Role of Ambient Conditions on Organotin Cluster Based Extreme Ultraviolet Resist Chemistries

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Lithography Uncertainty Principle

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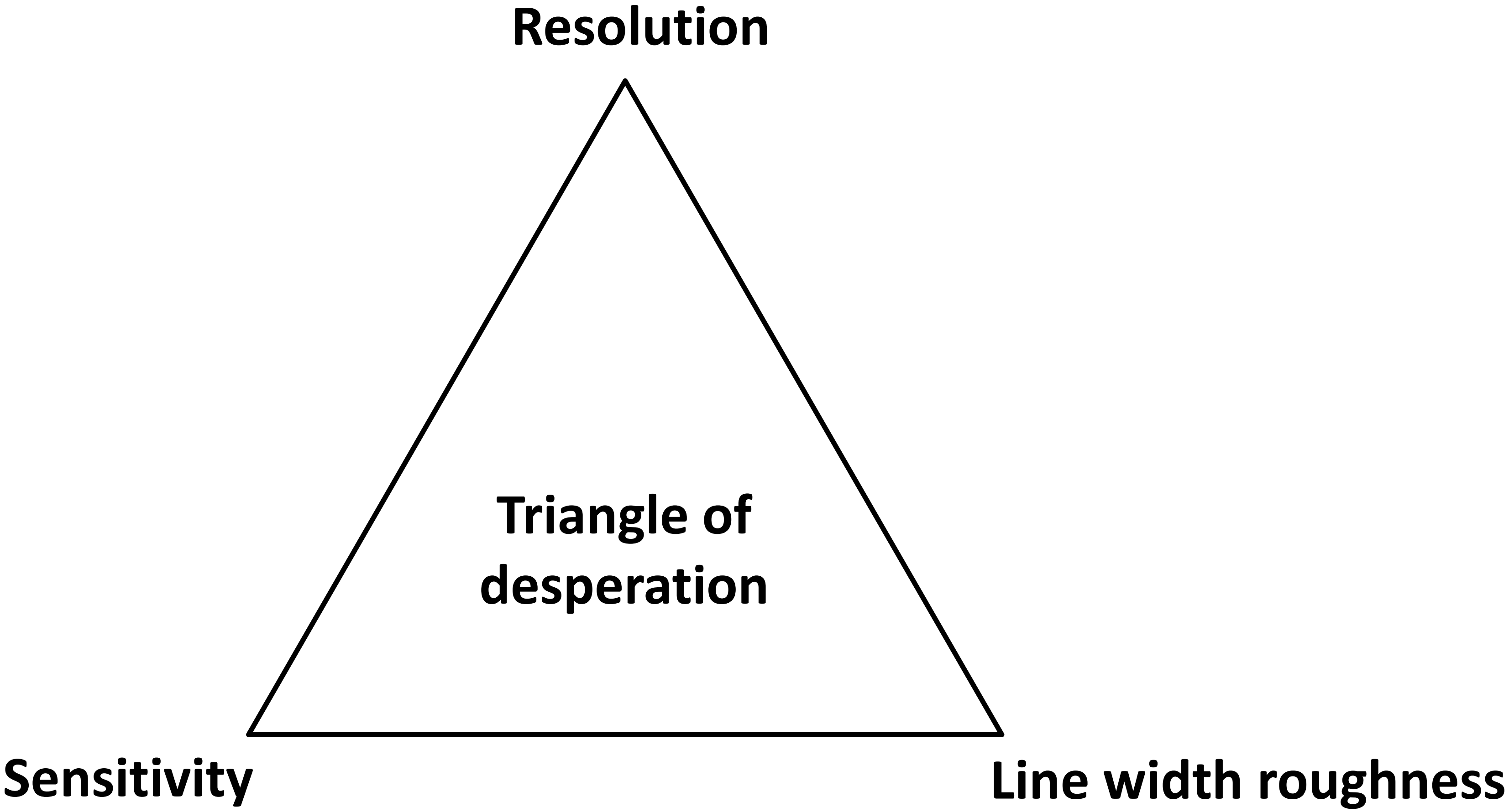

O.R. Wood, *EUVL: Challenges to Manufacturing Insertion*, J. Photopolym. Sci. Technol. **30**, 599-604 (2017).

Lithography Uncertainty Principle

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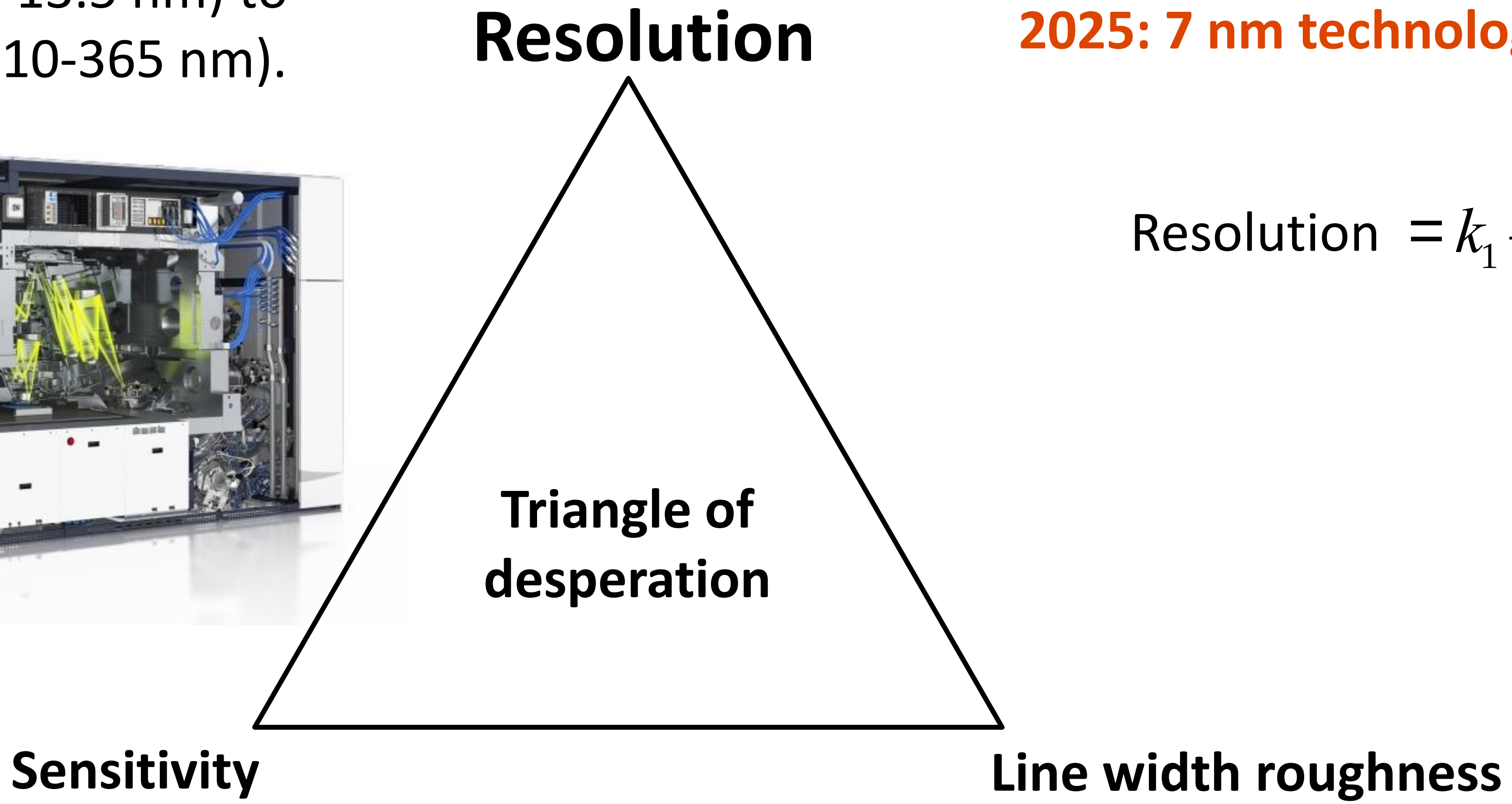
EUV Radiation (λ = 13.5 nm) to replace DUV (λ = 210-365 nm).

ASML NXE:3350B Technical Specifications

EUV light	13.5 nm
NA	0.33
Resolution	≤ 16 nm
Productivity	≥ 125 wph

www.asml.com



2025: 7 nm technology node

$$\text{Resolution} = k_1 \frac{/}{NA}$$

O.R. Wood, *EUVL: Challenges to Manufacturing Insertion,* J. Photopolym. Sci. Technol. **30**, 599-604 (2017).

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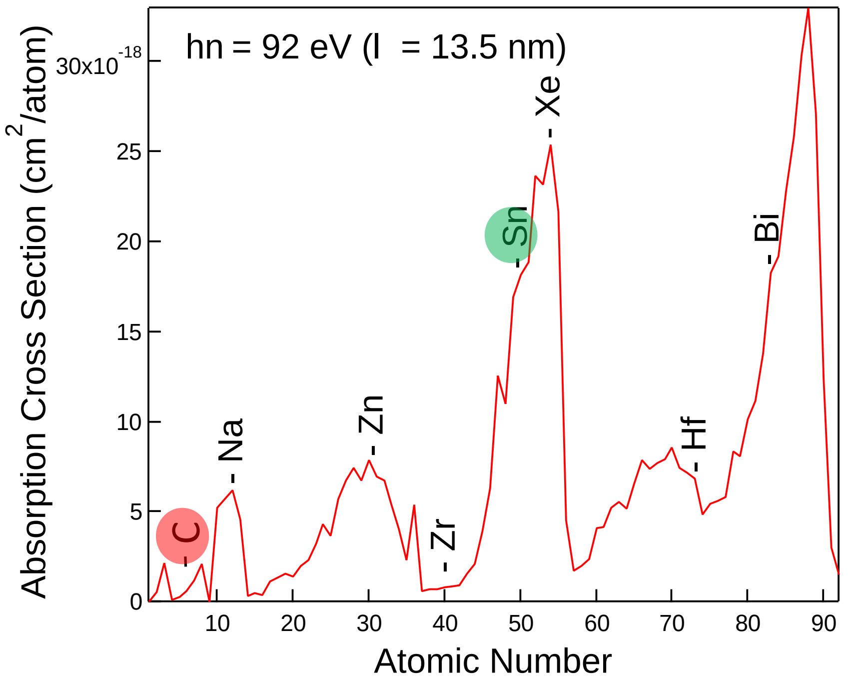
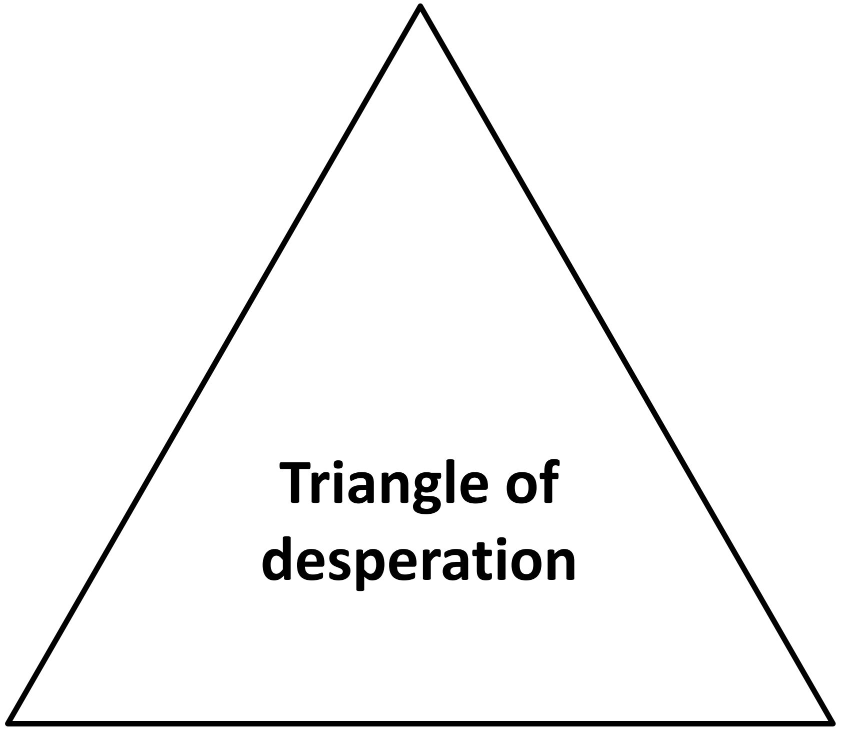
EUV Atomic Absorption Cross Sections



henke.lbl.gov/optical_constants/pert_form.html

Resolution

2025: 7 nm technology node



Sensitivity

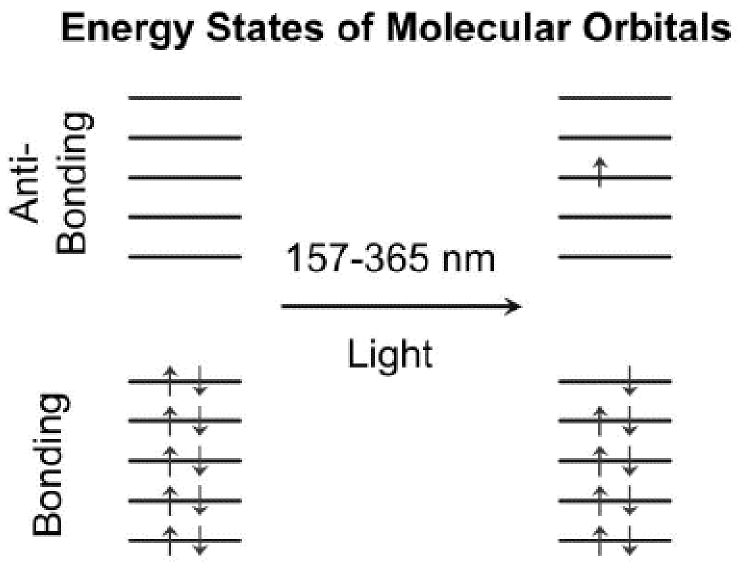
Line width roughness

Printing of ~1000 wafers per day per exposures tool at the dose required for a product (~35 mJ/cm^2)

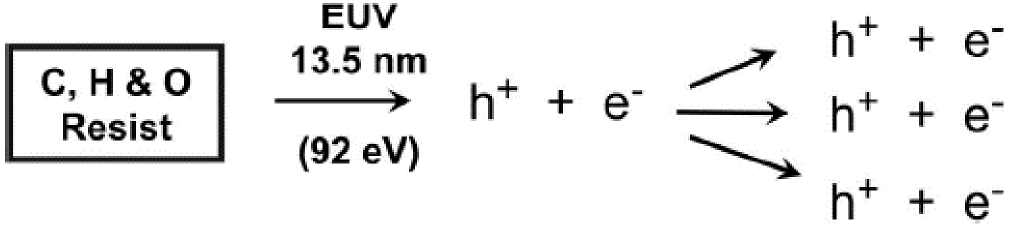
O.R. Wood, *EUVL: Challenges to Manufacturing Insertion*, J. Photopolym. Sci. Technol. **30**, 599-604 (2017).

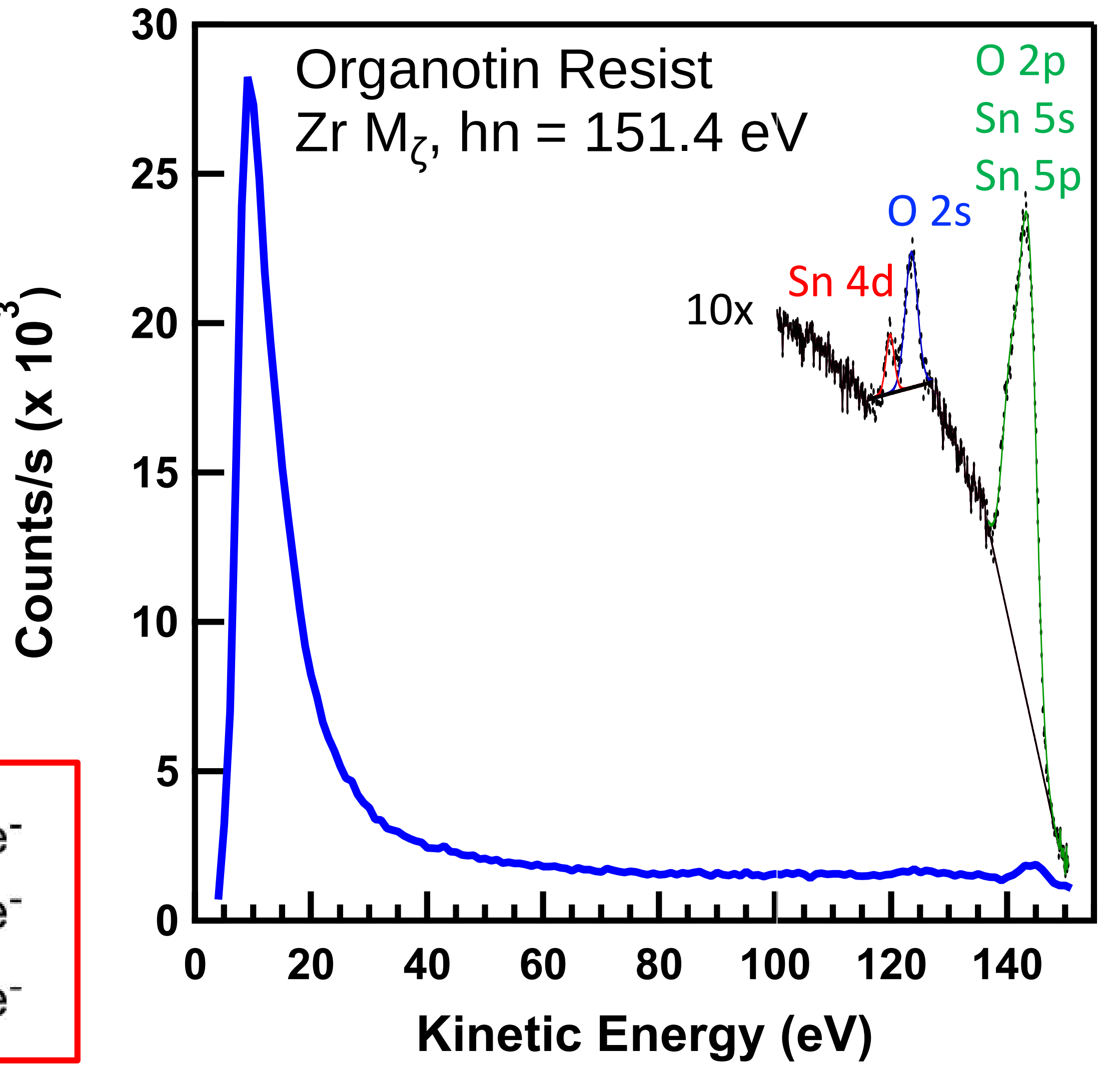
Exposure Mechanisms

DUV



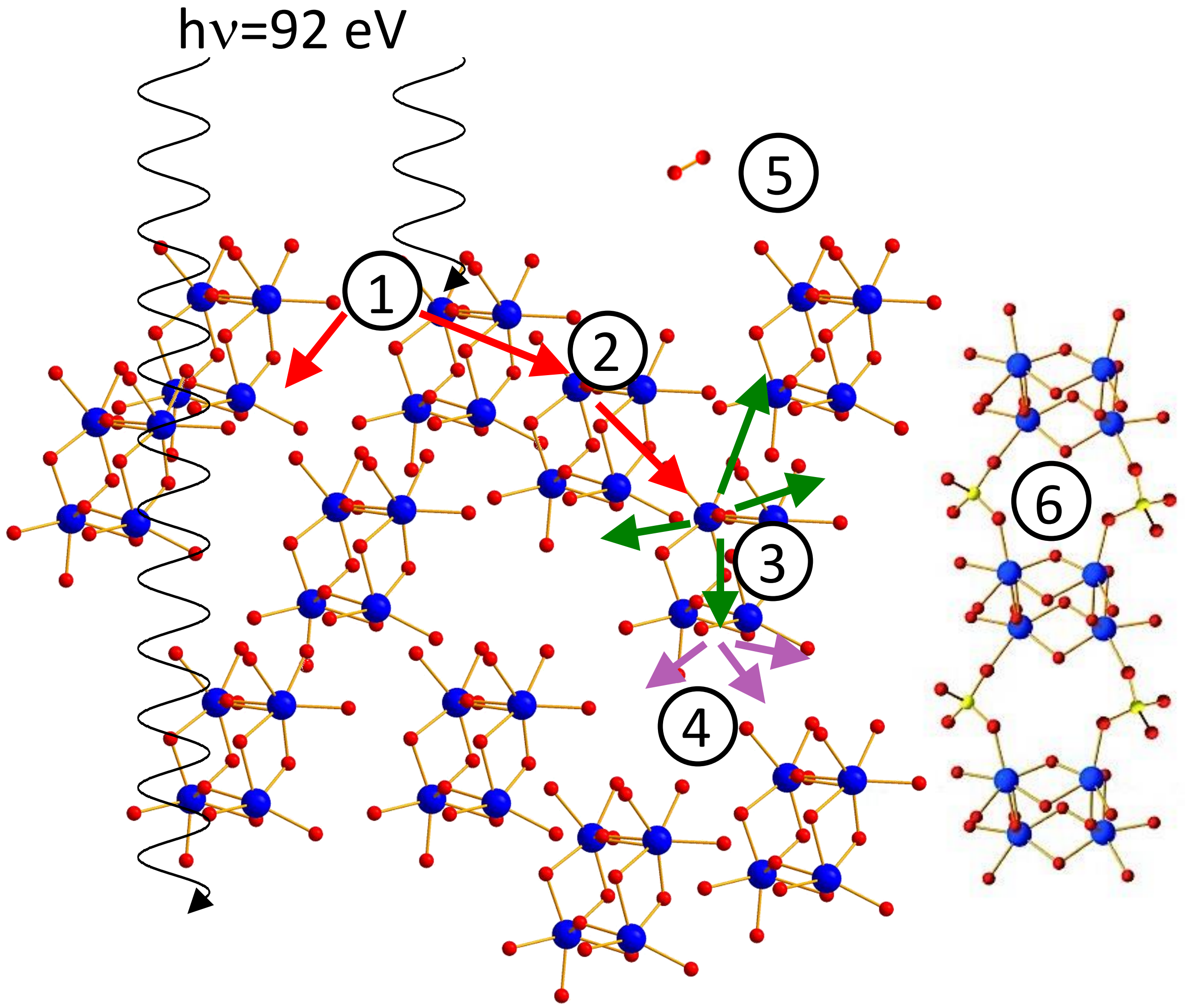
EUV





EUV Lithography, SPIE, editor V. Bakshi, Chap. 8, R. L. Brainard

Inorganic EUV Resist Model



Anisotropic

1. Photon absorption (high Sn absorption cross section)
2. Electron scattering

Isotropic

3. Secondary electrons (E_{kin} ~ 20-80 eV)
4. Thermal electrons (E_{kin} < 15 eV)
5. Desorption
6. Reactions

Expected yield > 4 e^-/photon

Organotin Photoresists (ß-$NaSn_{13}$)

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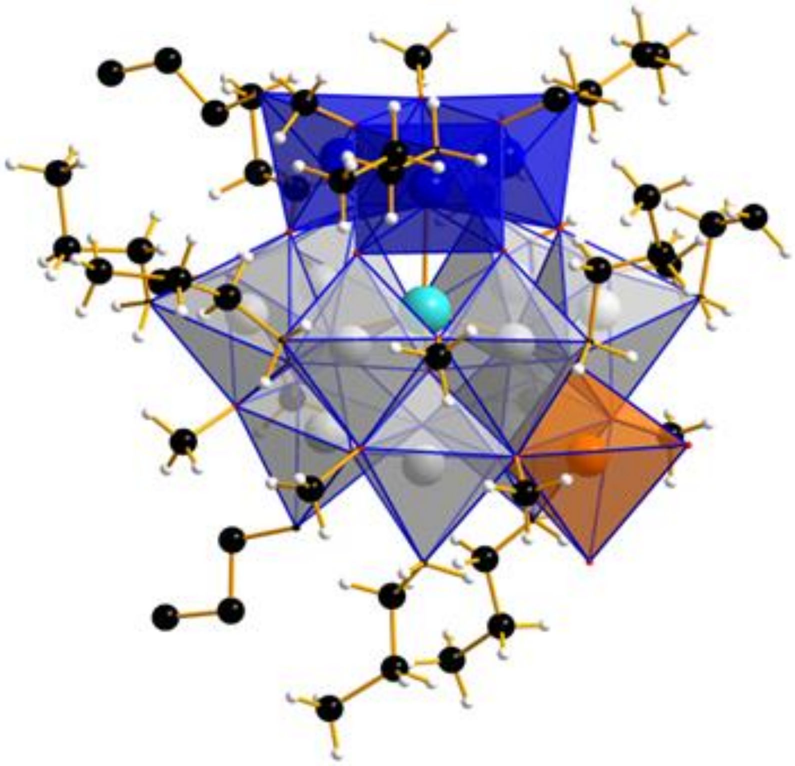
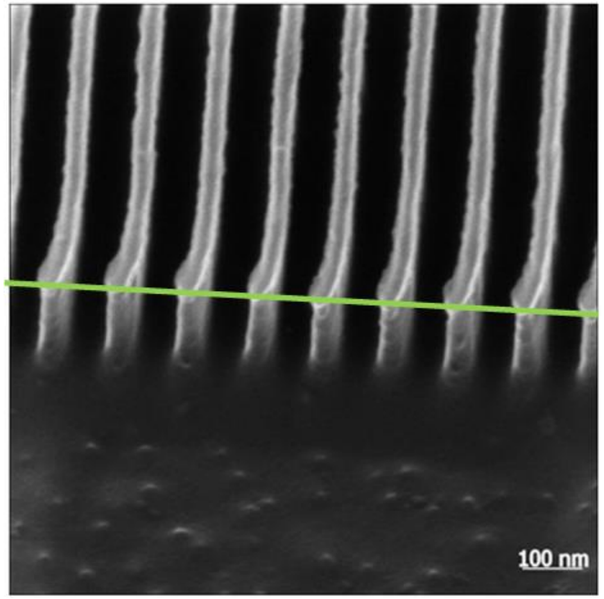


$NaO_4(BuSn)_{12}(OH)_3(O)_9(OCH_3)_{12}[Sn(H_2O)_2]$

S. Saha, et al., Angew. Chem. Int. Ed. **56**, 10140-10144 (2017)

Hypothesis:

- Tin-carbon bond weak compared to carbon-carbon bond (2.0 eV vs 3.6 eV).
- Radiation induced homolytic cleavage of tin-carbon bond and conversion from organotin to tin oxide during post-exposure bake changes film polarity and relative solubility.

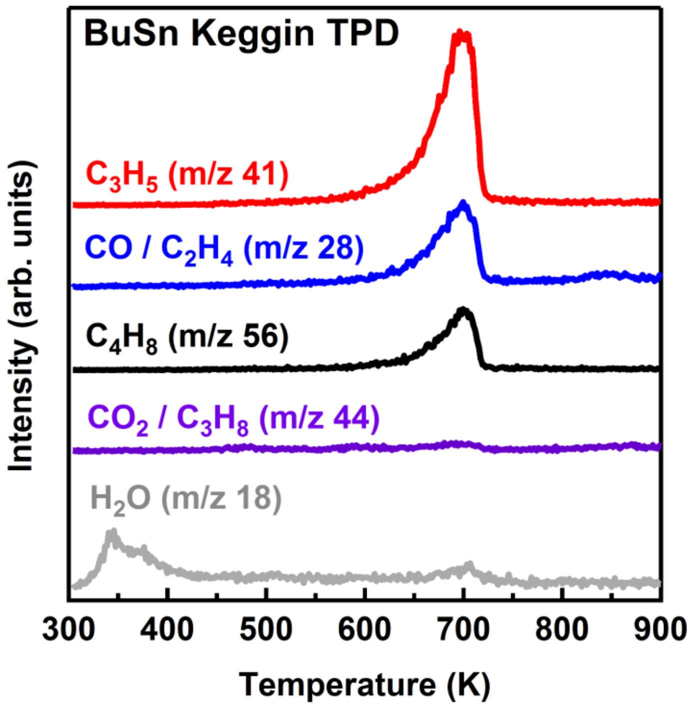


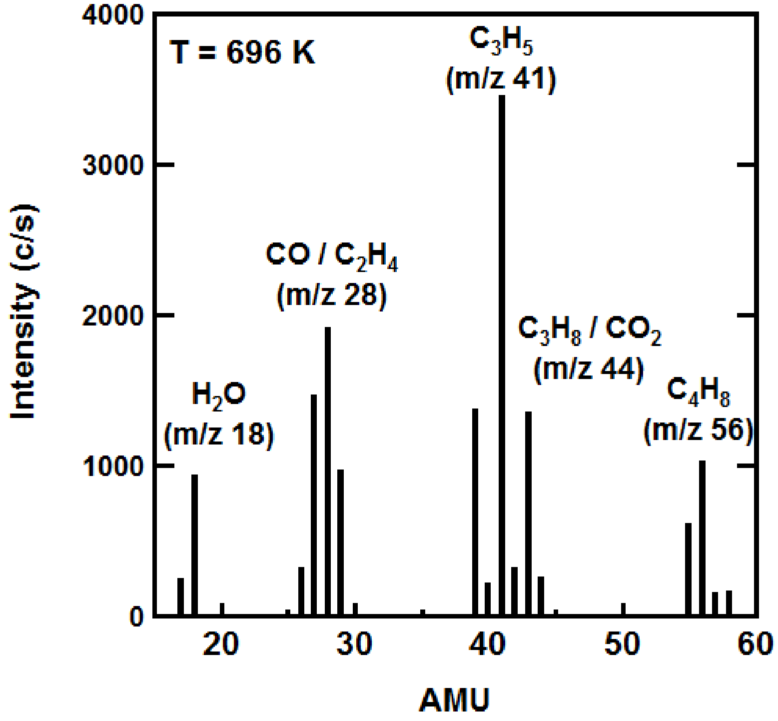
Resist above green line, silicon below

M. Li and E. Garfunkel (in preparation)

Thermal Stability Evaluated by TPD

Masses corresponding to C_3H_5, C_2H_4, C_4H_8 are due to cracking of the butyl fragment in the mass spectrometer ionizer.





- Main desorption peak at ~696 K during temperature programmed desorption (TPD)
- m/z 18 desorption occurs at ~350 K, corresponding to hydroxyl recombination and/or water desorption

R.T. Frederick, et al., ACS Appl. Mat. Int. **11**, 4514-4522 (2019)

Radiation Chemistry Evaluated by ESD

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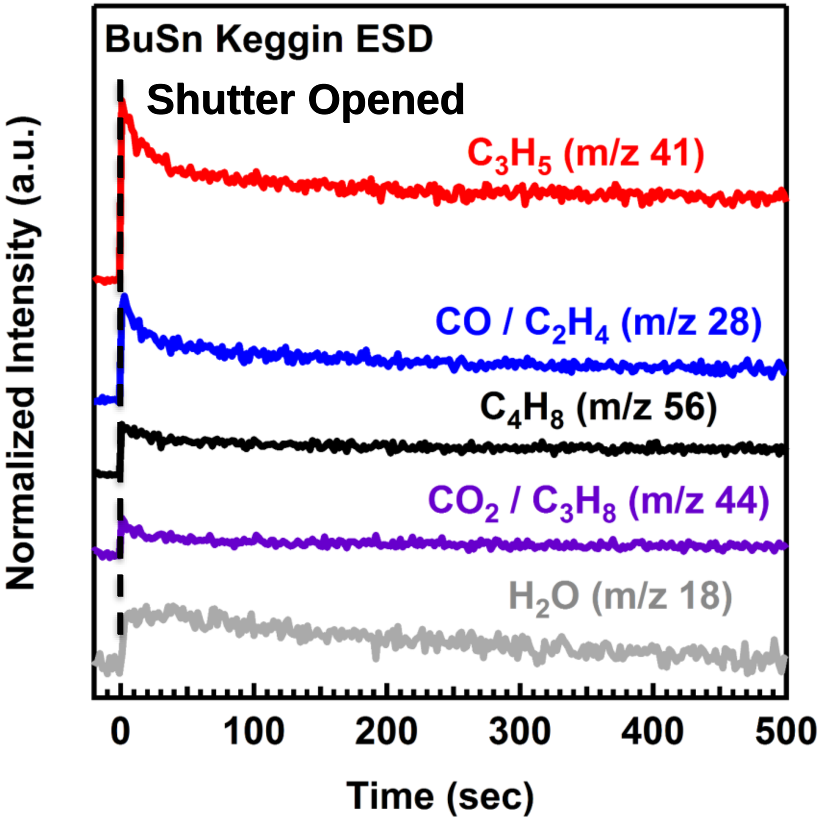

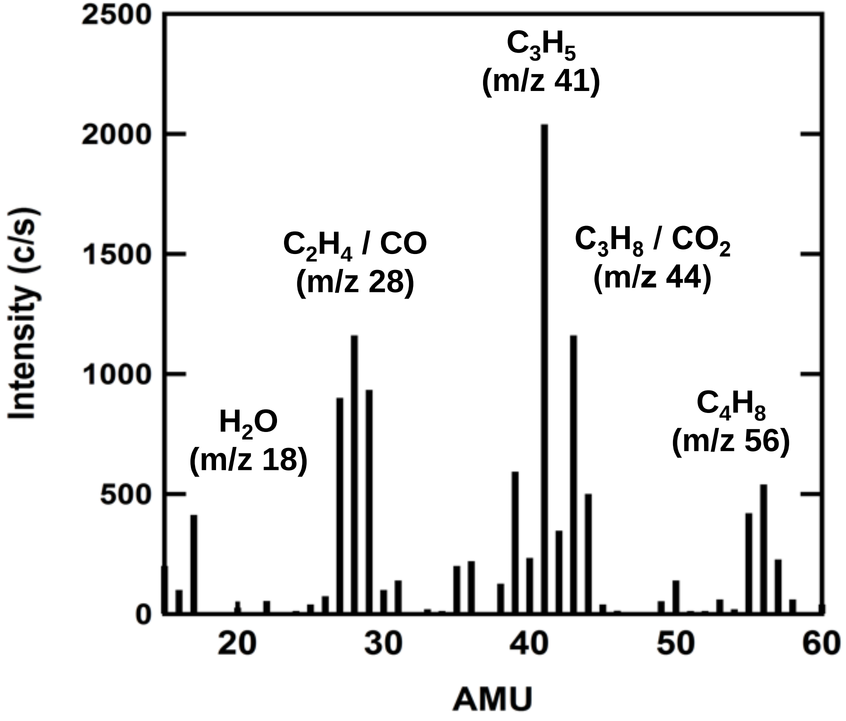

- Low energy electron beam (E_{kin} = 80 eV) used for electron stimulated desorption (ESD)
- Desorption occurs immediately when shutter is open

R.T. Frederick, et al., ACS Appl. Mat. Int. **11**, 4514-4522 (2019)

ESD Cross Section Analysis

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Desorption Cross Sections (Q):
Calculate from Log Intensity of m/z 41 vs. time plot.

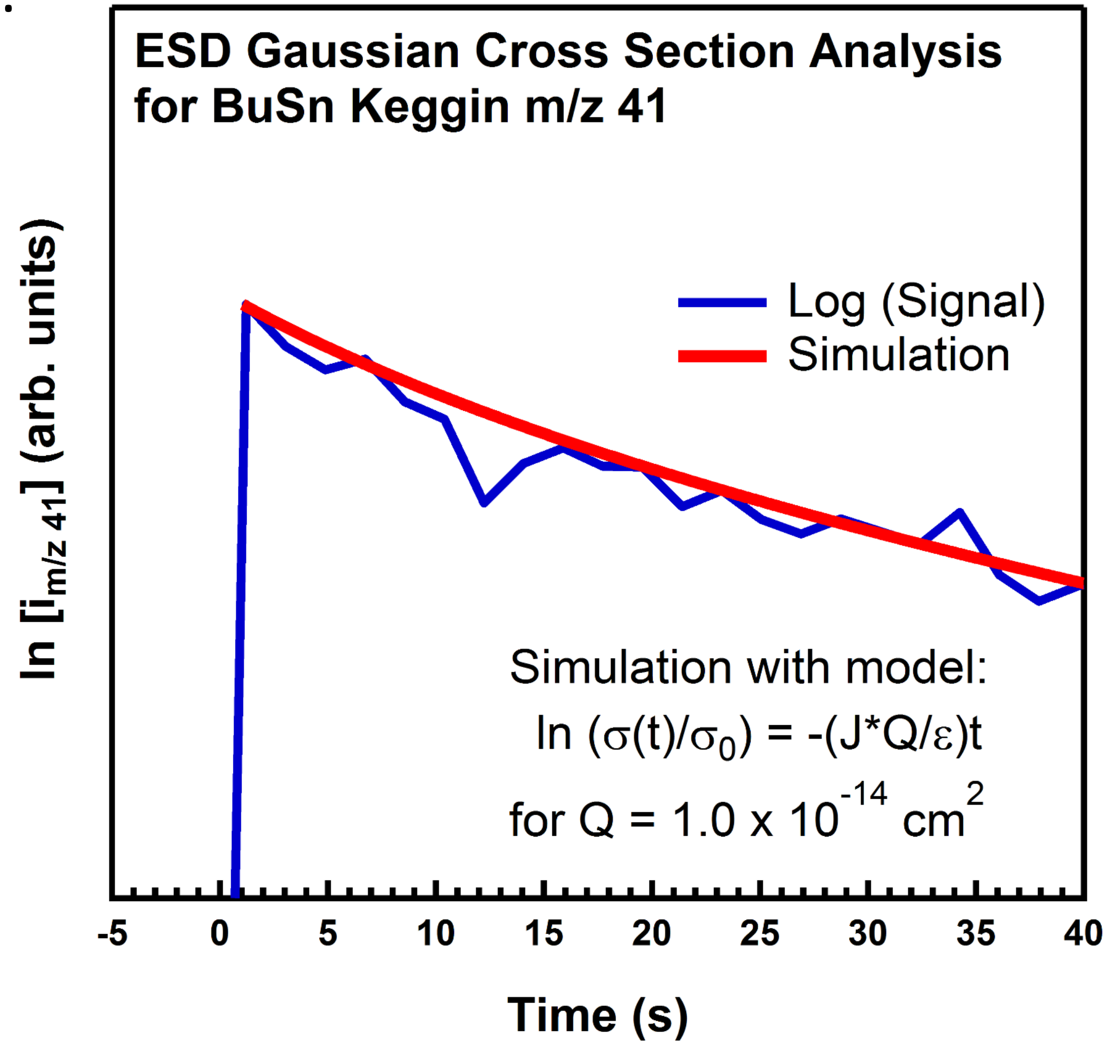
$$\ln\left(\frac{i}{i_0}\right) = -\left(\frac{JQ}{\epsilon}\right)t$$

J = electron radiation primary current density

σ = surface coverage

t = time

ε = electron charge



Effect of Ambient Gases

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- Desire to increase sensitivity of resists to meet EUV dose goals.
- Recent advances for EUV steppers include a dynamic gas lock (DGL) membrane located between the projection optics and the wafer stage.
- Instead of changing resist composition, try changing ambient conditions.
- Reaction of O_2 with electrons during exposure may result in reactive oxygen radicals.

Effect of Ambient Oxygen

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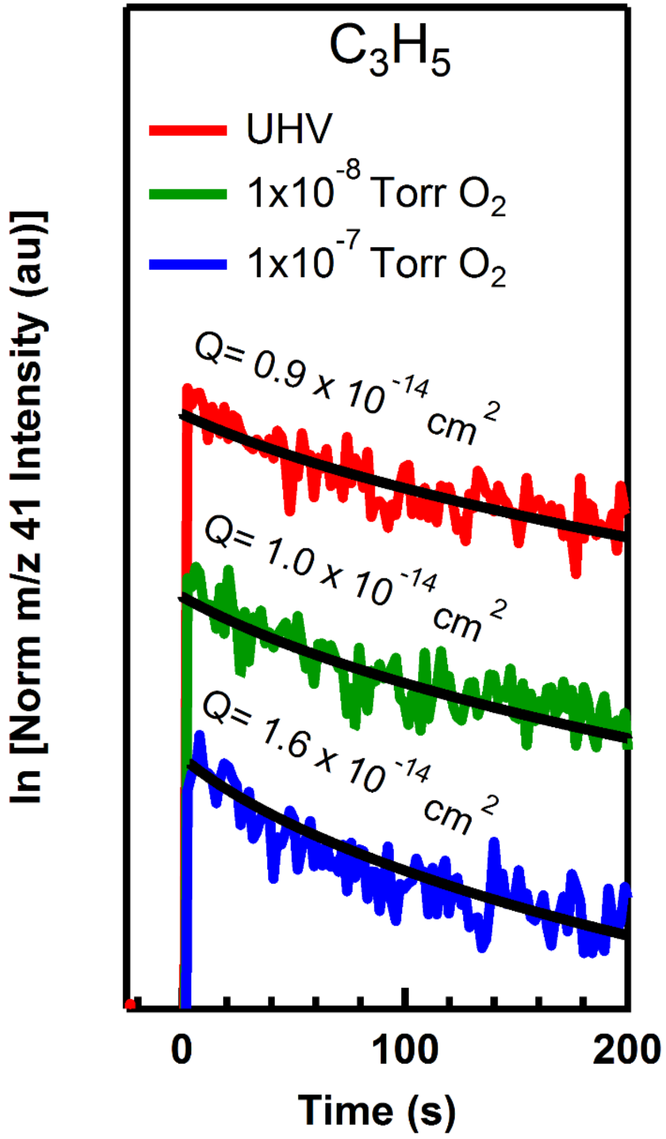
Pressure (Torr)	Average Cross Section (cm^2) $x10^{-14}$	
	C_3H_5 m/z 41	C_4H_8 m/z 56
UHV	0.9	0.9
$1x10^{-8}$ O_2	1.0	1.1
$1x10^{-7}$ O_2	1.6	1.6

- Oxygen ambient influences radiation chemistries, even for low impingement rates ($3.6x10^{13}$ O_2/cm^2s) compared to $8.9x10^{16}$ Sn atoms/cm^2 for 20 nm thick film.



R.T. Frederick, et al., ACS Appl. Mat. Int. **11**, 4514-4522 (2019)

AP-XPS SSRL Beamline 13-2

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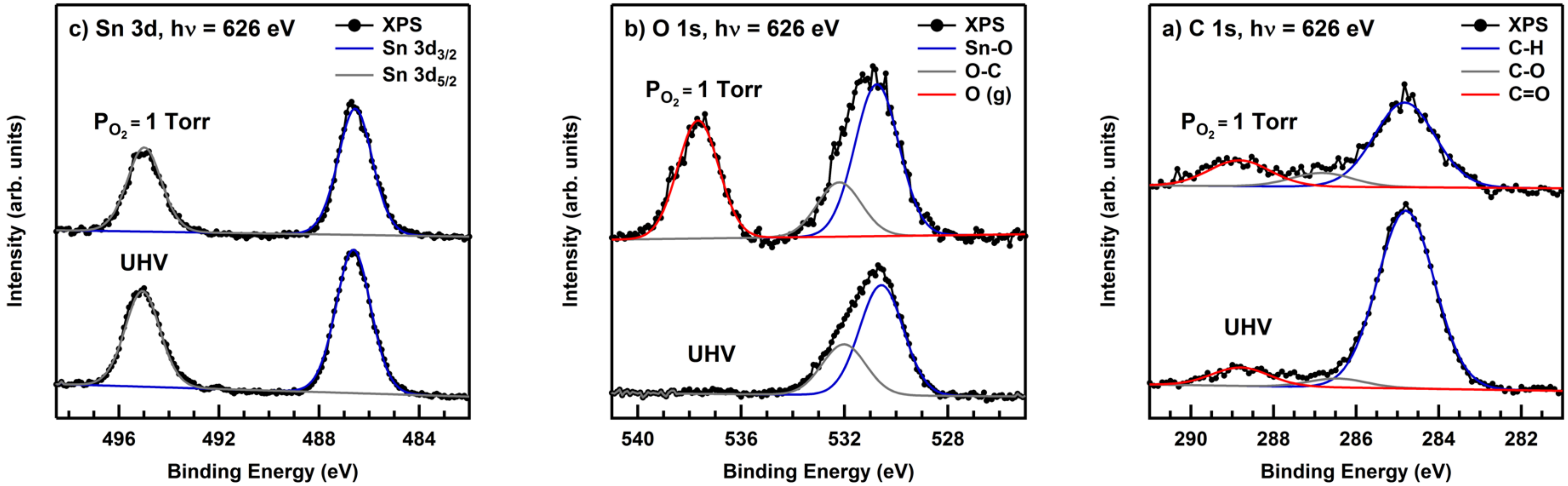
β-$NaSn_{13}$



No significant changes in spectra other than peak from O_2 gas and reduction in C 1s intensity.

J.T. Diulus, et al., ACS Appl. Mat. Int. **11**, 2526-2534 (2019)

Tracking C 1s & O 1s Intensities

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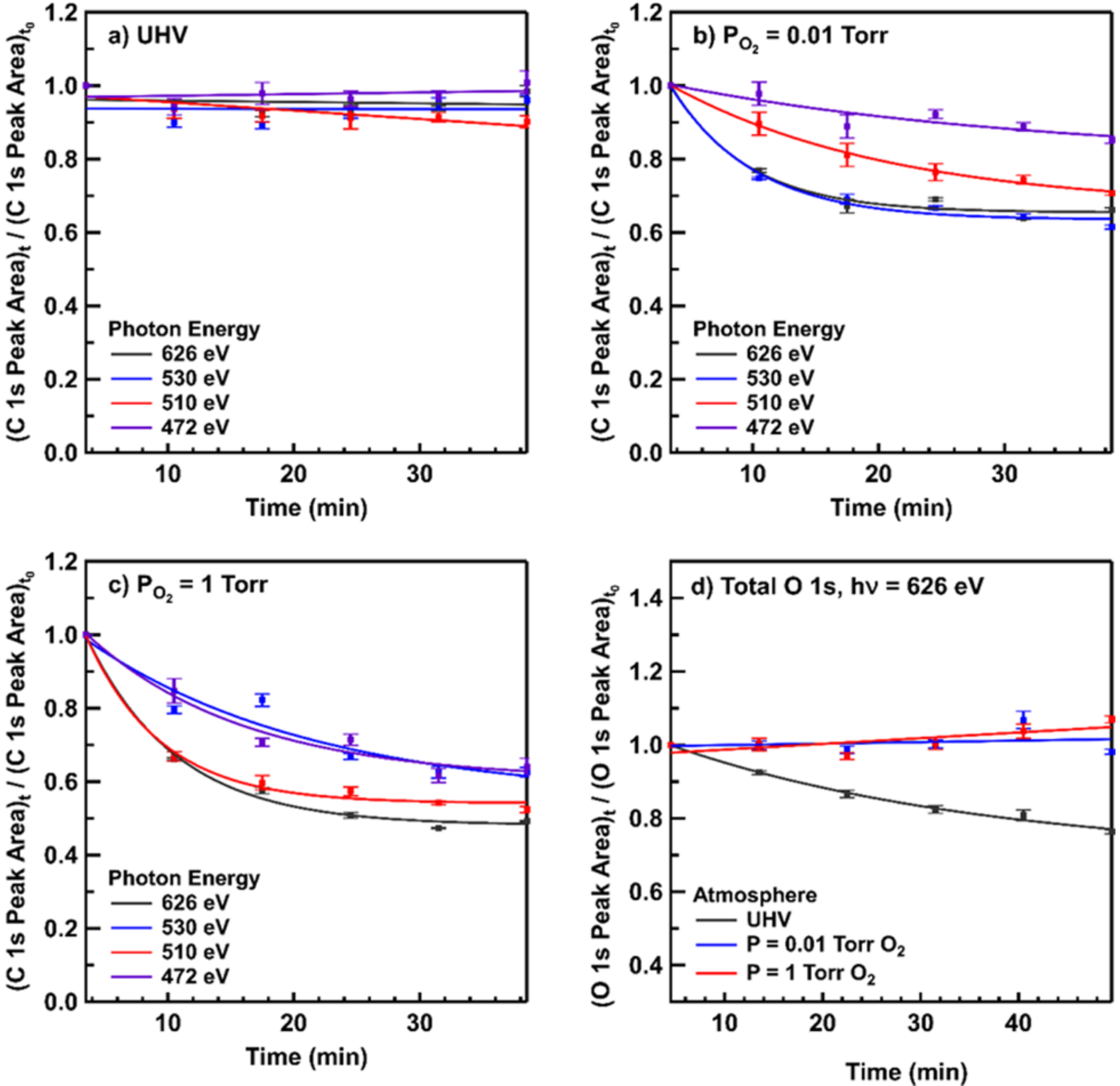
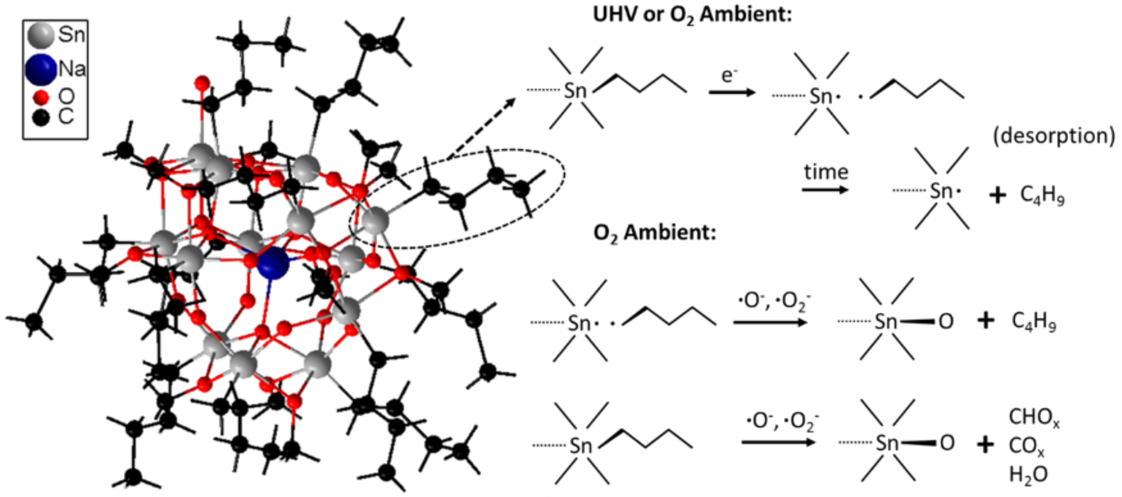


$$I(t) = I_0 exp[-\sigma\varphi t] + I_\infty$$

σ ranges from 8 x 10^{-18} to 4 x 10^{-17} cm^2



J.T. Diulus, et al., ACS Appl. Mat. Int. **11**, 2526-2534 (2019)

OSU Ambient-Pressure XPS/STM

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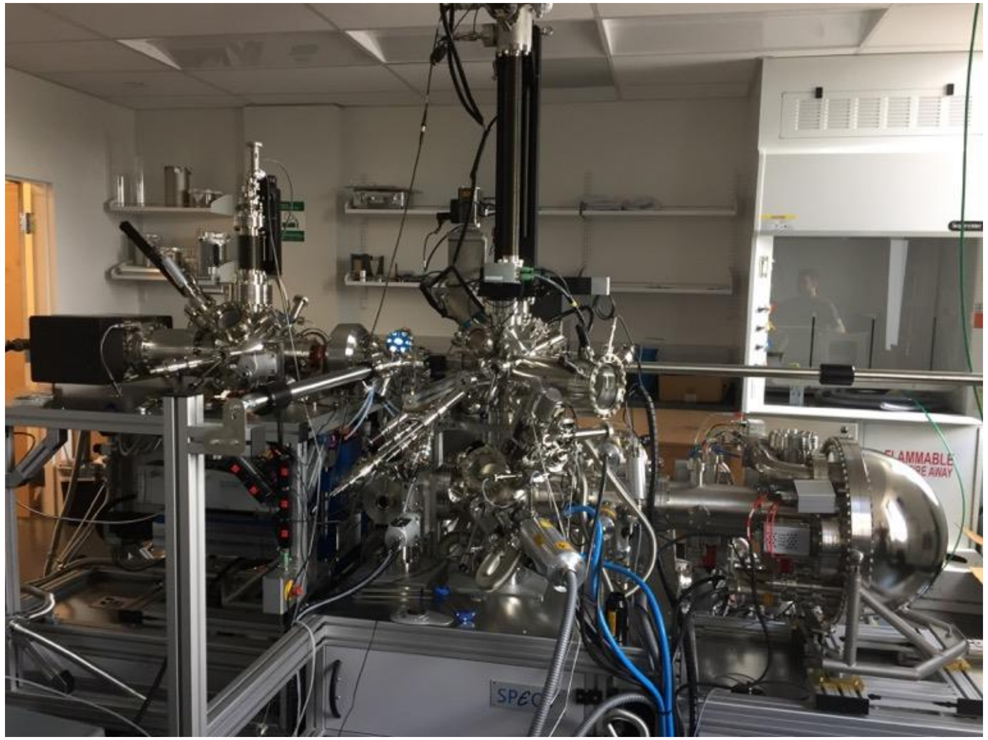
- AP-XPS
  - Pressure: < 25 torr O_2, H_2, N_2, H_2O
  - Temperature: 200 to 873 K (25 torr) and 120 to 1073 K (UHV)
  - Photon energies: $h\nu$ = 21.2, 40.8, 151.4, 1486.4, 2984.3 eV
- AP-STM
  - Pressure: < 100 torr O_2, H_2, N_2, H_2O
  - Temperature: 298 to 523 K (10 torr) and 220 to 773 K (UHV)
- Preparation Chamber
  - LEED, Auger, EELS
  - 4-pocket e-beam evaporator



Access available to external users through NNCI.

National Nanotechnology Coordinated Infrastructure

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Contrast Curves using Al Kα Radiation

β-$NaSn_{13}$

Thickness measured with ellipsometer.

UHV

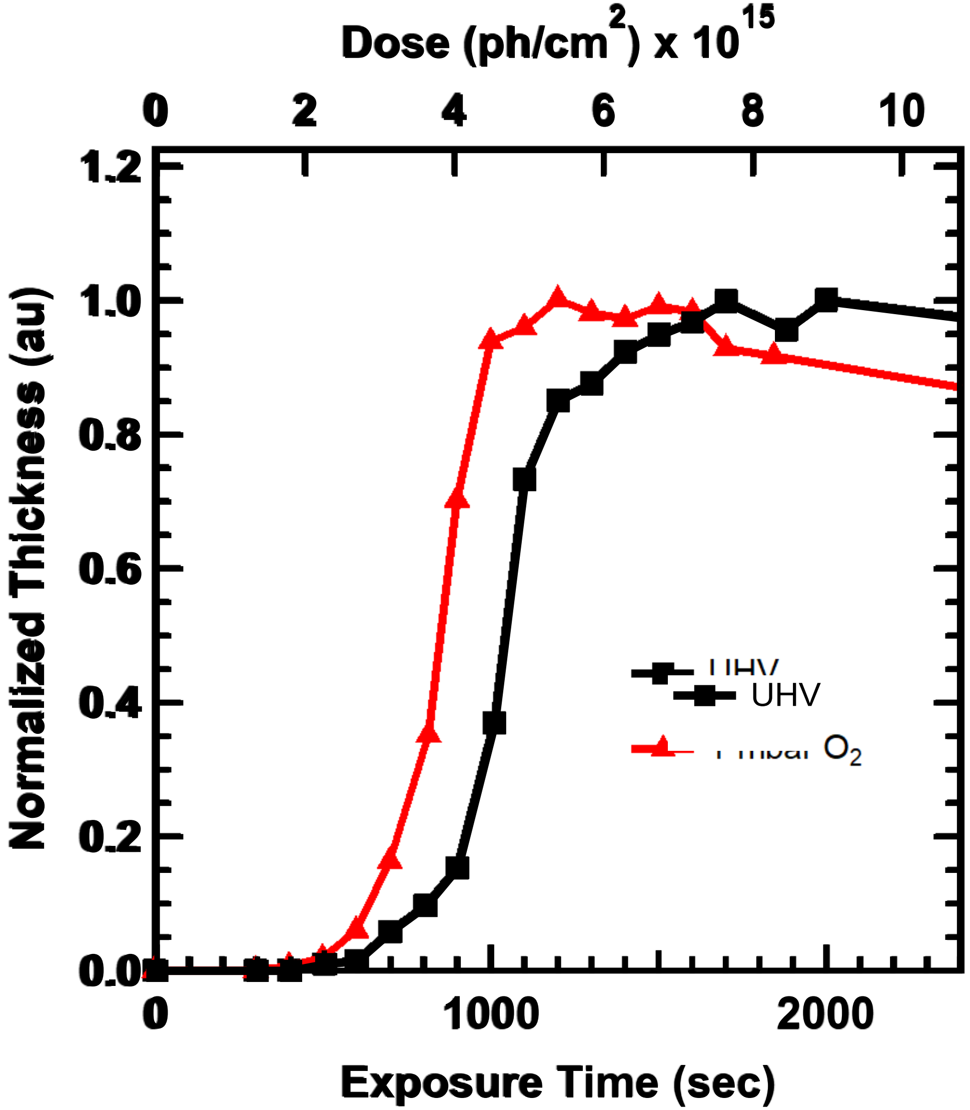
300 s

600 s

900 s

1200 s

1500 s



Contrast Curves Different Ambients

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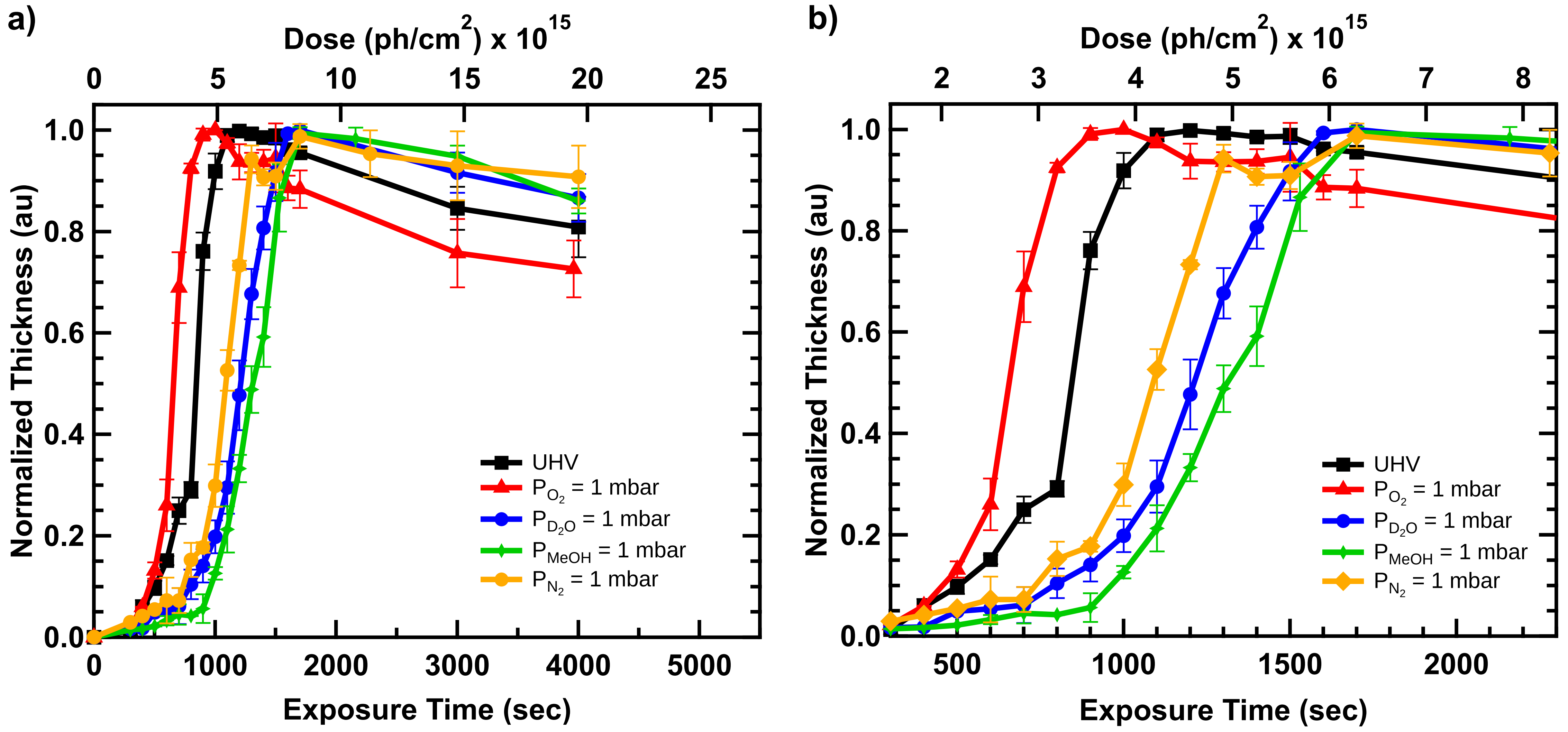
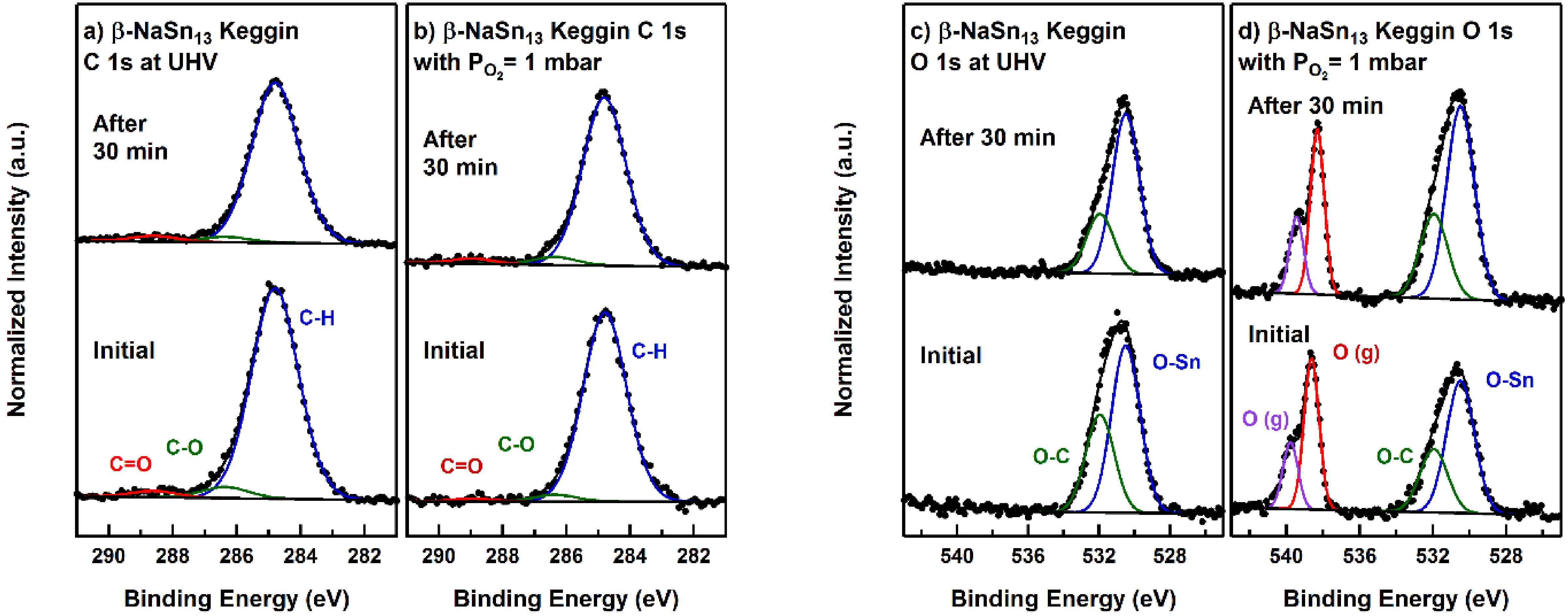
β-$NaSn_{13}$



AP-XPS Using Al Kα Radiation



R.T. Frederick, et al., Proc. SPIE 10586, Advances in Patterning Materials and Processes XXXV, 1058607 (2018)

Composition Before/After Exposure

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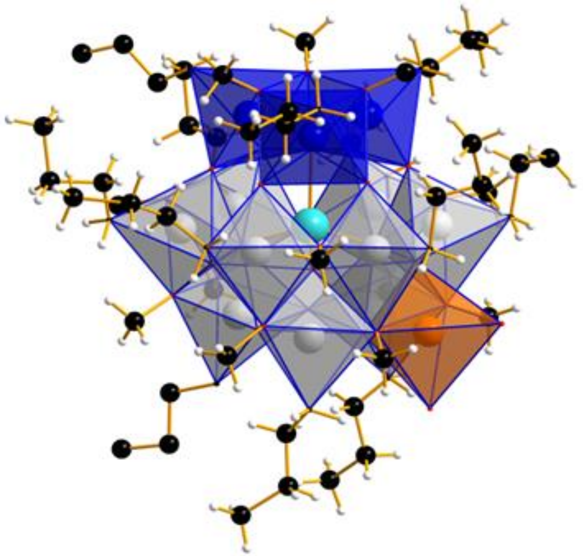
β-$NaSn_{13}$



Expected atomic concentrations: 13% Sn, 58% C, and 29% O

	Element	Initial Atomic %	After 30 min Atomic %
Exposure in UHV	Sn	14 %	18 %
	C (Total)	59 %	55 %
	C-H	54 %	52 %
	C-O	3.0 %	1.8 %
	C=O	1.6 %	1.9 %
	O (Total)	27 %	29 %
	O-Sn	17 %	19 %
	O-C	10 %	7.2 %
Exposure in Po_2 = 1 mbar	Sn	16 %	17 %
	C (Total)	57 %	49%
	C-H	55 %	45 %
	C-O	1.2 %	2.2 %
	C=O	1.3 %	1.5 %
	O (Total)	26 %	35 %
	O-Sn	18 %	24 %
	O-C	8.5 %	11 %

R.T. Frederick, et al., Proc. SPIE 10586, Advances in Patterning Materials and Processes XXXV, 1058607 (2018)

Composition Before/After Anneal

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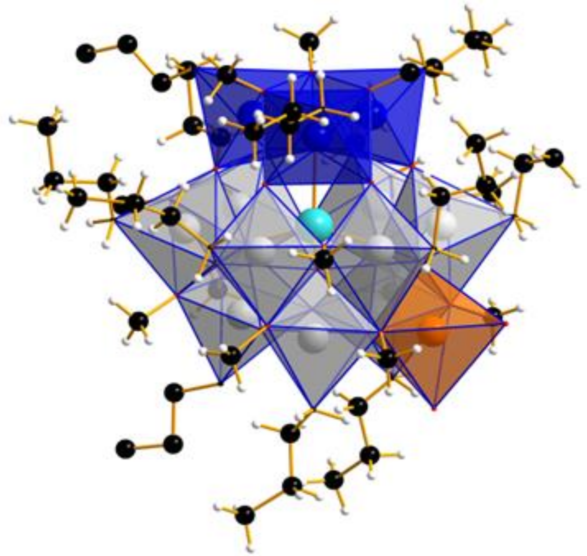
β-$NaSn_{13}$



Expected atomic concentrations:
13% Sn, 58% C, and 29% O

		Initial	After 170 °C anneal, no exposure	After 30 min exposure, 170 °C anneal
	Element	Atomic %	Atomic %	Atomic %
Annealed in UHV	Sn	14 %	17 %	18 %
	C (Total)	61 %	59 %	57 %
	C-H	57 %	56 %	53 %
	C-O	2.6 %	1.5 %	2.2 %
	C=O	1.3 %	1.0 %	1.5 %
	O (Total)	25 %	24 %	25 %
	O-Sn	17 %	18 %	20 %
	O-C	8.4 %	6.4 %	5.3 %
Annealed in P_{O_2} = 1 mbar	Sn	15 %	16 %	18 %
	C (Total)	60 %	61%	57 %
	C-H	56 %	58 %	53 %
	C-O	2.5 %	1.8 %	2.2 %
	C=O	1.3 %	0.7 %	1.2 %
	O (Total)	26 %	23 %	26 %
	O-Sn	17 %	18 %	19 %
	O-C	8.7 %	5.1 %	6.1 %

R.T. Frederick, et al., Proc. SPIE 10586, Advances in Patterning Materials and Processes XXXV, 1058607 (2018)

β-$NaSn_{13}$ EUV Resist Chemistries

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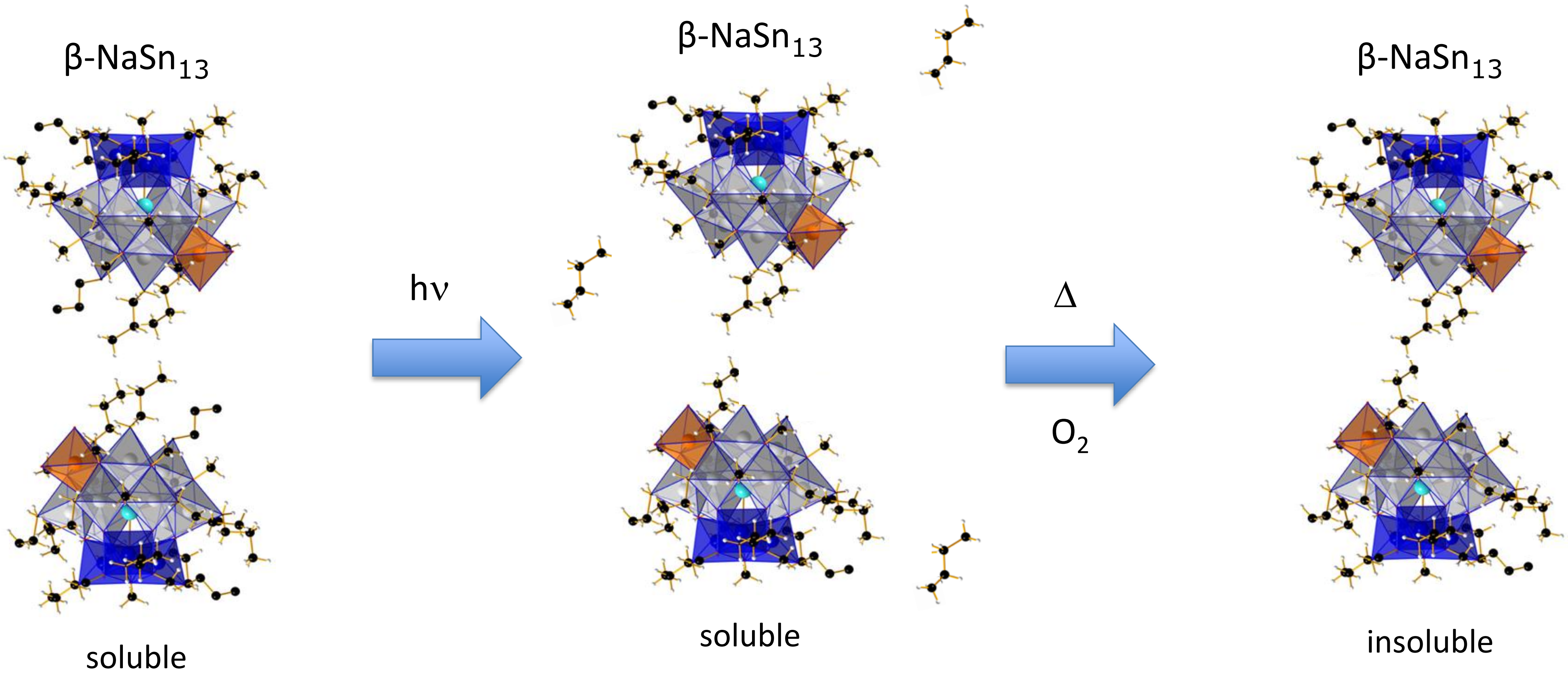

polymerization through radical hydrogen abstraction and radical – radical coupling reactions

Conclusions

- Low kinetic energy electrons (E_{kin} = 80 eV) are effective for simulating EUV radiation chemistries.

- Temperatures above 400 °C are required to desorb butyl groups, suggesting good thermal stability during EUV exposures and bake steps.

- Presence of oxygen increases cross sections and rate of BuSn homolytic cleavage of Sn-C bond.

- Contrast curves and AP-XPS results suggest that radical hydrogen abstraction and radical - radical coupling reactions result in polymerization of organotin species.

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