EUV Radiation Chemistry Fundamentals: Novel Probing Techniques

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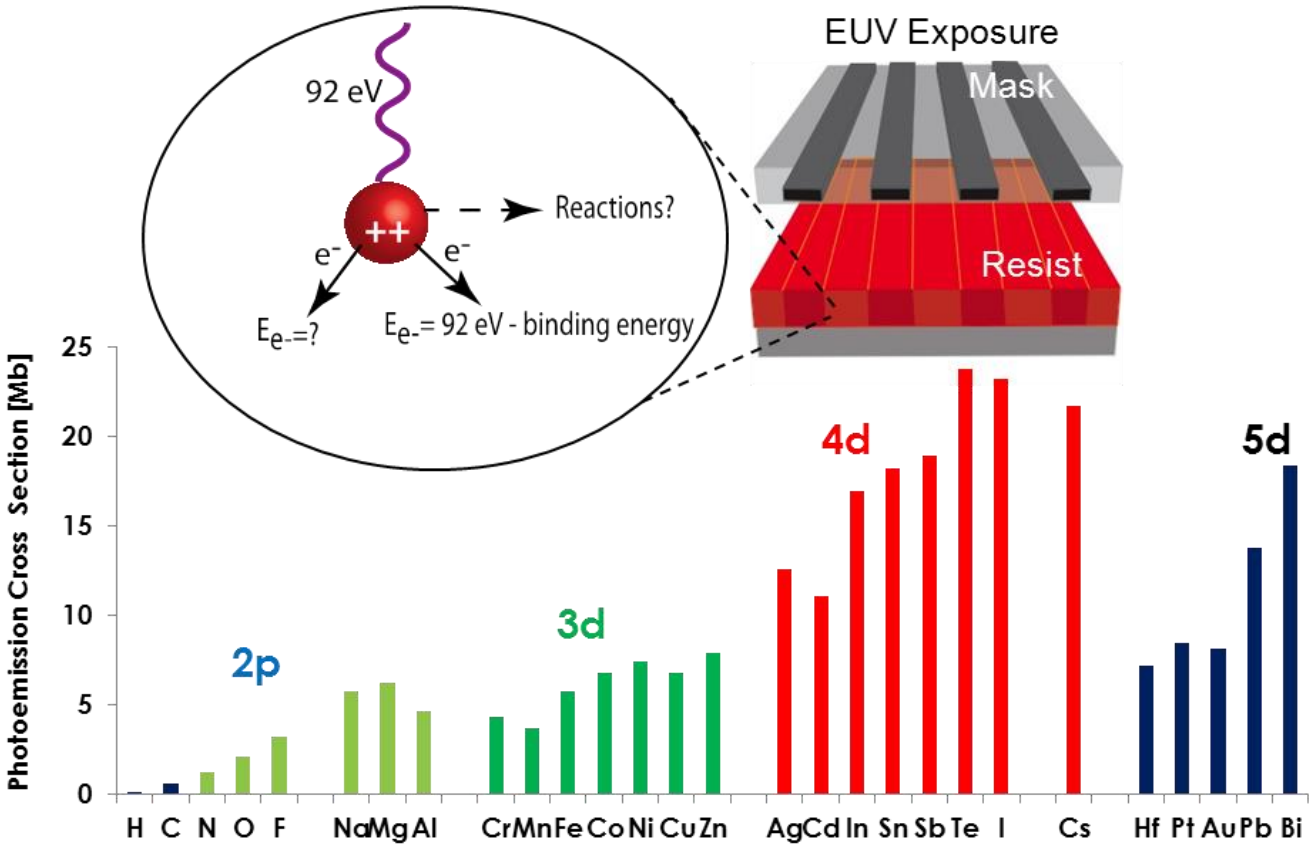
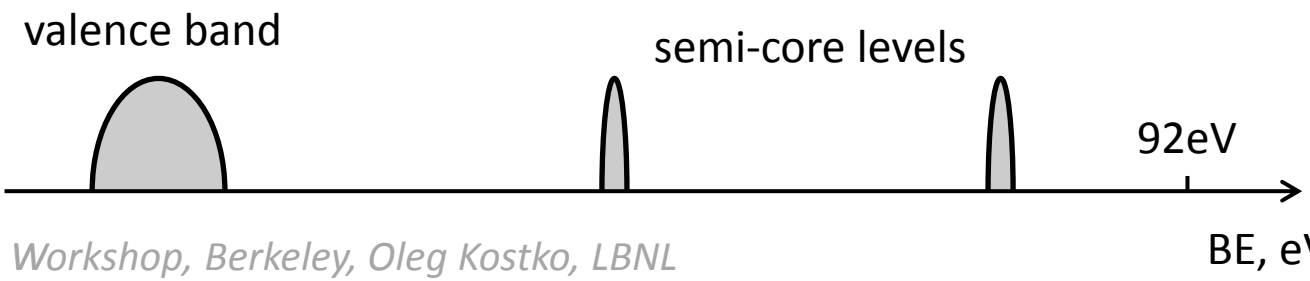
Motivation


92 eV
++
Reactions?
e⁻
e⁻
E_e-=?
E_e-= 92 eV - binding energy
EUV Exposure
Mask
Resist
Photoemission Cross Section [Mb]
25
20
15
10
5
0
2p
3d
4d
5d
H C N O F
Na Mg Al
Cr Mn Fe Co Ni Cu Zn
Ag Cd In Sn Sb Te I
Cs
Hf Pt Au Pb Bi


valence band
semi-core levels
92eV
BE, eV

The Problem

"…it is technically nearly impossible to directly observe the reactions induced in ultrathin resist films by 92.5 EUV radiation…"

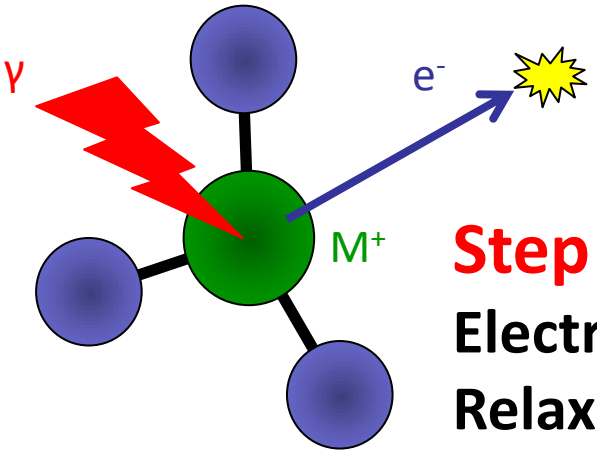
Kozawa & Tagawa EUV CAR review
Jpn J Appl Phys 2010

Processes After EUV Photon Absorption

Step 1

Photoionization

$M + h\nu \rightarrow M^+ + e^-$

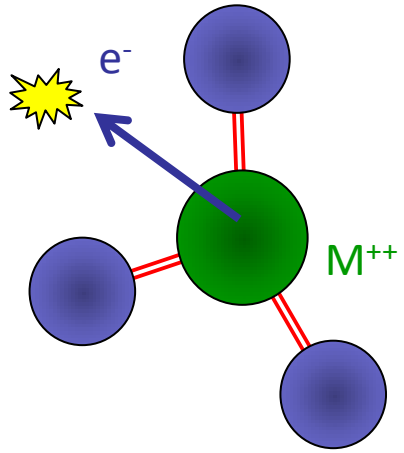


Step 2

Electronic Relaxation

Auger process ?

$M^+ \rightarrow M^{++} + e^-$

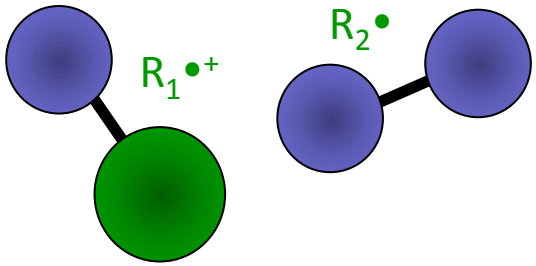


Step 3

Atomic Relaxation

Fragmentation?

$M^+ \rightarrow R_1\bullet^+ + R_2\bullet$

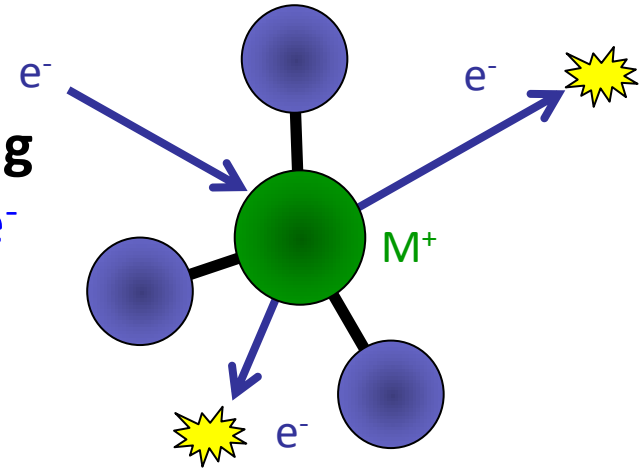


Step 4

Inelastic Scattering

$M + e^- \rightarrow M^+ + 2\ e^-$

and more steps…



Our Approach

Gas-phase ⇨ Nanoparticles ⇨ Thin films

Step 1 **Photoionization**

$M + h\nu \rightarrow M^+ + e^-$

Step 2 **Electronic Relaxation**

Auger process ?

$M^+ \rightarrow M^{++} + e^-$

Step 3 **Atomic Relaxation**

Fragmentation?

$M^+ \rightarrow R_1\bullet^+ + R_2\bullet$

Step 4 **Inelastic Scattering**

$M + e^- \rightarrow M^+ + 2\ e^-$

and more steps…

Photoelectron spectroscopy:

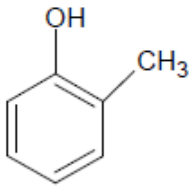
1. Electron kinetic energies
2. Electron yield

Mass spectrometry:

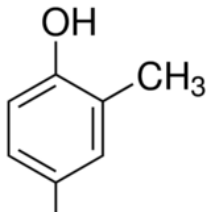
1. Fragmentation pattern after EUV photon absorption
2. Fragmentation pattern after e^- collision

Samples

Resist prototype molecules

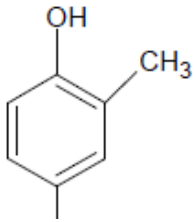


2-methylphenol



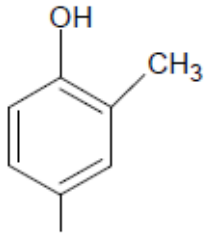
F

4-**fluoro**-
2-methylphenol



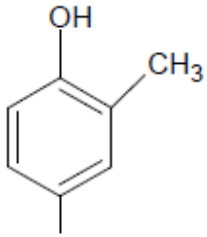
Cl

4-**chloro**-
2-methylphenol



Br

4-**bromo**-
2-methylphenol



I

4-**iodo**-
2-methylphenol

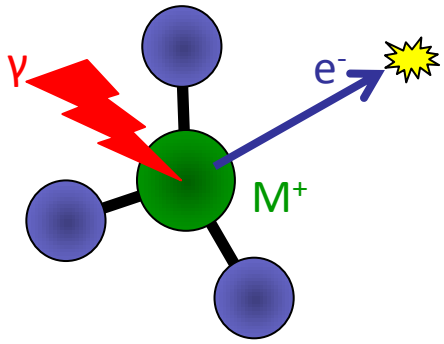
Photoelectron Spectroscopy

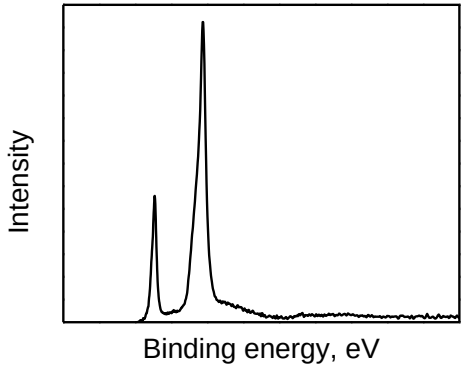
Velocity Map Imaging (VMI) Photoelectron Spectrometer

Step 1

Photoionization

$M + h\nu \rightarrow M^+ + e^-$





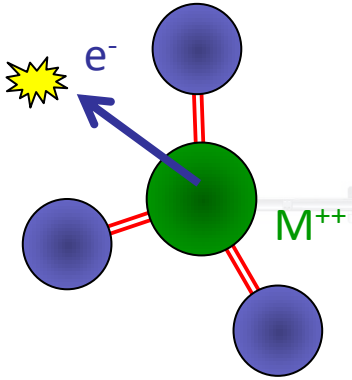
Step 2

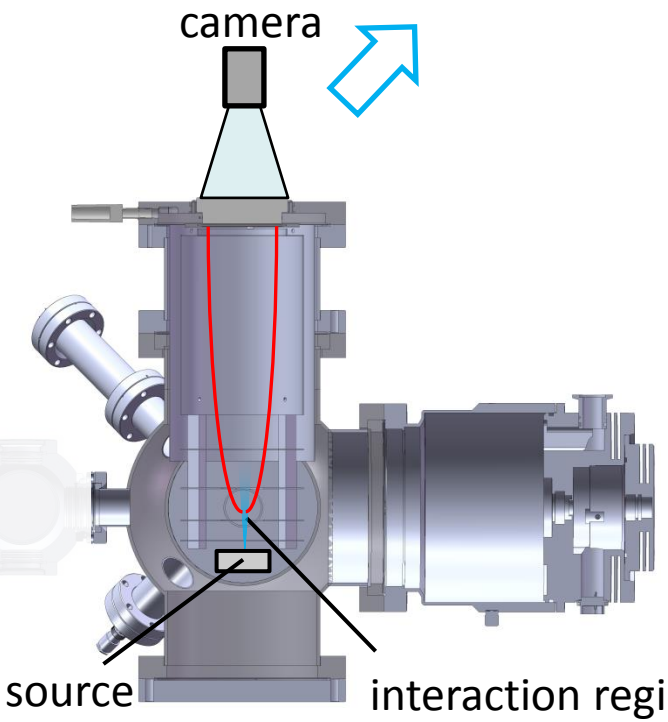
Electronic

Relaxation

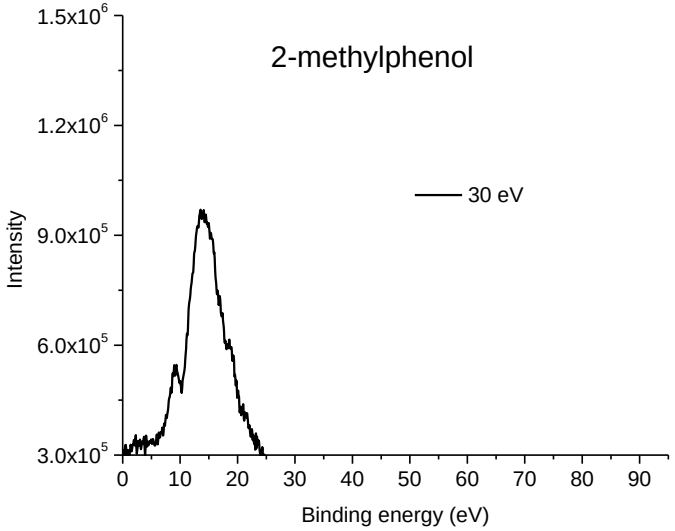
Auger process ?

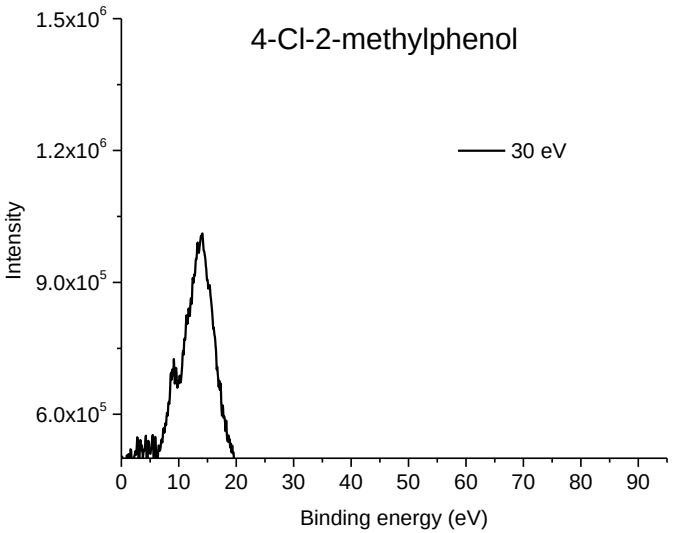
$M^+ \rightarrow M^{++} + e^-$

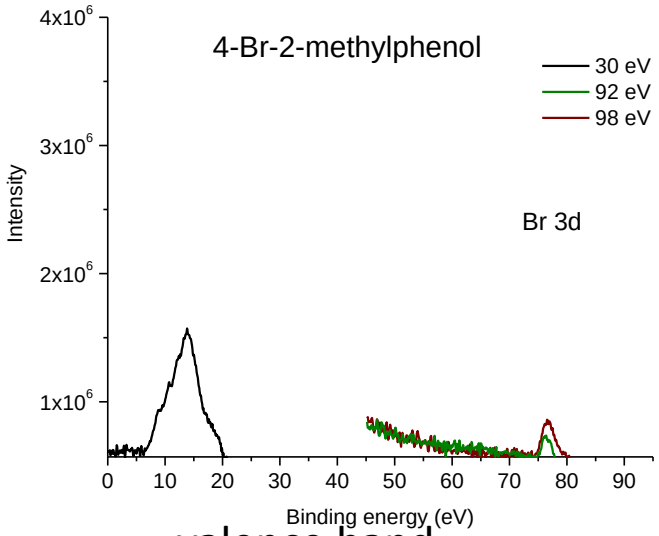


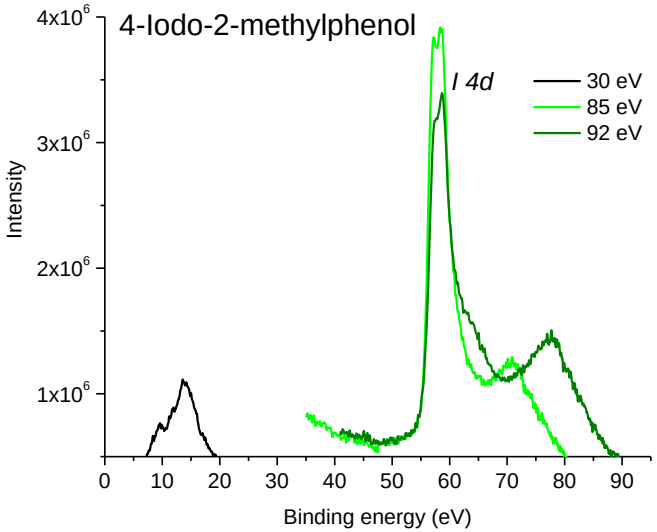


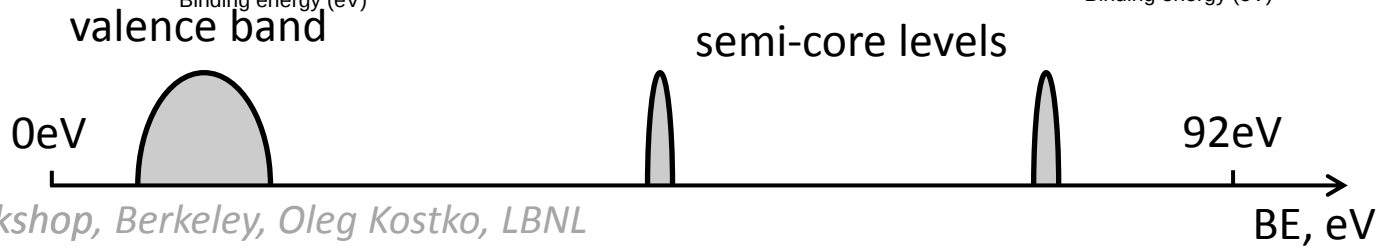
PES of Methylphenols



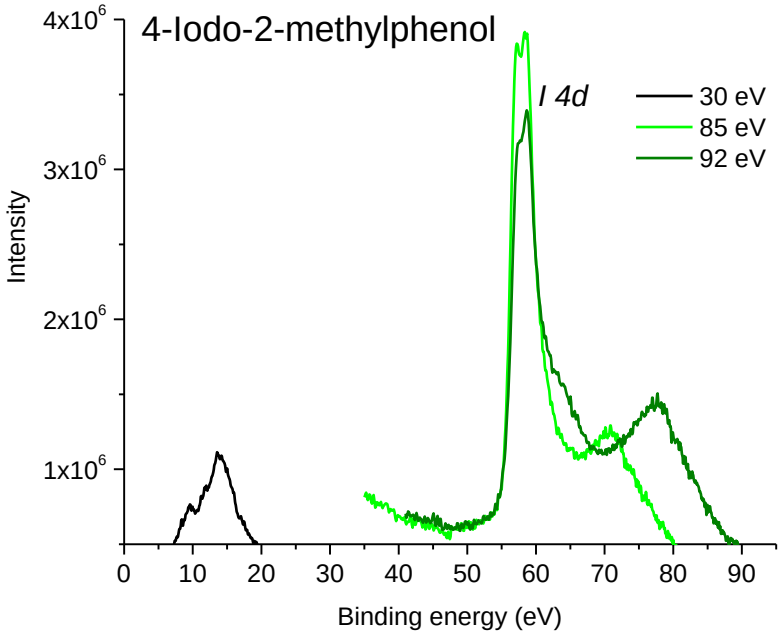


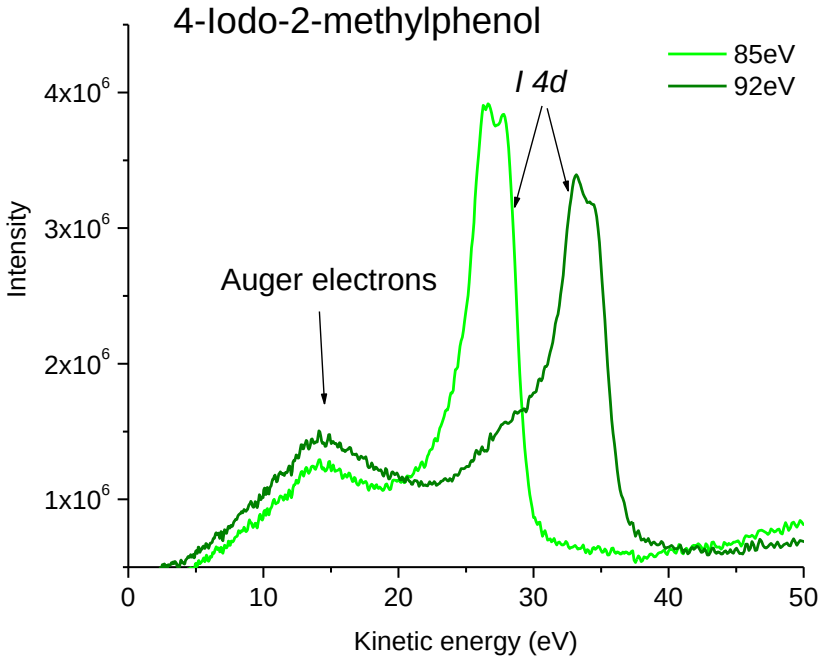


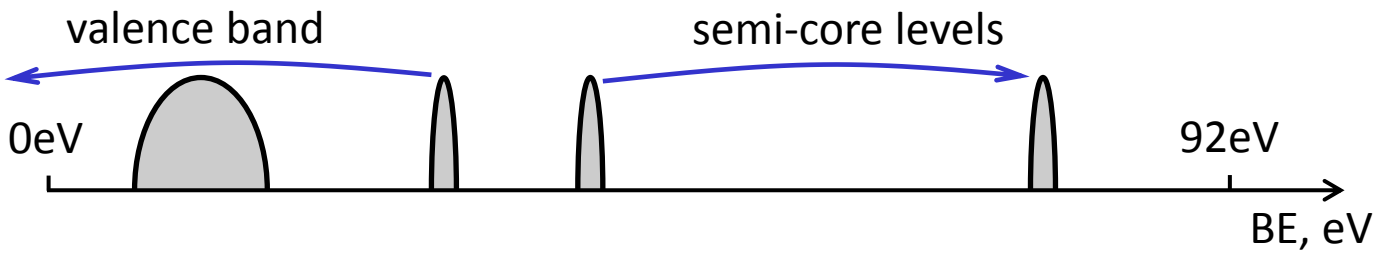




PES of 4-Iodo-2-Methylphenol





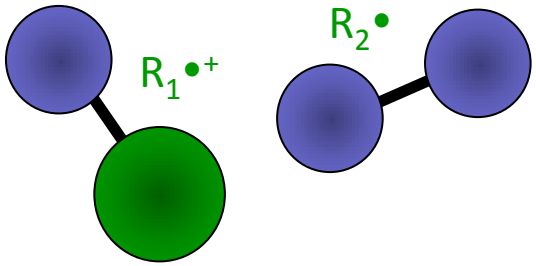


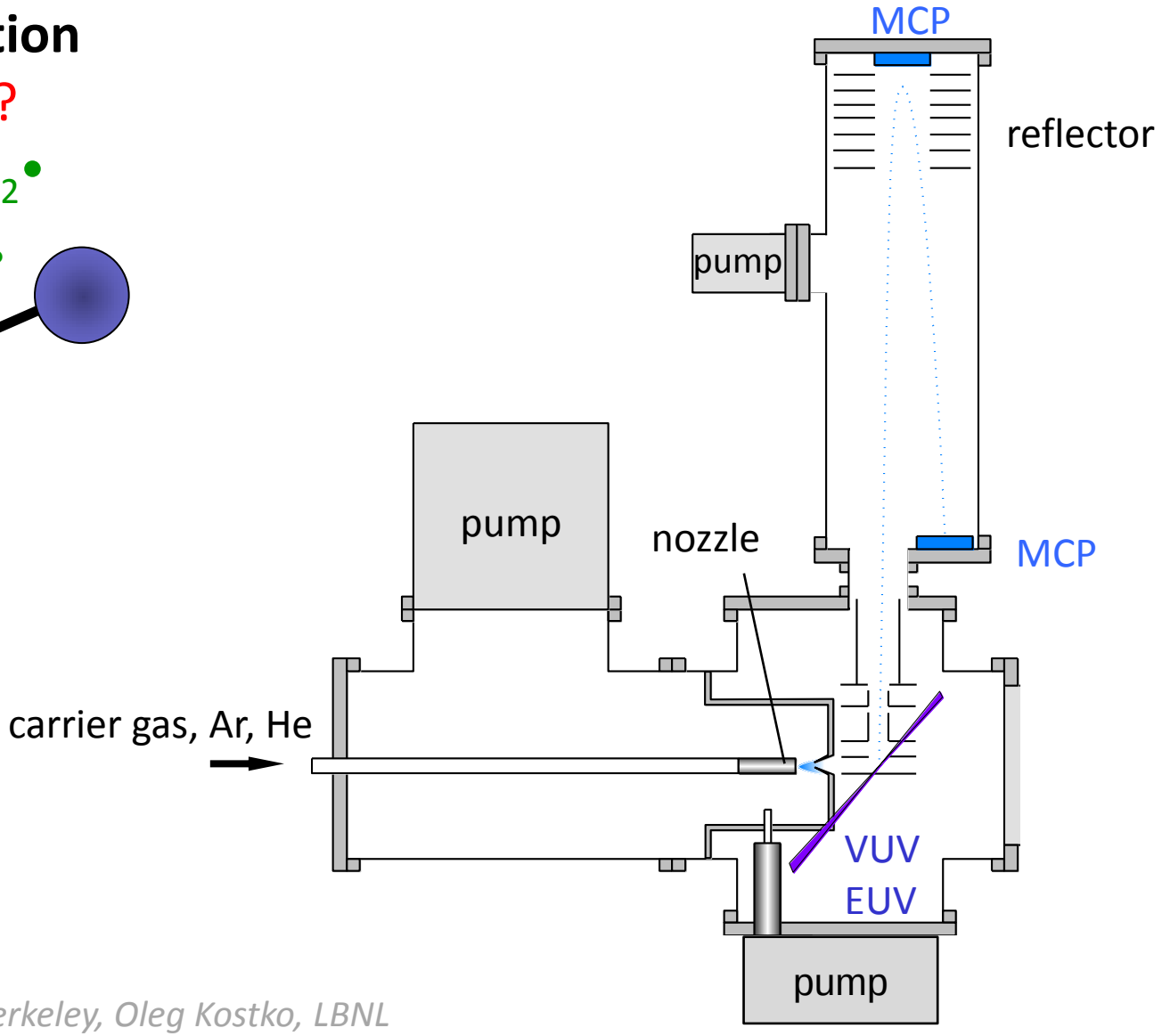
Step 3

Atomic Relaxation

Fragmentation?

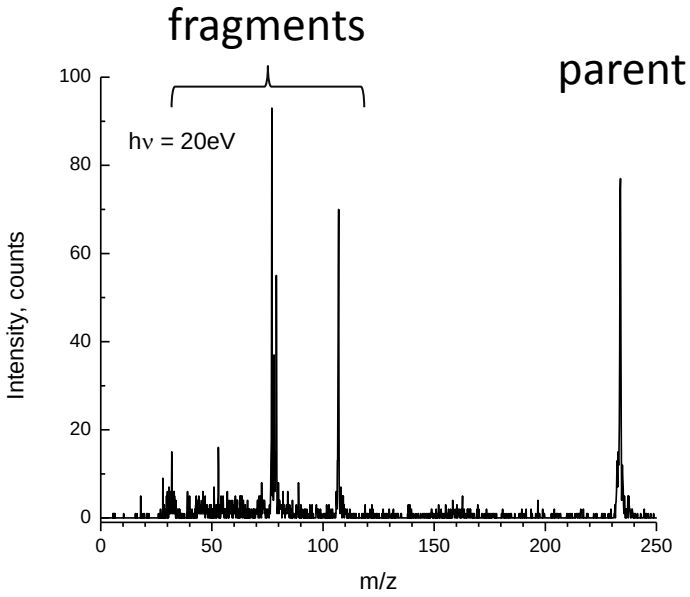
$M^+ \rightarrow R_1\bullet^+ + R_2\bullet$



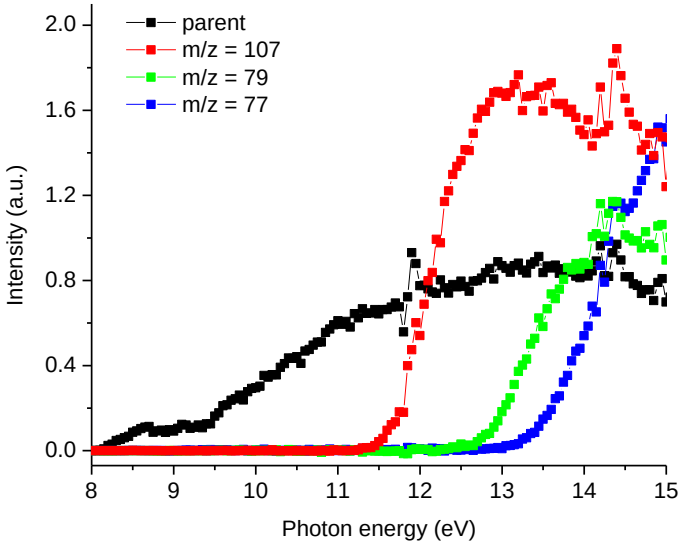


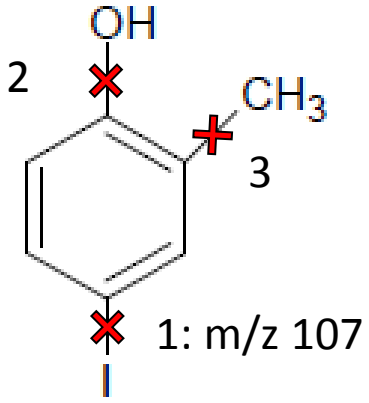
Mass-Spec Data: Photons

Mass spectra



Photoionization efficiency curves (PIEs)





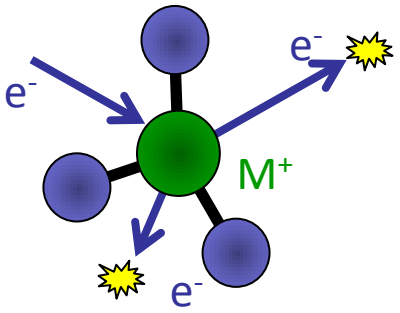
Mass-Spec Data: Electrons

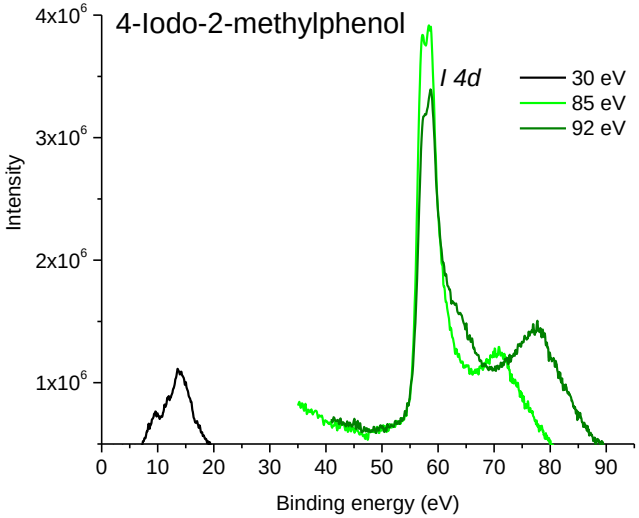
Step 4

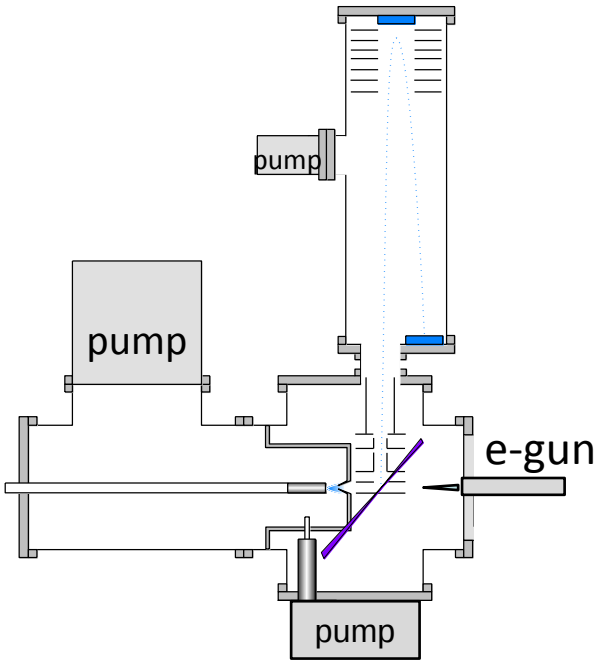
Inelastic Scattering

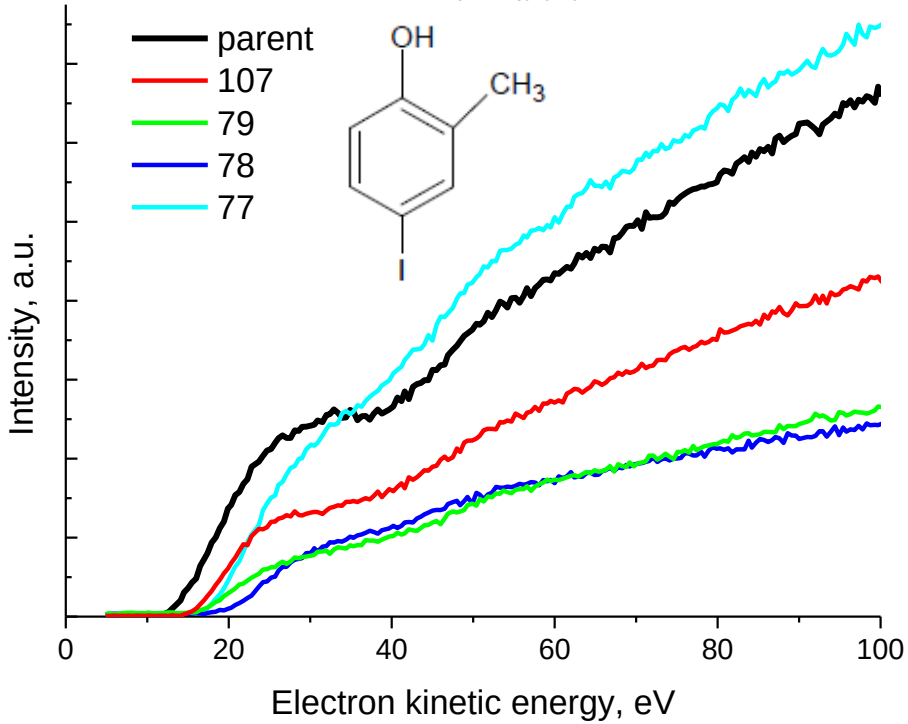
$M + e^- \rightarrow M^+ + 2\ e^-$

and more steps…









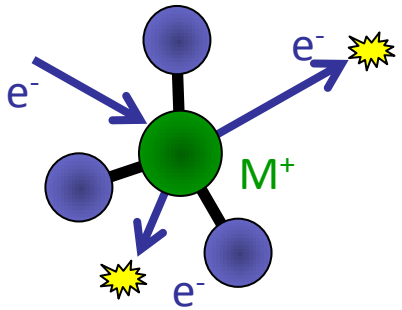
Slow Electron Attachment

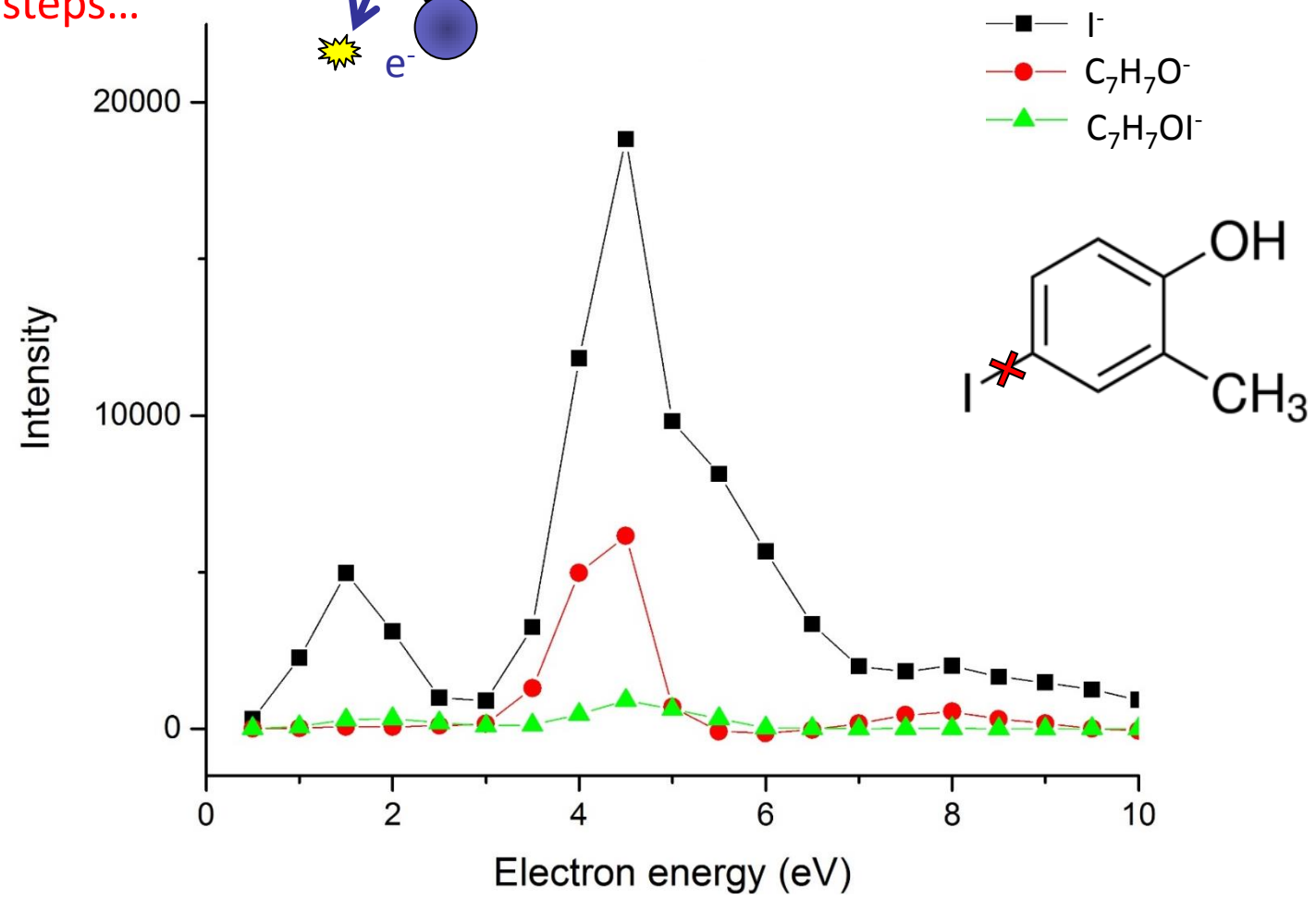
Step 4

Inelastic Scattering

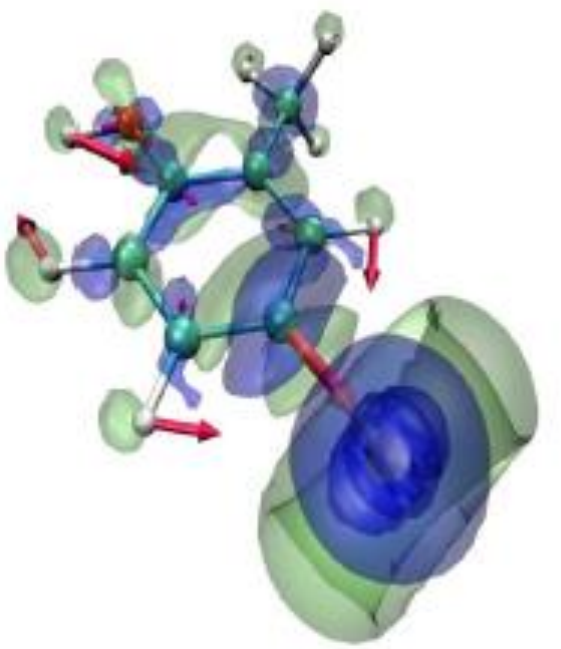
$M + e^- \rightarrow M^+ + 2\ e^-$

and more steps…





Computations



I 4d level is ionized,
Molecular orbital density increases (blue) or decreases (green)

This generates forces on the atoms (red arrows) and fragmentation, (probable loss of I radical)

Other orbitals produce OH radicals or stable ions

Modeling the Interaction of EUV radiation with Photoresist Materials (P71)

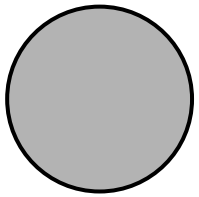
Kristina D. Closser, David Prendergast

From Gas-Phase to Real World

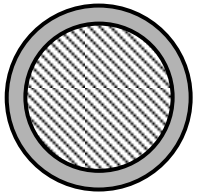
Gas-phase ⇨ Nanoparticles

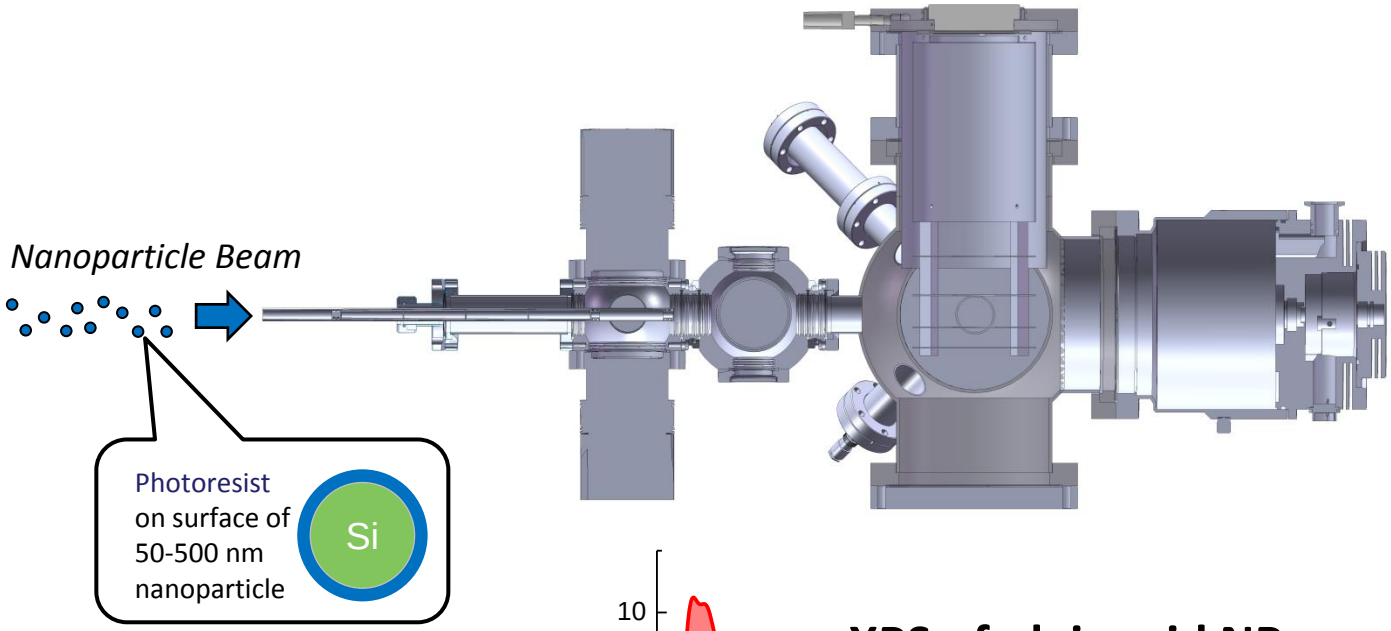
Nanoparticles:

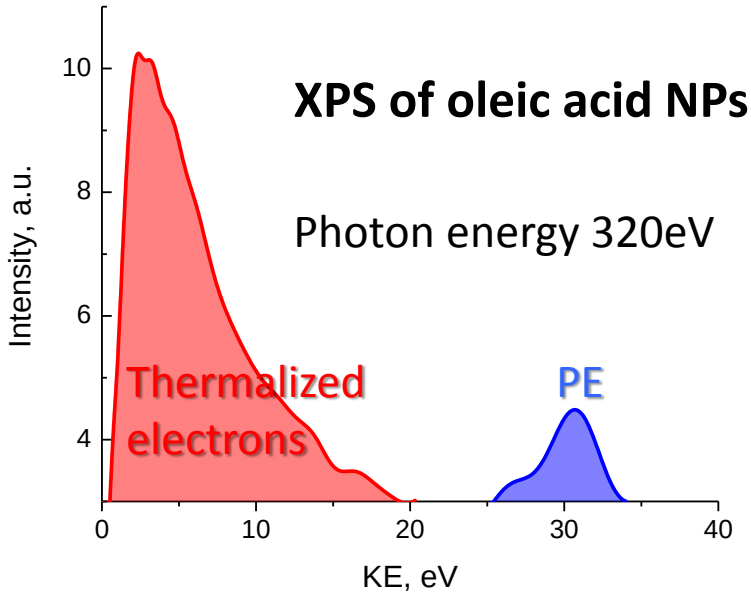
uniform



core-shell







Summary

We have techniques, able to probe:

- Energies and yield of electrons, emitted after EUV photon absorption
- Fragmentation pattern of molecules by EUV irradiation
- Fragmentation of molecules after collisions with emitted electrons
- Effect of thermalized electrons on resist molecules
- Condensed resist material using nanoparticles

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