Mean free path of electrons in EUV photoresist in the energy range 20 – 450 eV

… and other experiments in lithography

Roberto Fallica, Thierry Conard, Anja Vanleenhove, Danilo De Simone (**imec**)
Nicola Mahne, Stefano Nannarone (**CNR-IOM**)

LEE 2023
20 November 2023, Università Tor Vergata, Roma

EUV lithography

IMEC headquarter in Leuven (Belgium)

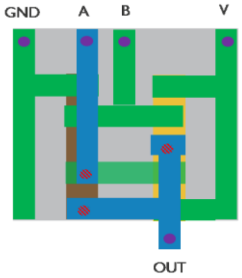
200 mm cleanroom

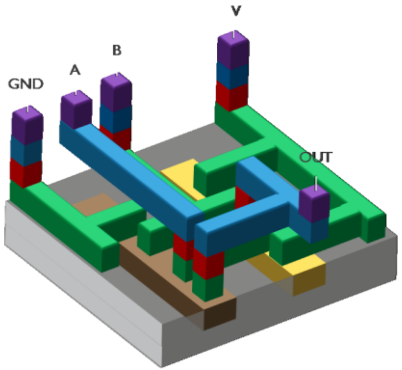
Imec tower

Office buildings (~3000 pp)

300 mm cleanroom

Semiconductors = high volume manufacturing



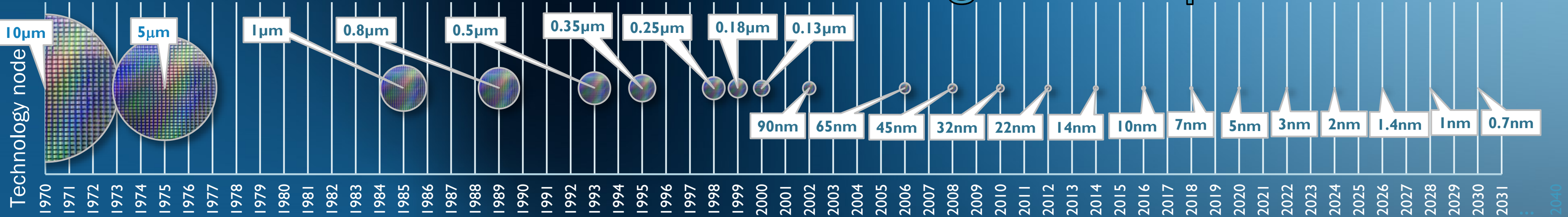


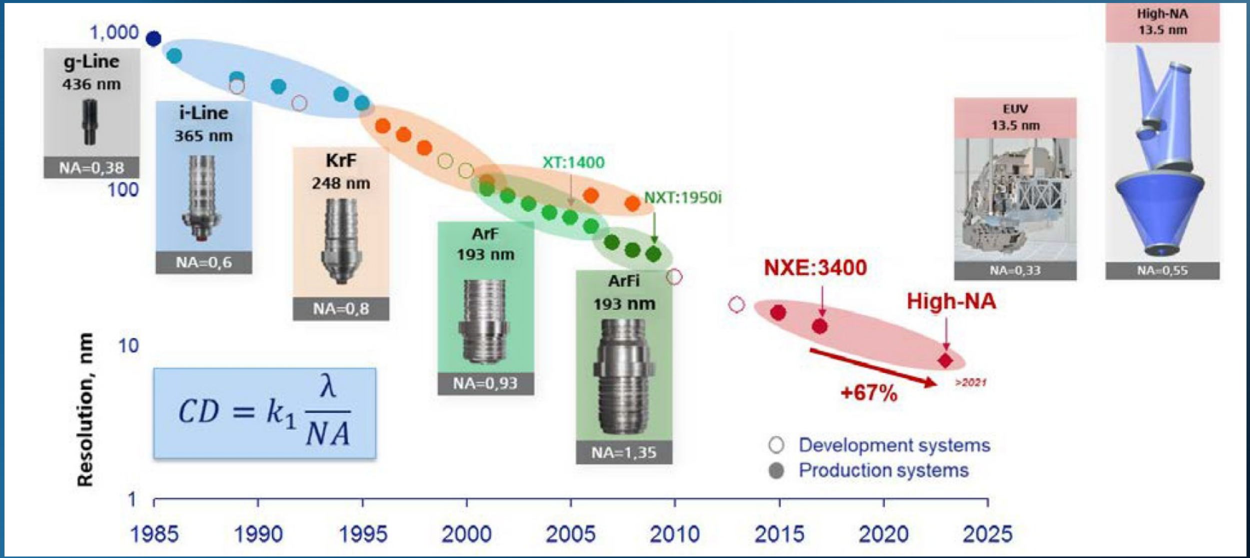
<u>Semiconductor scaling brings faster, smaller devices but is limited by our capacity to build smaller, denser devices.</u>

Minimum printable size = Critical Dimension CD

C. Smeets et al., Proceedings Volume PC12051, Optical and EUV Nanolithography XXXV; PC1205103 (2022)
J. Van Schoot et al., Proc. SPIE 11517, EUV Lithography 2020, 1151712 (2021)
Y. Vesters, PhD thesis, KU Leuven, Belgium.

Semiconductor scaling roadmap





Courtesy Danilo De Simone, AVS 69th Advanced Patterning and Plasma-Engineered Materials Session

EUV lithography (13.5 nm, 92 eV)

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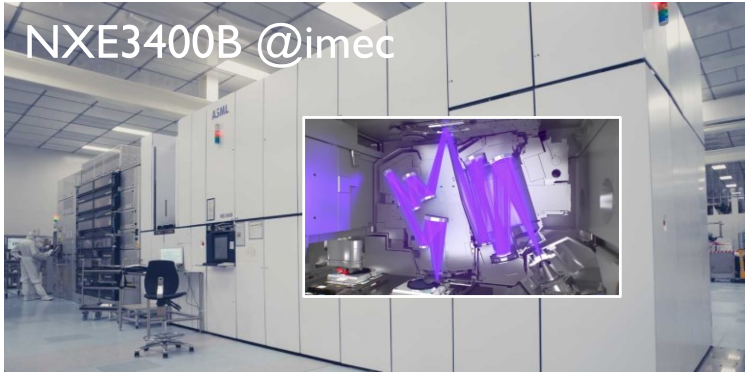

[https://www.imec-int.com/en/press/imec-pushes-single-exposure-patterning-capability-033na-euvl-its-extreme-limits]

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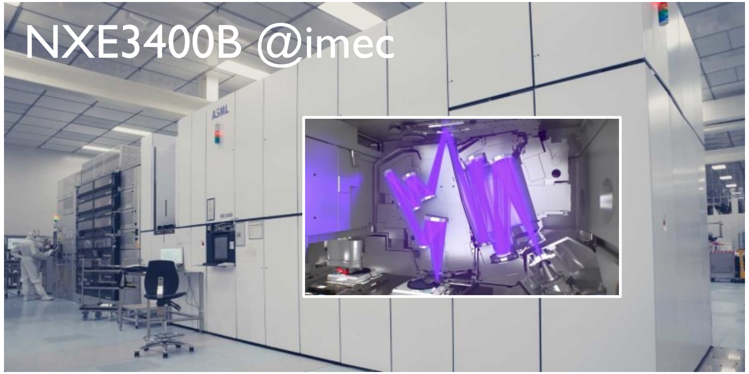
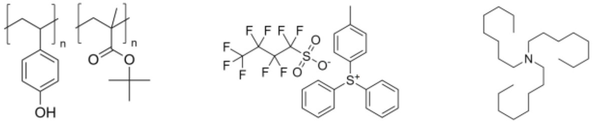
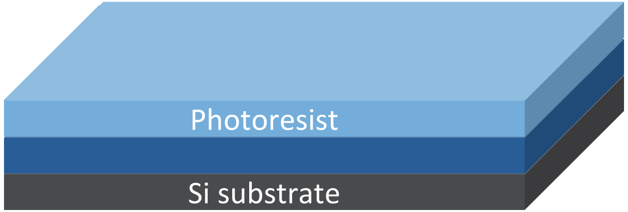


Polymer + PAG + Quencher





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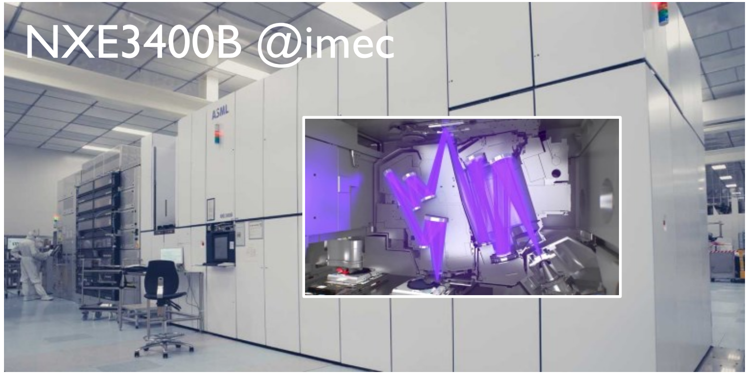

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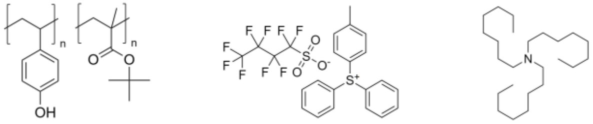

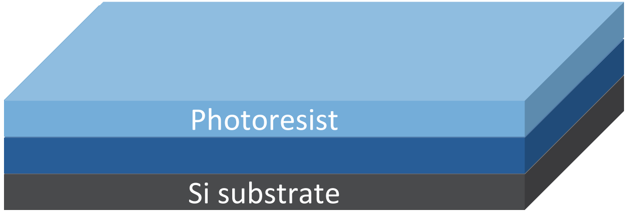

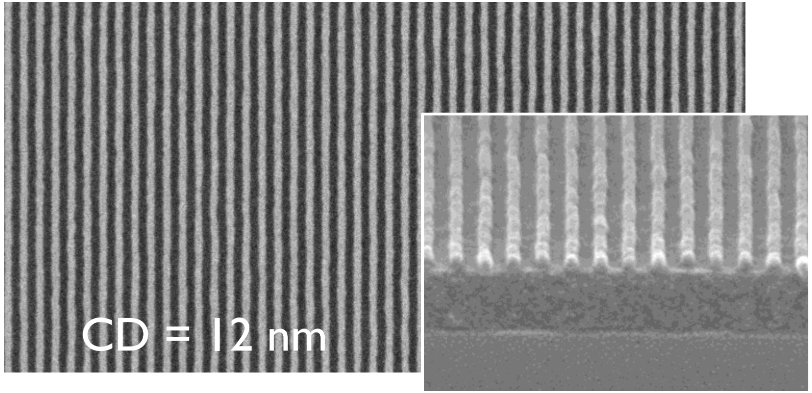

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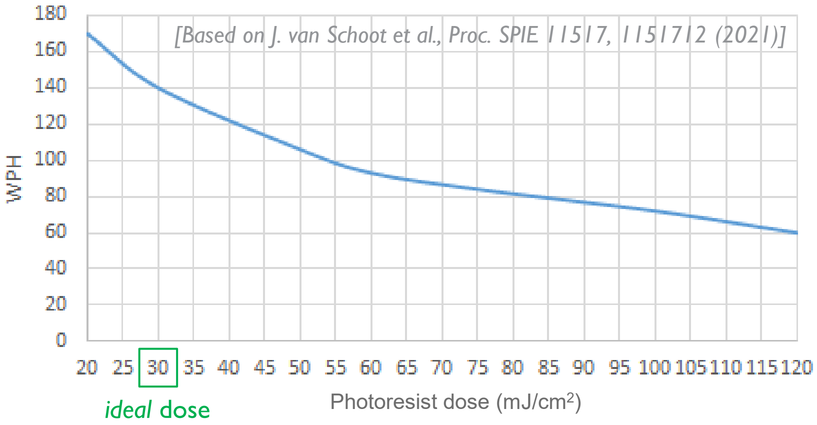
Lithography challenges are … photoresist challenges!

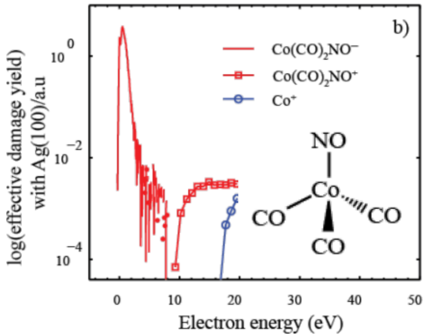
ASML EUV scanner (model 3400B) in imec cleanroom



Low photo-sensitivity = high dose → low throughput (wph)

Need for highly efficient photoresists →

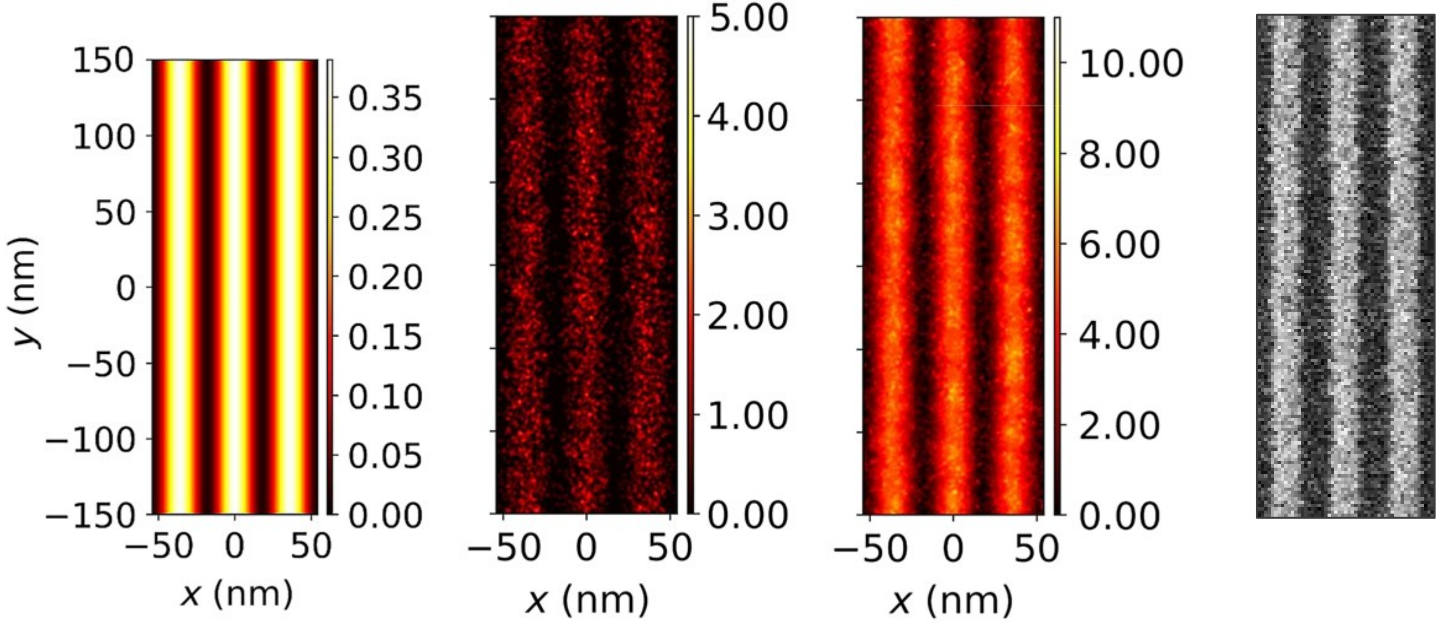
Role of electrons in the chemistry



DEA (dissociative electron attachment)

[R. Thorman et al., Beilstein J. Nanotechnol. 6, 1904 (2015)]

Lithography challenges are … photoresist challenges!

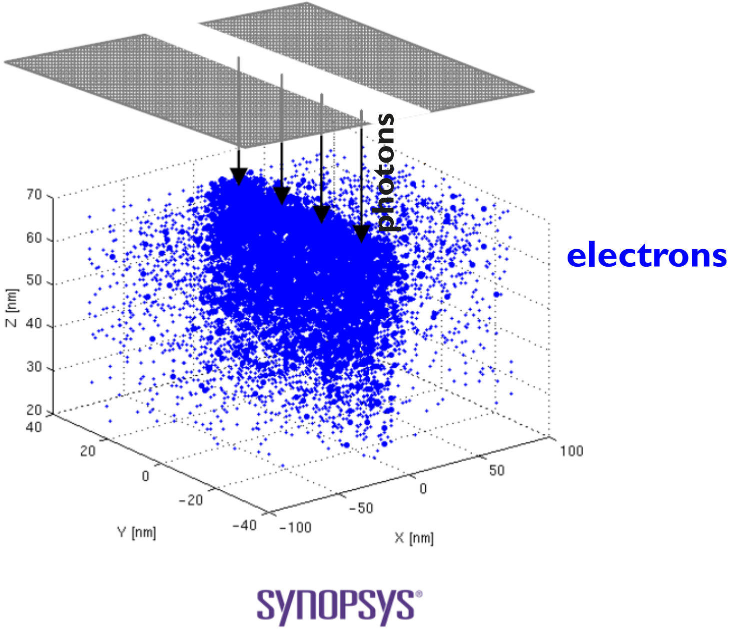


EUV intensity EUV absorption Secondary electrons Resist image

[Z. Belete et al., J. Micro/Nanopattern. Mater. Metrol. 20(1), (2021) 014801-1]

Electron mean free path: the problem

Electron mean free path

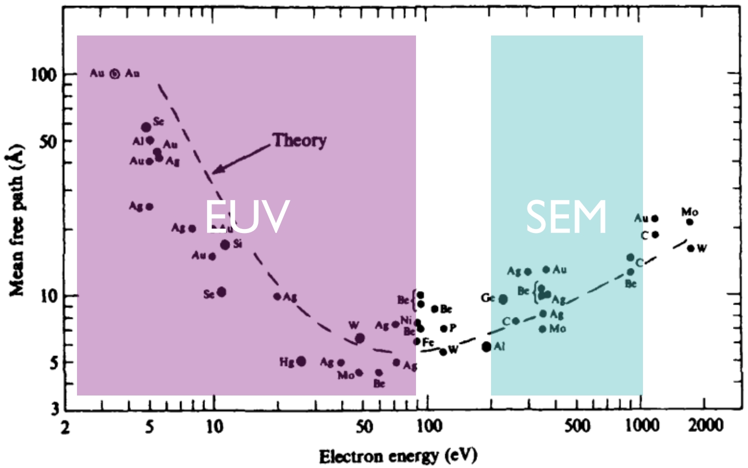


Electron blur is caused by electrons moving away from the photoabsorption location: **loss of resolution!**

Courtesy Alex Vaglio Pret (KLA), Ulrich Welling (Synopsys).

The ‘universal curve’ of electron mean free path

Fig. 2.1. Universal curve of electron mean free path: experiment (Rhodin & Gadzuk, 1979; Somorjai, 1981); theory (Penn, 1976).



1. Universal MFP curve = minimum MFP of *most materials*

2. MFP is not just one number: we need to evaluate across all energy range

See for example: Villarrubia et al., Proc. SPIE 6518, 65180K (2007)

BEAR beamline at Elettra

BEAR: Bending magnet for Emission Absorption and Reflectivity

Analysis of "particles (electrons and photons) yield" expressed as num. particles / num. incident photons possibly resolved in energy and angle

- *ENERGY RANGE* 2.8 - 1600 eV
- *SPOT SIZE*: (*vertical*) 400 μm - ~ 15 μm (mono vertical exit slit/slope errors)
  (*horizontal*) 400 μm - ~ 5 μm
- *DIVERGENCE* : ≤ 20x20 (*h x v*) mrad^2
- *POLARIZATION*: variable from ~ linear to elliptical (right and left/RCP-LCP)
- *FLUX and RESOLUTION* 2.8-40 eV (GNIM) (*peak*)~10^{10} ph/s at 20 eV (ΔE/E ~5000)
  35-1600 eV (G1200) 10^{11} ph/s at 100 eV (E/ΔE~3000)
- *HIGHER ORDER REJECTION*: Filters (B270, SiO_2, LiF, In, Sn, Al, Si, B, C, Ti) and monochromator deviation angle
- **Dose control in Watt/cm² or (photon per s)/cm²**

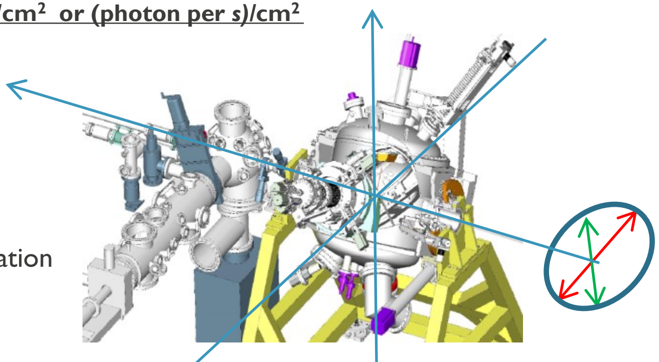
Spectroscopies

Optical absorption (XAS, NEXAFS, EXAFS)
•Transmission
light beam
•Drain (emission) current mode/Total electron yield
•Fluorescence (excitation curves – scanning photon energy)
•Luminescence (excitation curves – scanning photon energy)
•Auger yield

Light scattering/Reflectivity
•Specular reflectivity (θ-2 θ – Diffraction gratings calibration)
•Diffuse reflectivity (→ roughness)

Photon emission
•Fluorescence
•Luminescence (XEOL)

Photoemission
- UPS/XPS
- Partial electron yield



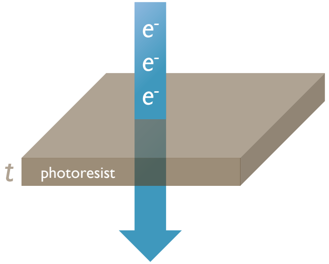
BEAR experimental station

Measuring electron mean free path

History of MFP experiments and models

Tanuma et al., Surf. Interface Anal. 21(3), 165 (1994)
Vaglio Pret et al., Proc. SPIE 10146, 1014609 (2017)
Kostko et al., J. Chem. Phys. 151, 184702 (2019)
Santaclara et al., Proc. SPIE 11323, 113231A (2020)
Kozawa et al., Jpn. J. Appl. Phys. 50, 030209 (2011)
Grzeskowiak et al., J. Vac. Sci. Technol. B 33(6), 06FH01 (2015)

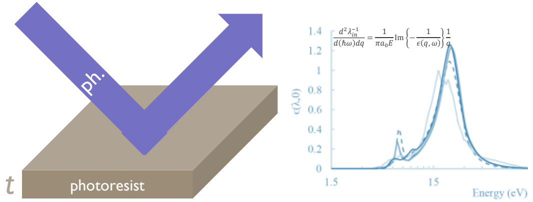
Electron beam transmission



$$T_X = e^{-\frac{t}{\lambda}}$$

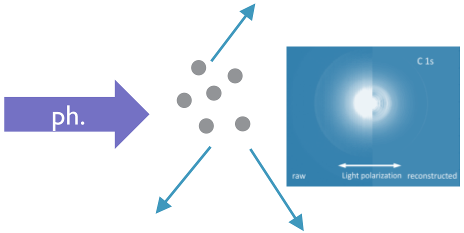
Only applicable to
μm film and > 1 keV electrons.

Dielectric formalism

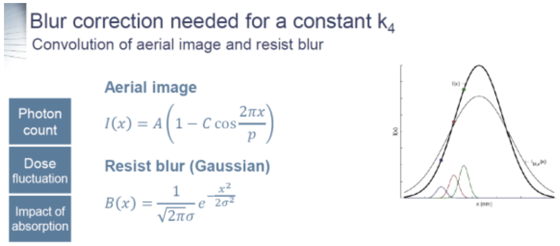


Optical dielectric constant, but only valid in the optical limit (q = 0).

Velocity map imaging



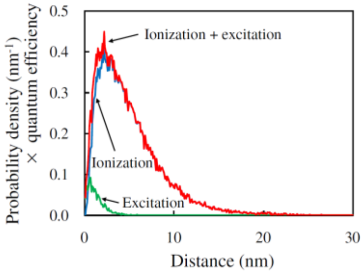
Requires synchrotron and vapor phase molecules, monomers.



$$I(x) = A\left(1 - C\cos\frac{2\pi x}{p}\right)$$

$$B(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{x^2}{2\sigma^2}}$$

Resist blur as degradation of the aerial image

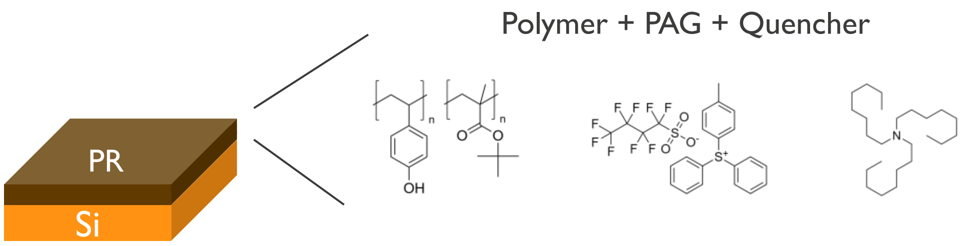


Montecarlo simulations of the thermalization distance

Measuring the electron MFP: at BEAR beamline using substrate

https://doi.org/10.1021/acsami.3c05884

Measuring the electron MFP



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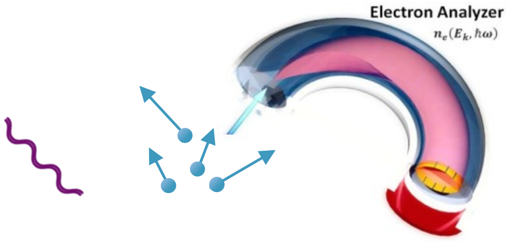
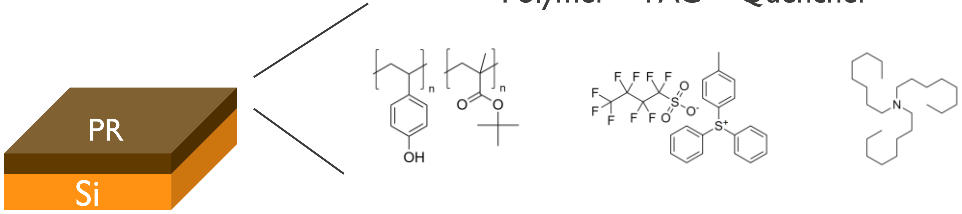


Polymer + PAG + Quencher



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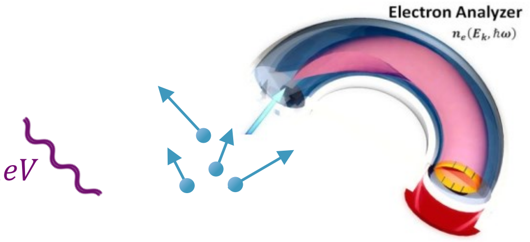
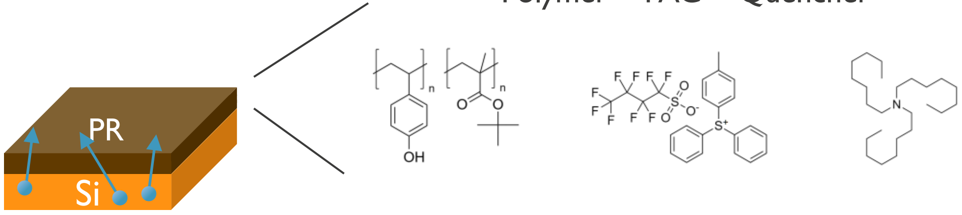
Measuring the electron MFP

$\hbar\omega > 101eV$



Using light above the Si2*p* absorption edge, photoemission is mainly from the Si, not PR

Polymer + PAG + Quencher



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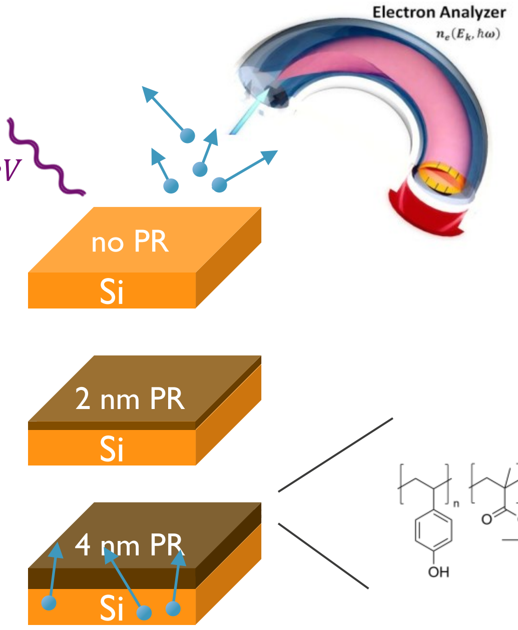

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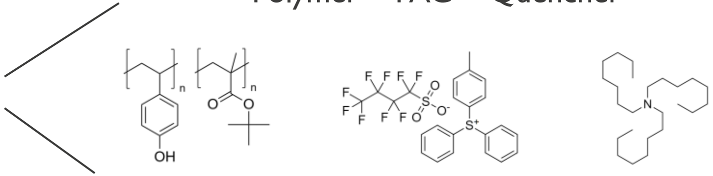

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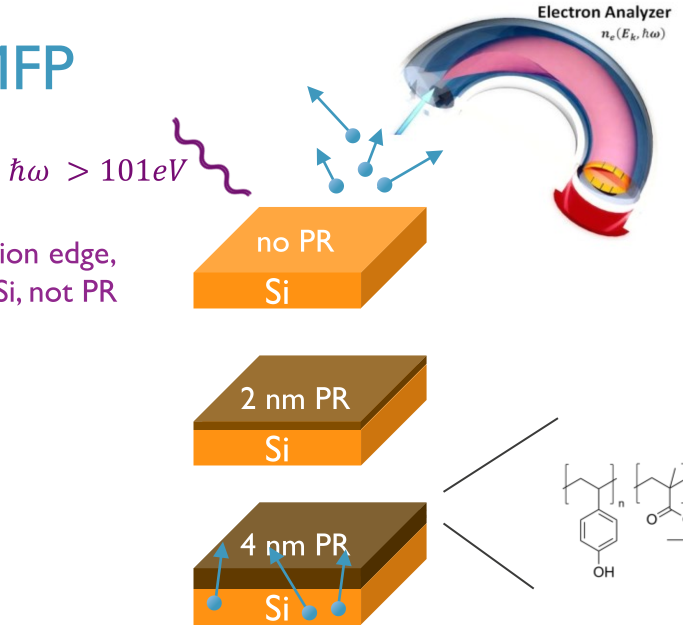

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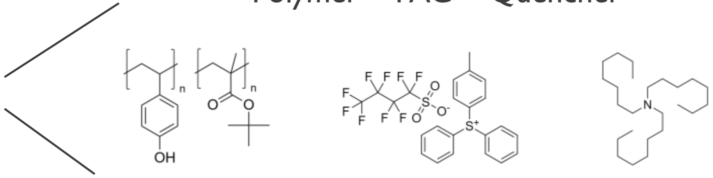

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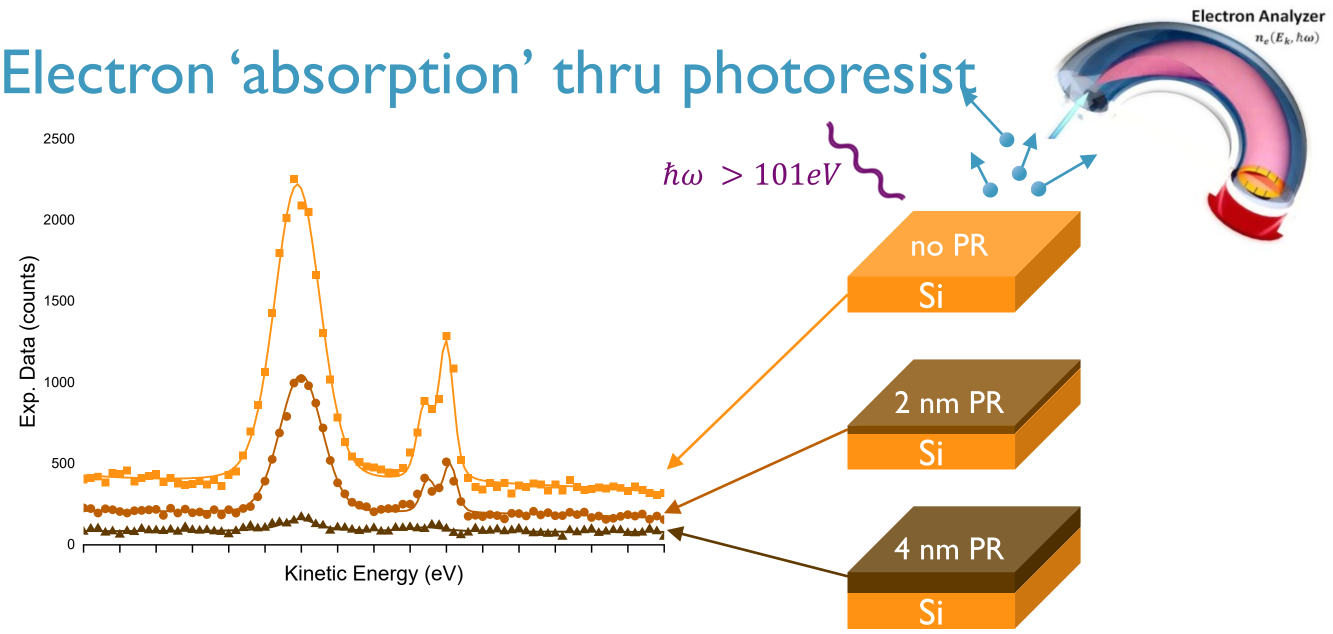
public

Electron ‘absorption’ thru photoresist



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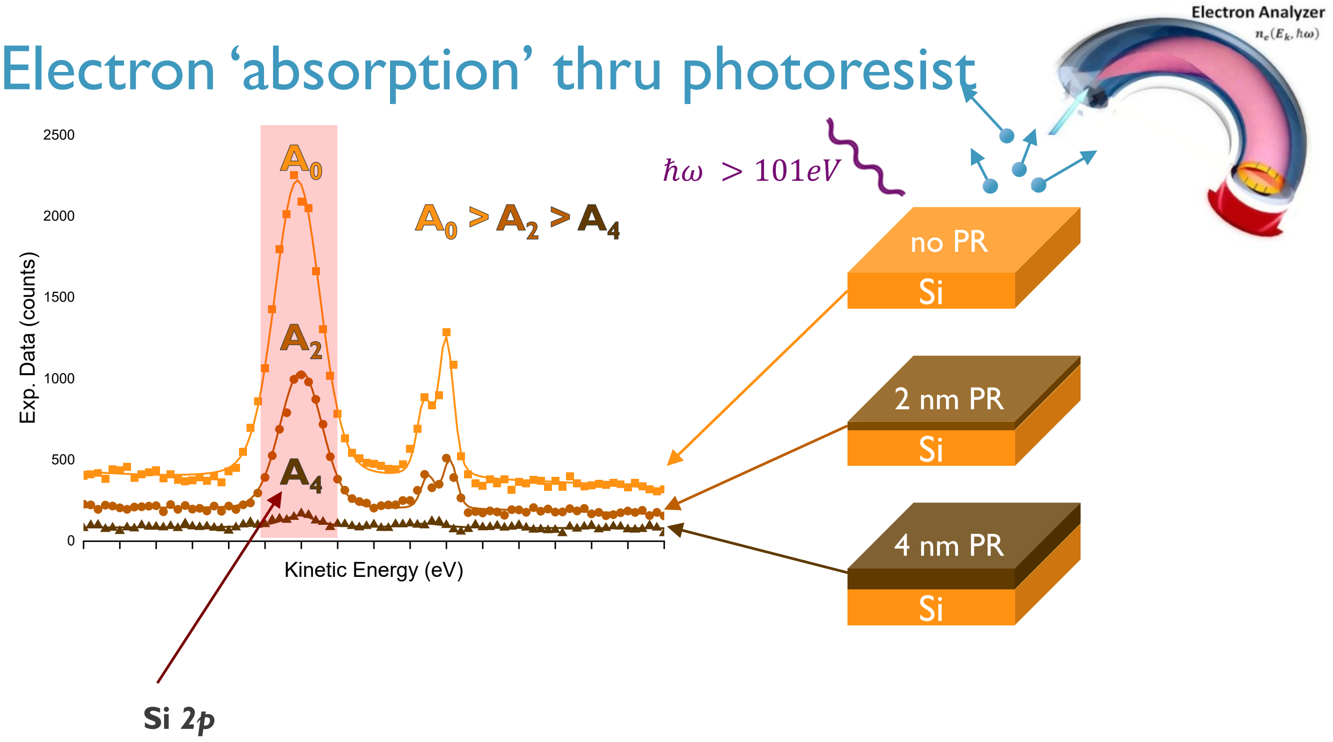

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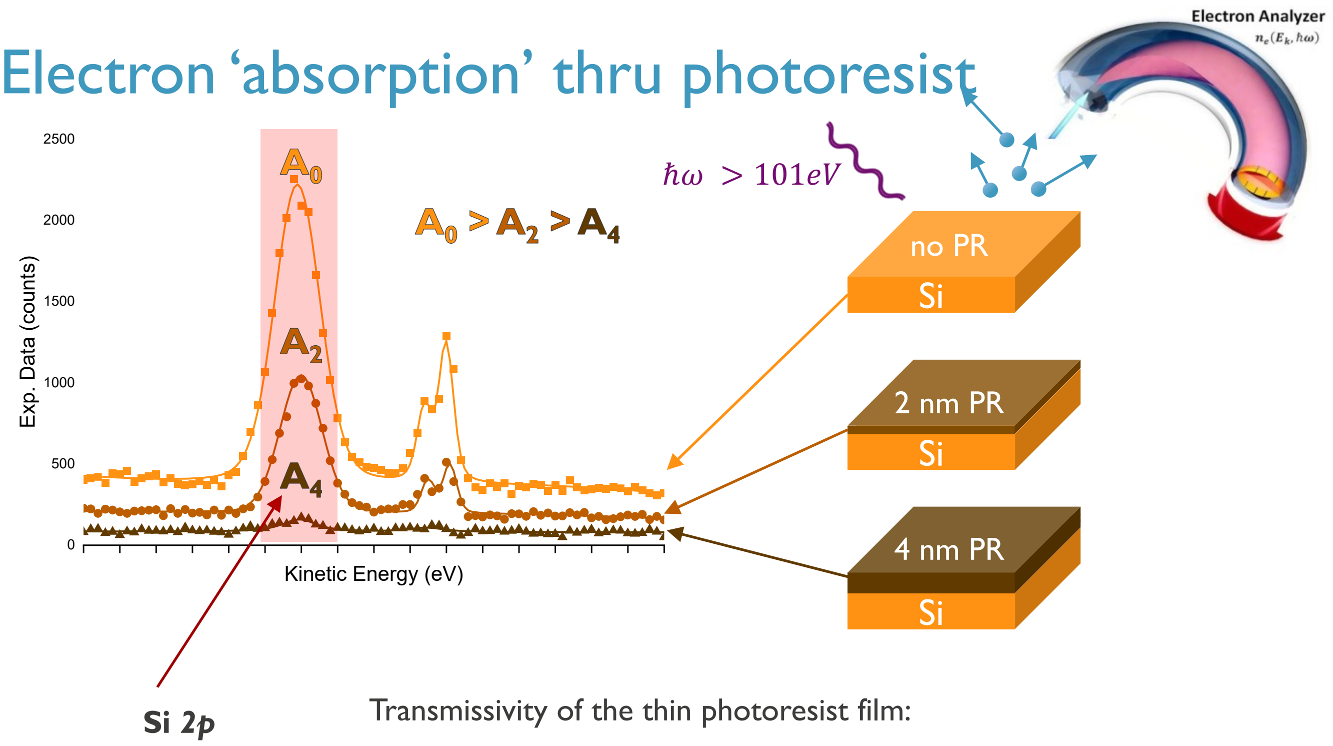

Transmissivity of the thin photoresist film:

$$T_x = \frac{A_t}{A_0} = e^{-\frac{t}{\lambda}}$$

Mean free path:

$$MFP = \left(-\frac{1}{t} \cdot \ln \frac{A_t}{A_0}\right)^{-1}$$

Thickness measured by XPS

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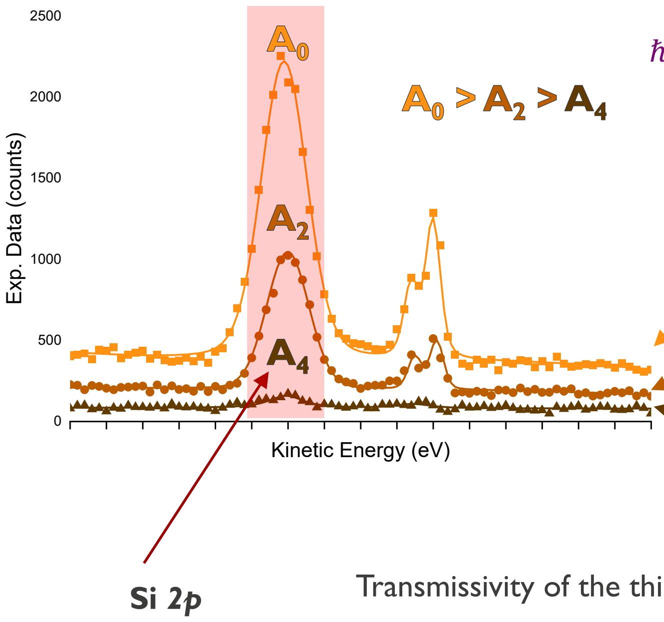

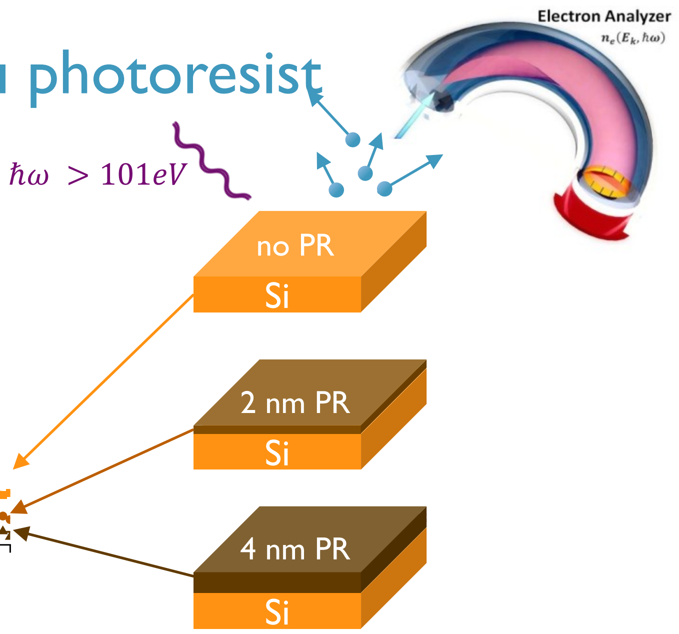

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Thickness measured by XPS

The electron mean free path is measured as attenuation (‘absorption’) of electrons photoemitted from the substrate and passing thru photoresist.

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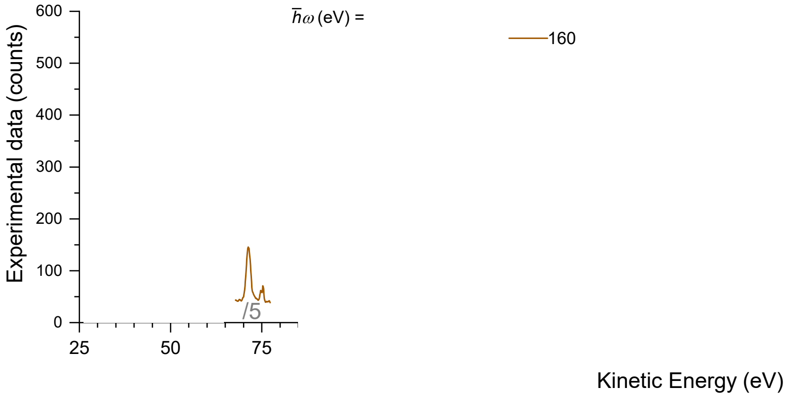
Measuring the electron MFP



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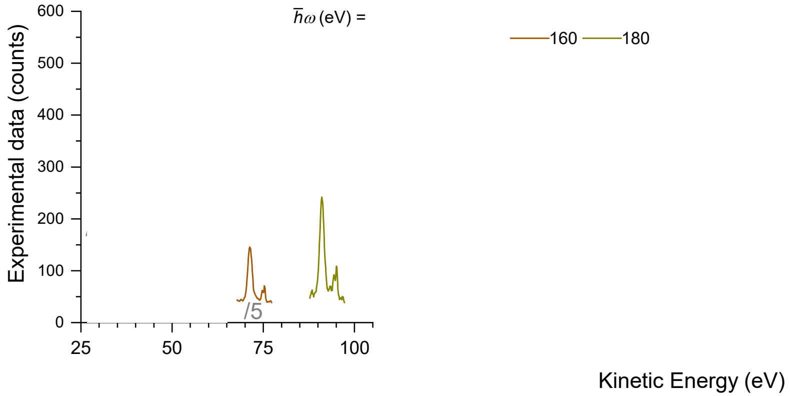
where kinetic energy $E_K = E_b - \hbar\omega - \Delta\Phi$

Measuring the electron MFP



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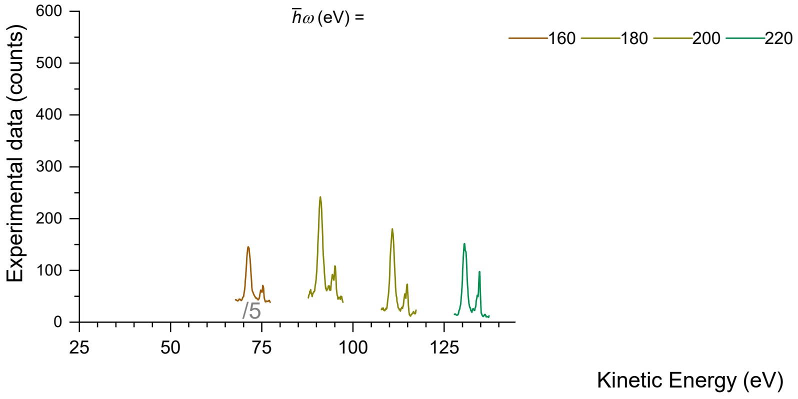

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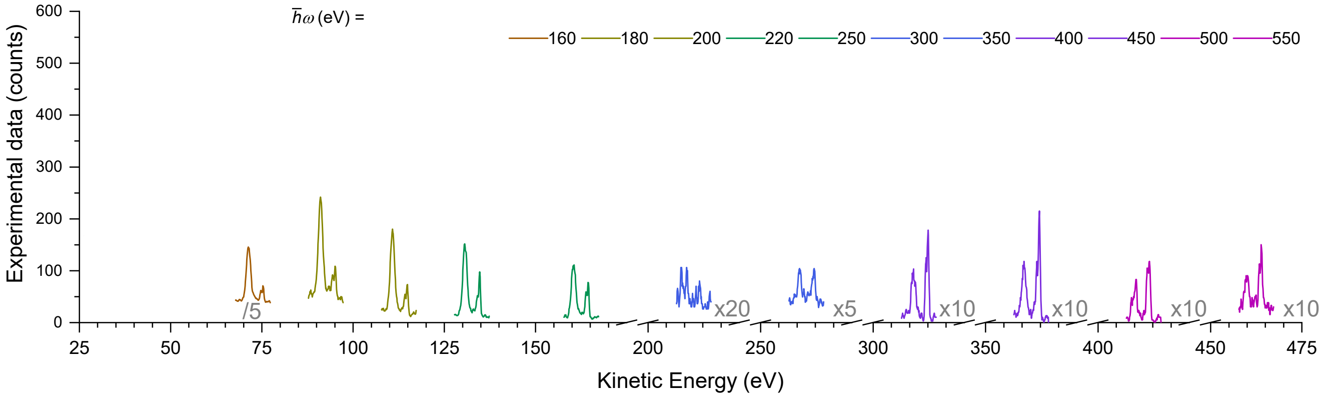

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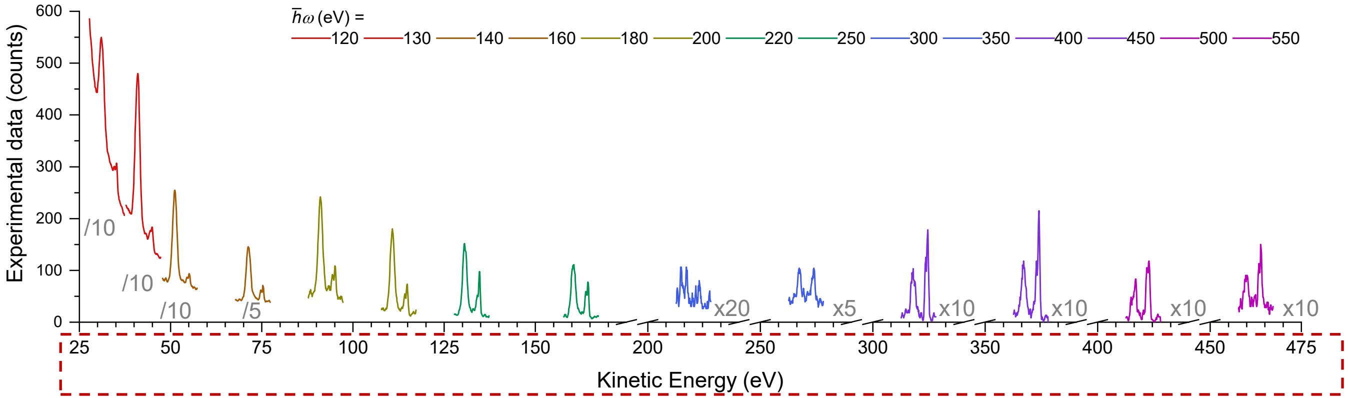

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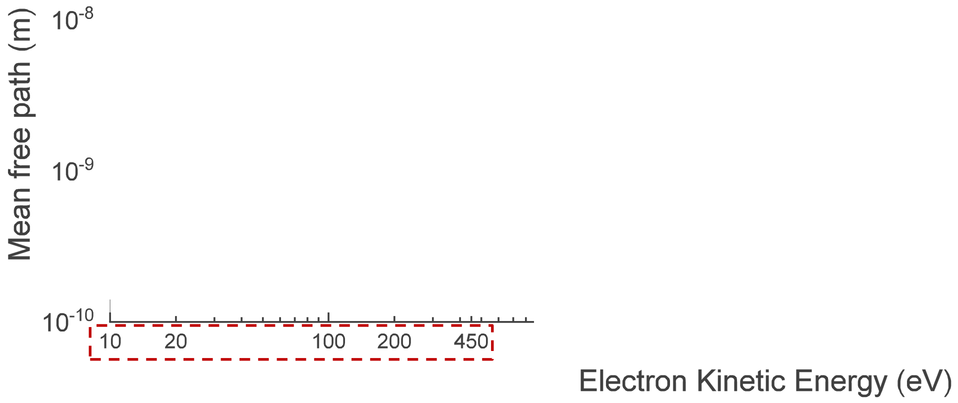
where kinetic energy $E_K = E_b - \hbar\omega - \Delta\Phi$

MFP in a EUV chemically amplified resist

Polymer only | Polymer + PAG | Polymer + PAG + Q



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MFP in a EUV chemically amplified resist

Polymer only

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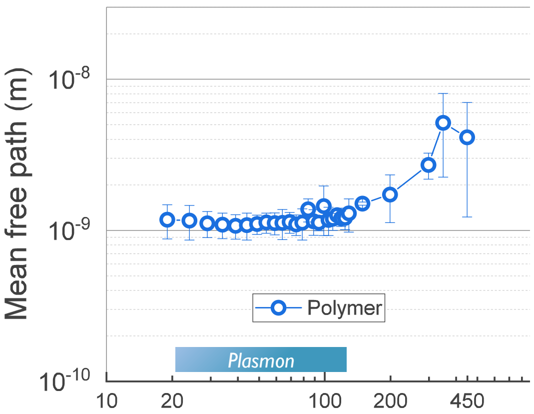

Electron Kinetic Energy (eV)

https://doi.org/10.1021/acsami.3c05884

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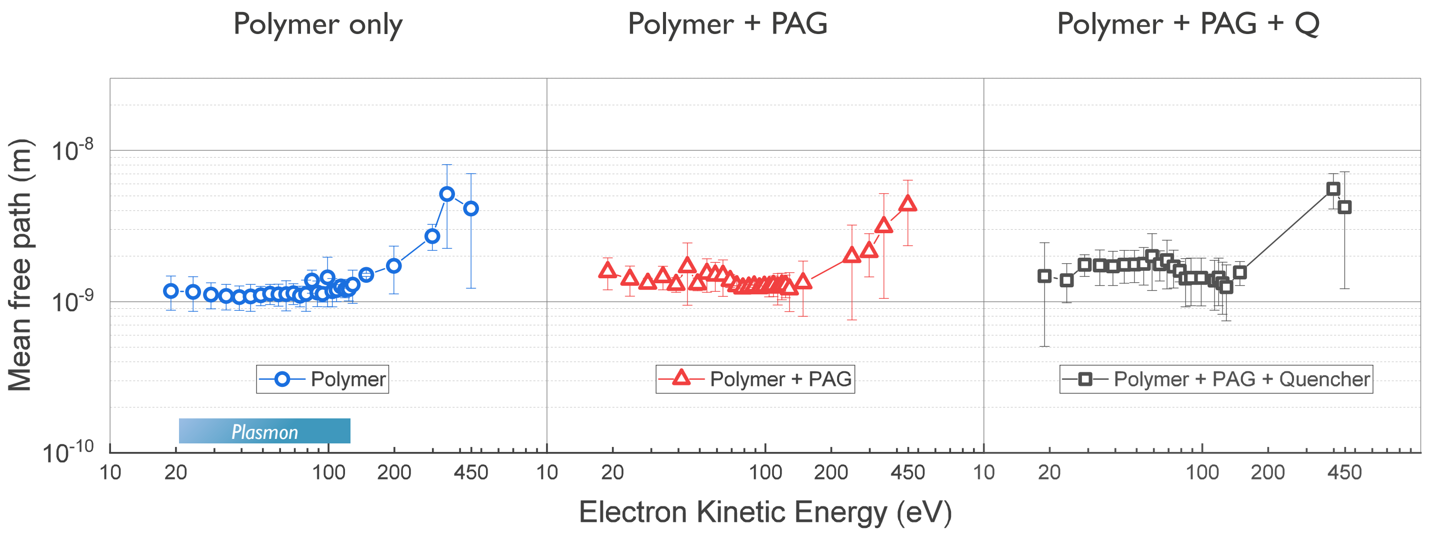
MFP in a EUV chemically amplified resist

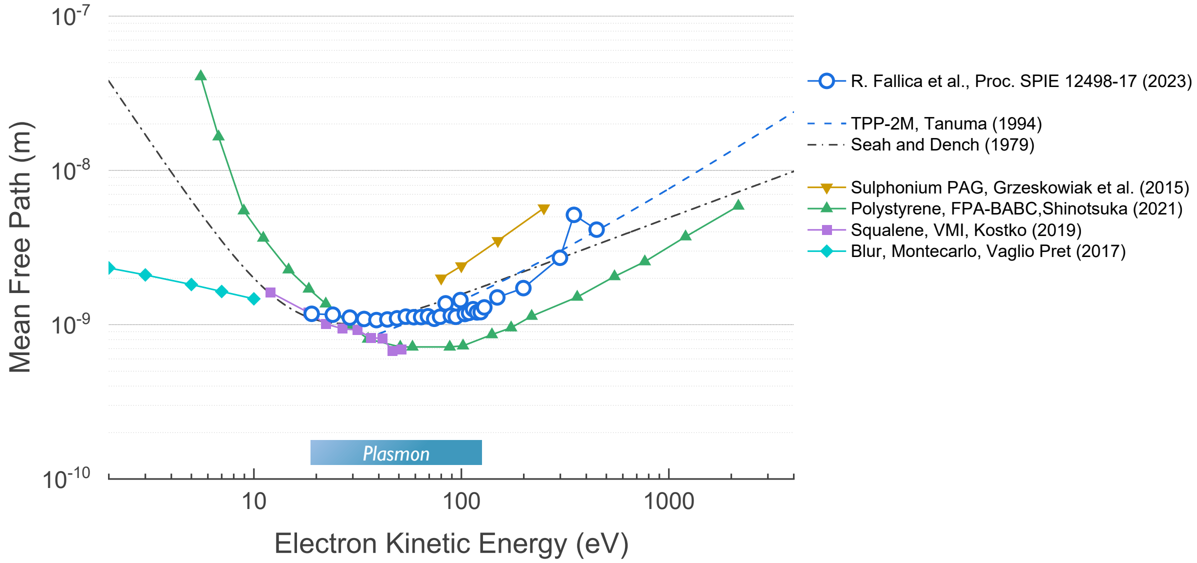


- ➢ MFP = 1 ~ 2 nm in EUV-relevant range
- ➢ MFP does not change with PAG and quencher (inelastic scattering with plasmon is ≈ unchanged)
- ➢ No chemical effects from PAG dissociation until 20 eV (dissociative electron attachment, DEA)

where kinetic energy $E_K = E_b - \hbar\omega - \Delta\Phi$

https://doi.org/10.1021/acsami.3c05884

Comparison with previous studies



The thermalization distance was determined to be 3.2 ± 0.6 nm.

Kozawa and Tagawa, Jpn. J. Appl. Phys. 50 (2011) 030209

The EAL value obtained in the current study for PHS of 3.10 ± 0.41 nm is close to the semi-empirical thermalization

Ma et al., J. Appl. Phys. 127, 245301 (2020)

Data fitting allowed for an extraction of image blur σ = 8.6 ± 0.6 nm,

Allenet et al., Proc. of SPIE 11517, 115170J (2020)

1. Our experimental data has same trend as 'optical' model (Tanuma, Penn, Powell, TPP-2M)
2. Discrepancy at low energy: experiments needed
3. Effective number of electrons in valence band → shifts the plasmon to higher energy.

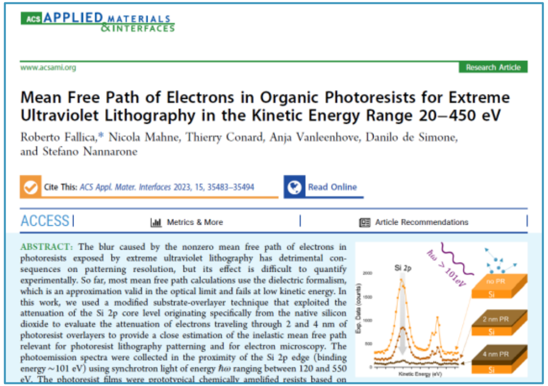
imec

https://doi.org/10.1021/acsami.3c05884

public

Conclusions

Conclusions



ACS APPLIED MATERIALS & INTERFACES

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Mean Free Path of Electrons in Organic Photoresists for Extreme Ultraviolet Lithography in the Kinetic Energy Range 20–450 eV

Roberto Fallica,* Nicola Mahne, Thierry Conard, Anja Vanleenhove, Danilo de Simone, and Stefano Nannarone

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ABSTRACT: The blur caused by the nonzero mean free path of electrons in photoresists exposed by extreme ultraviolet lithography has detrimental consequences on patterning resolution, but its effect is difficult to quantify experimentally. So far, most mean free path calculations use the dielectric formalism, which is an approximation valid in the optical limit and fails at low kinetic energy. In this work, we used a modified substrate-overlayer technique that exploited the attenuation of the Si 2p core level originating specifically from the native silicon dioxide to evaluate the attenuation of electrons traveling through 2 and 4 nm of photoresist overlayers to provide a close estimation of the inelastic mean free path relevant for photoresist lithography patterning and for electron microscopy. The photoemission spectra were collected in the proximity of the Si 2p edge (binding energy ~101 eV) using synchrotron light of energy ℏω ranging between 120 and 550 eV. The photoresist films were prototypical chemically amplified resists based on

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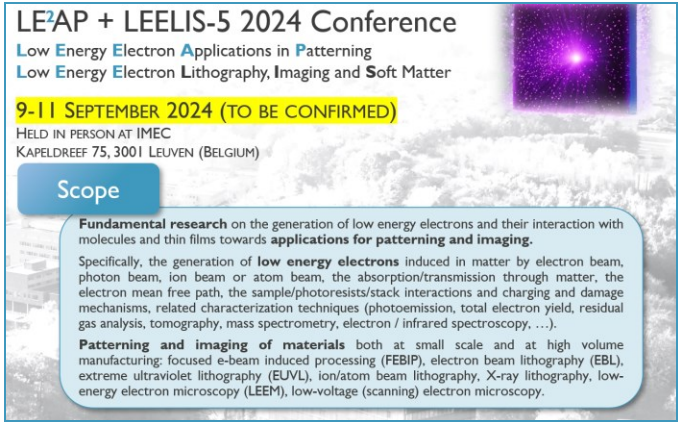

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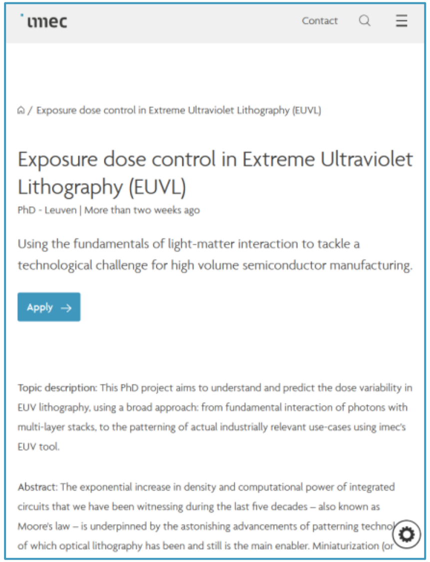

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roberto.fallica@imec.be

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