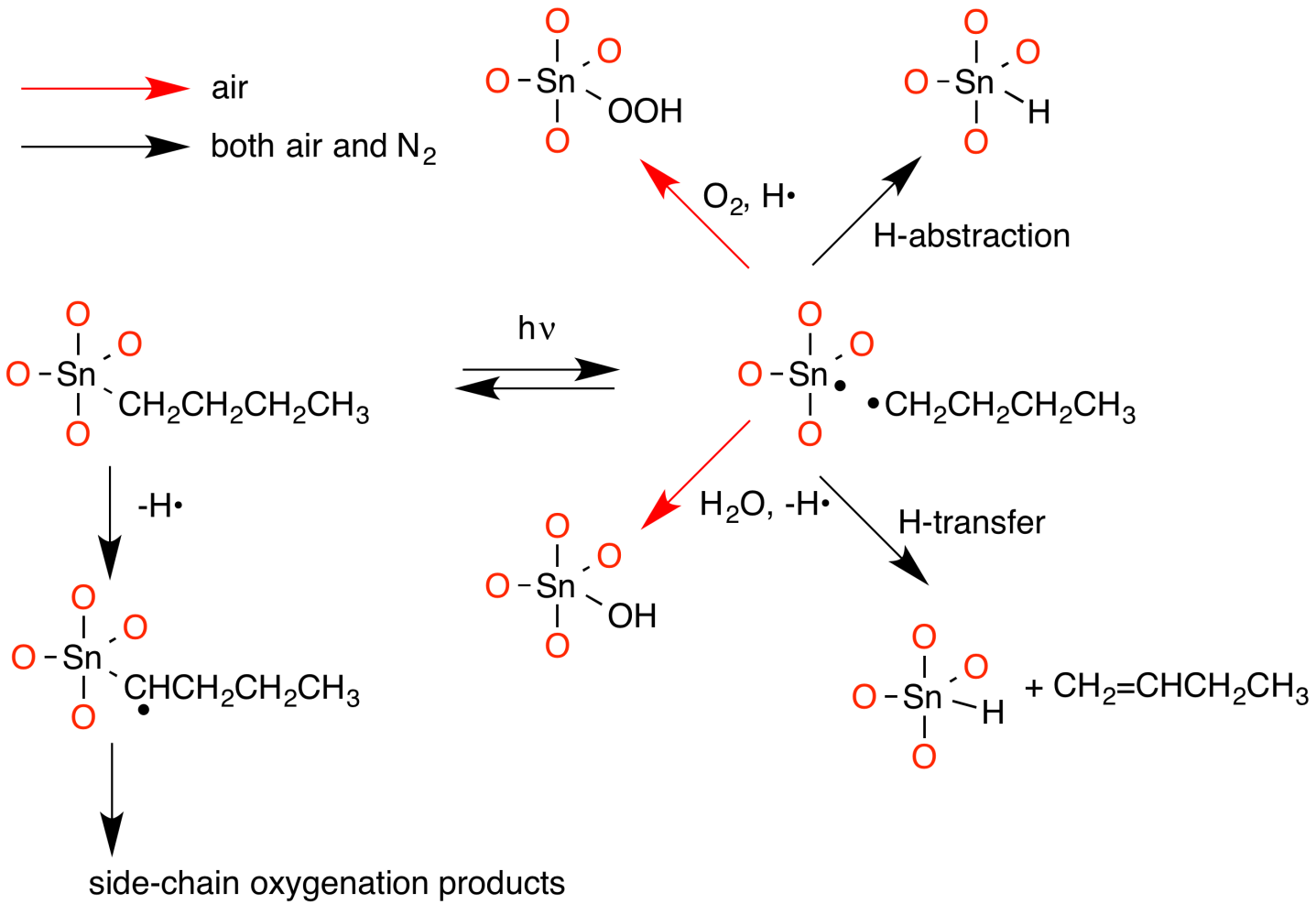
- Both DUV and hard X-ray lead to carbon chain loss.
- Oxydation state of Sn depends on atmosphere.





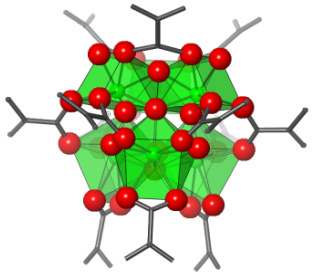
Y. Zhang, J. Haitjema, X. Liu, F. Johansson, A. Lindblad, S. Castellanos, N. Ottosson, A. M. Brouwer, Proc. SPIE Vol *10146, 10146-5; J Micro Nanolithogr MEMS MOEMS* **2017** *accepted*

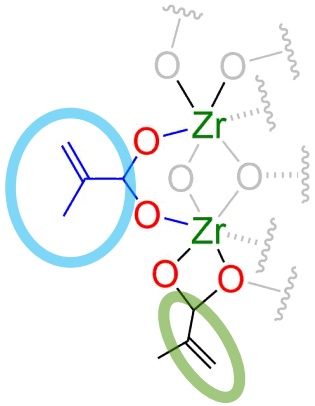
Proposed UV triggered mechanism

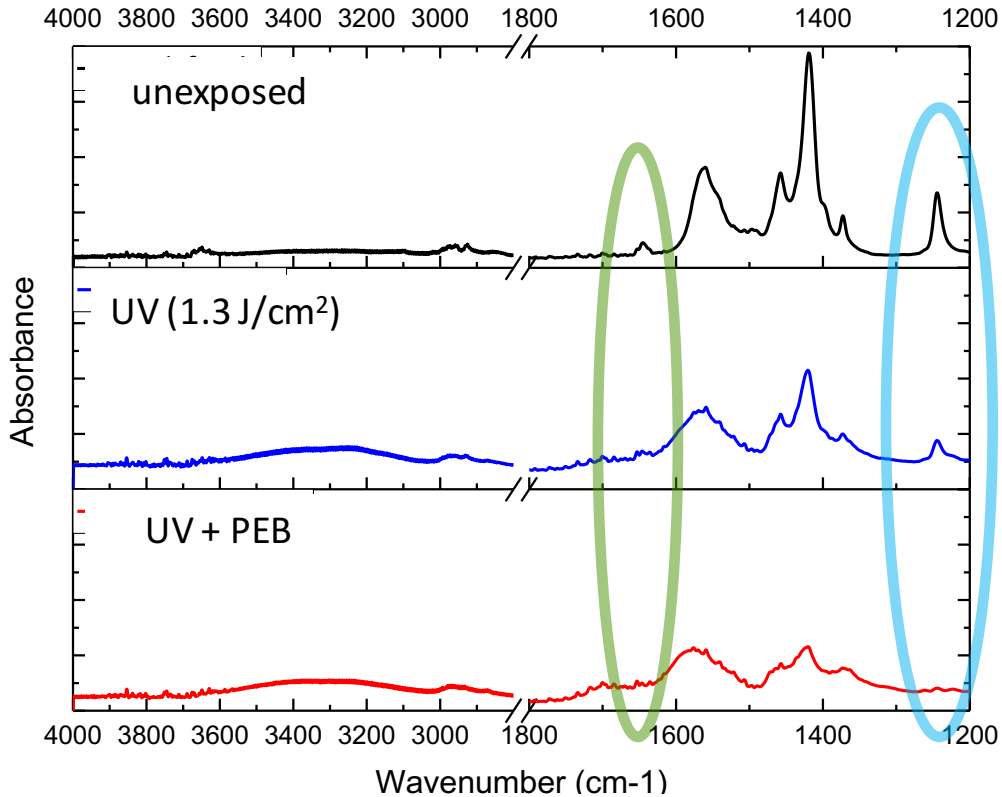


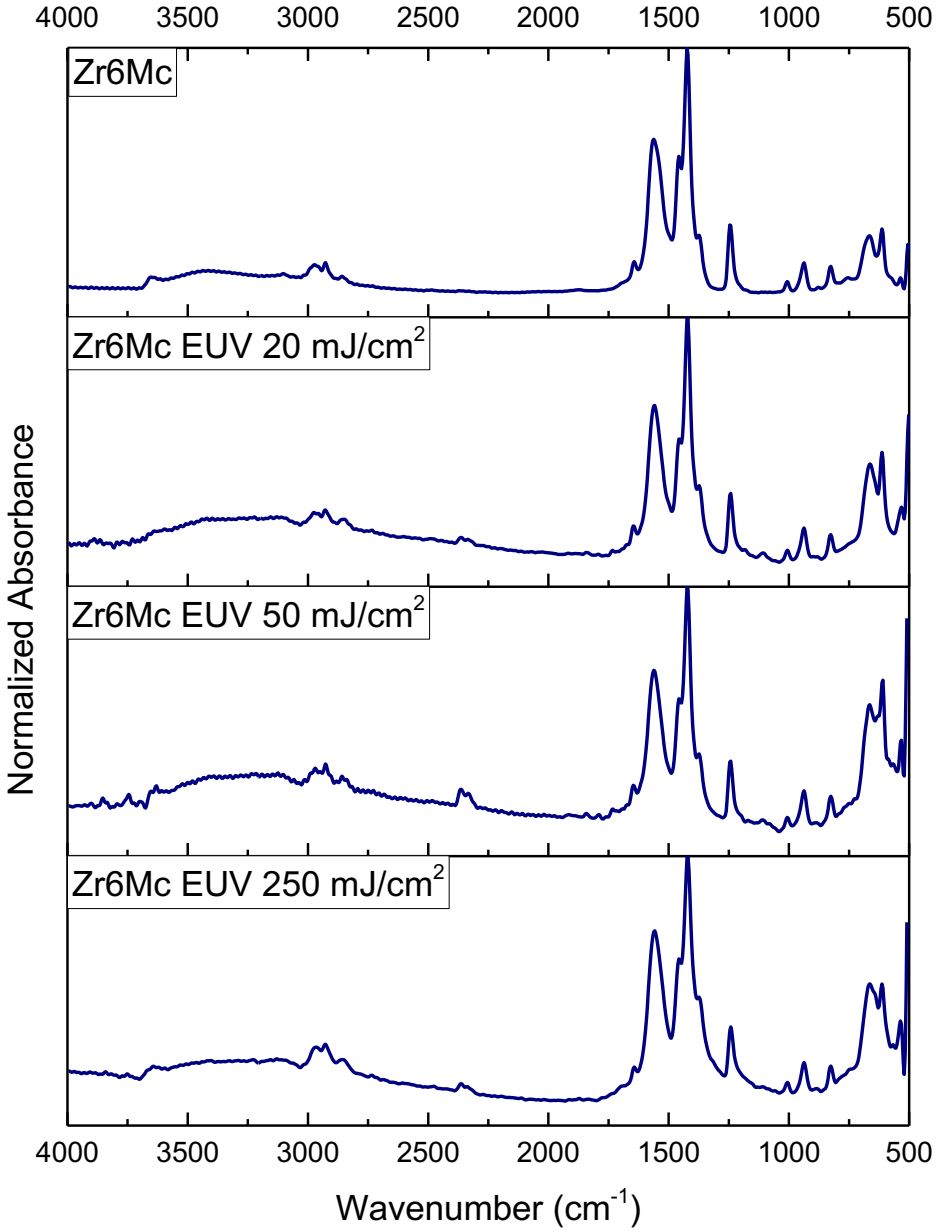
Y. Zhang, J. Haitjema, X. Liu, F. Johansson, A. Lindblad, S. Castellanos, N. Ottosson, A. M. Brouwer, Proc. SPIE Vol *10146, 10146-5; J Micro Nanolithogr MEMS MOEMS* **2017** *accepted*

Monitoring EUV photochemistry with FTIR









Conclusions

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Molecular design matters!!

- EUV **absorptivity** of molecular hybrid photoresists **can be tuned** through their chemical structure.
- **Higher absorptivity** of Sn-based material compared to Zr-based materials **does not lead to higher contrast**.
- Tin oxocages undergo **cleavage of Sn-C bonds** upon low energy and high energy light irradiation.
- **Intermediate photoproducts** of Sn-based compounds are further reactive upon heating.
- Solubility switch of Zr- and Hf- based oxoclusters might occur through partial **decarboxylation** and ligand loss. The mechanism is under study.

Acknowledgements

EUV Photoresists group:

L. Wu
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C. Werner-IJgosse

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Prof. Dr. F. Brouwer
Ing. van Leeuwen
J. Haitjema
B. Rocha Martins
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L. Metz
Paul Le Lan
Dr. A. Thete
Dr. R. Bloem

Paul Scherrer Institut:

D. Kazazis
M. Vockenhuber
R. Fallica

Molecular Photonics (UvA):

H. Sanders
M. Hilbers
P. Reijnders

Leiden University

D. Geelen
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