A NUMERIC MODEL FOR THE IMAGING MECHANISM OF METAL OXIDE EUV RESISTS

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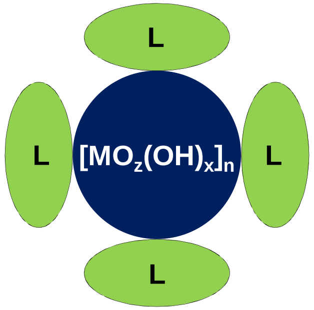
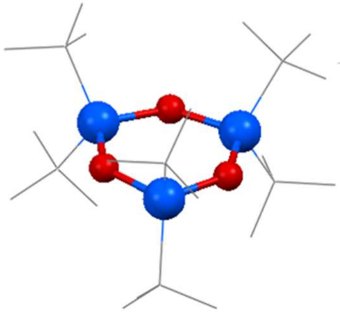
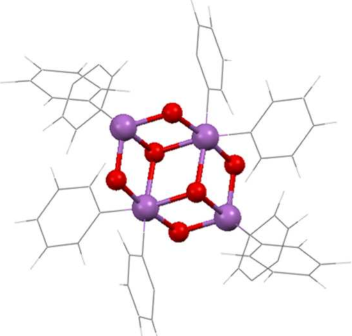
Metal Oxide (MOx) Cluster Resist Examples

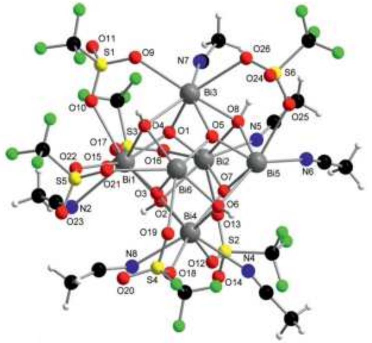




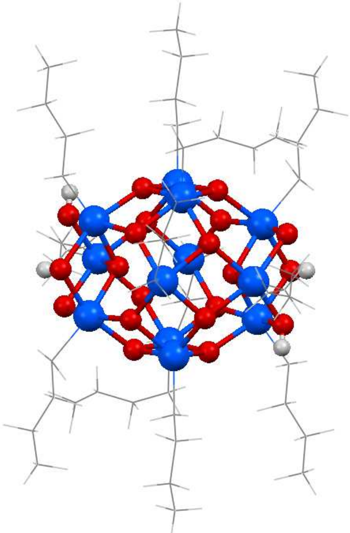
$[R_2SnO]_3$



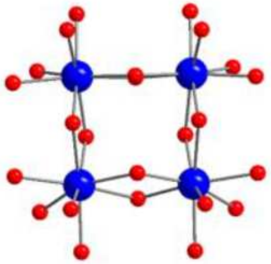
$[(R_2Sb)_2O_3]_2$



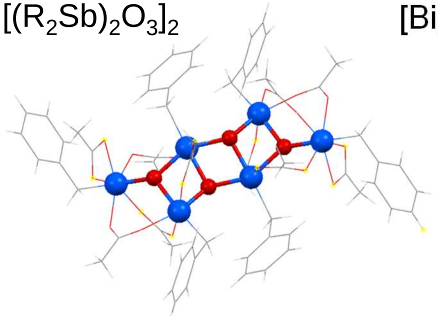
$[Bi_6O_4(OH)_4(OTf)_6(CH_3CN)_6]$



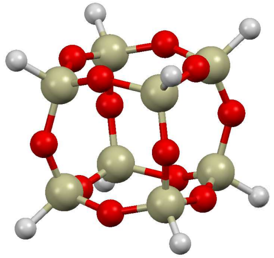
$[(RSn)_{12}O_{14}(OH)_6]^{+2}$



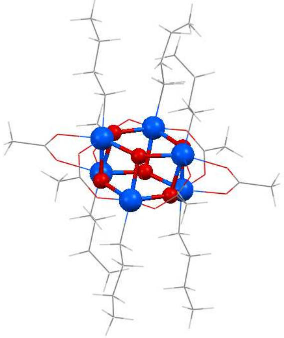
$[Hf_4(O_2)(OH)_7(SO_4)_3]^+$



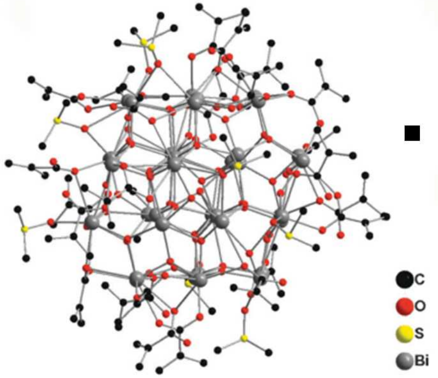
$[\{RSn(O)OOCR'\}_2\{RSn(OOCR')_3\}]_2$



$[H_8Si_8O_{12}]$

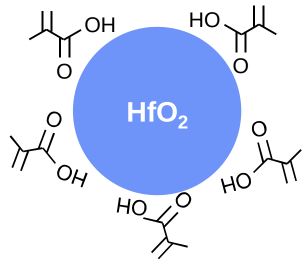


$[RSn(O)OOCR']_6$



$[Bi_{38}O_{45}(OMc)_{24}(DMSO)_9]$

■ ■ ■

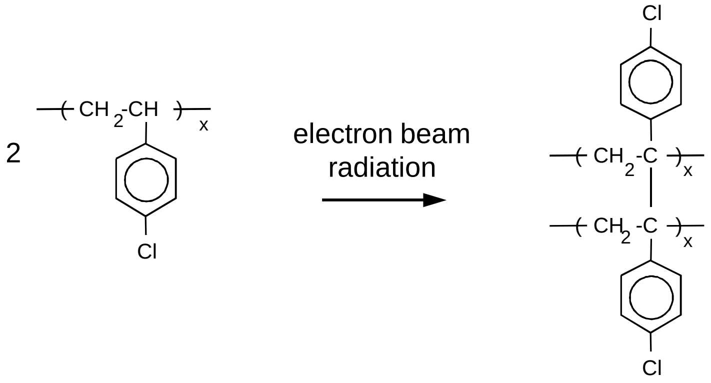


MO_2 Ligand-Stabilized nanoparticle

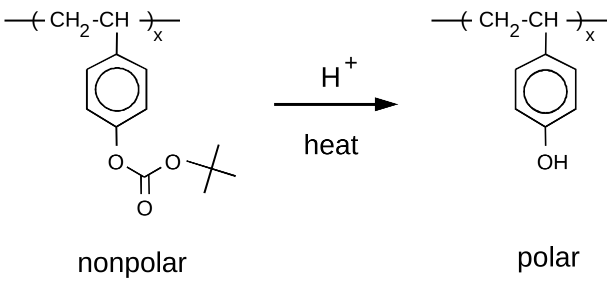
inpria

Negative Tone Resist Chemistries in Organic Polymers

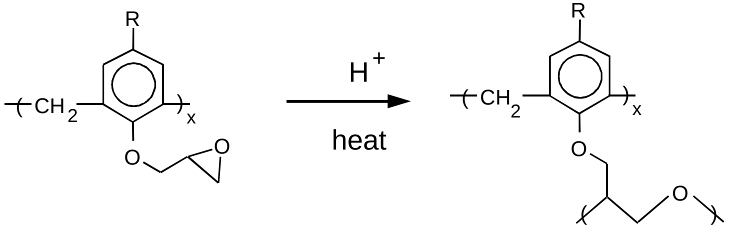
Direct crosslinking of polymer [poly(4-Cl-styrene)]



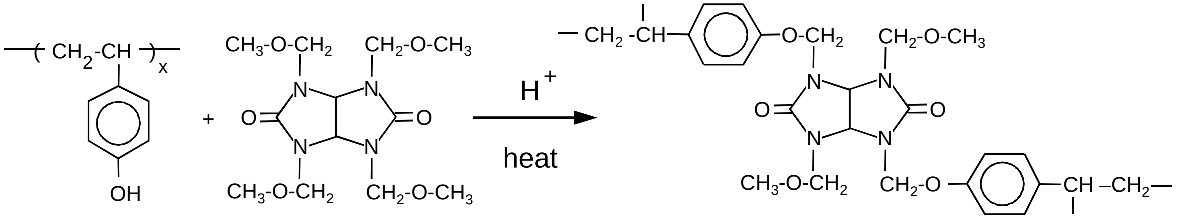
Polarity change [*t*-BOC, NTD resists]



Chain polymerization [Riston, SU-8]



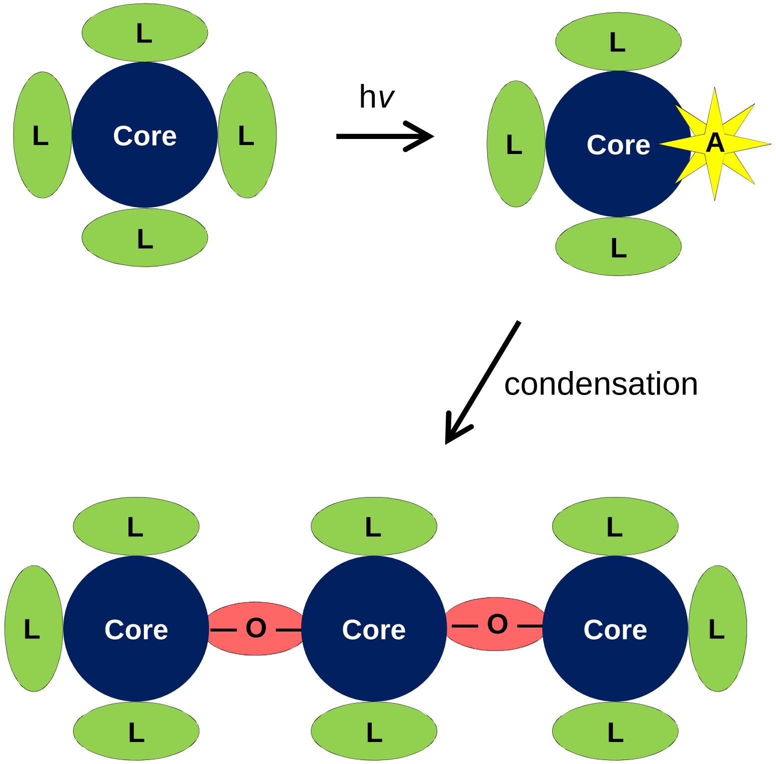
Crosslinking by multifunctional additive [CGR, bis-azide]



None of these describe the primary imaging mechanism in MOx resists

A Generic Imaging Model for MOx Resist Systems

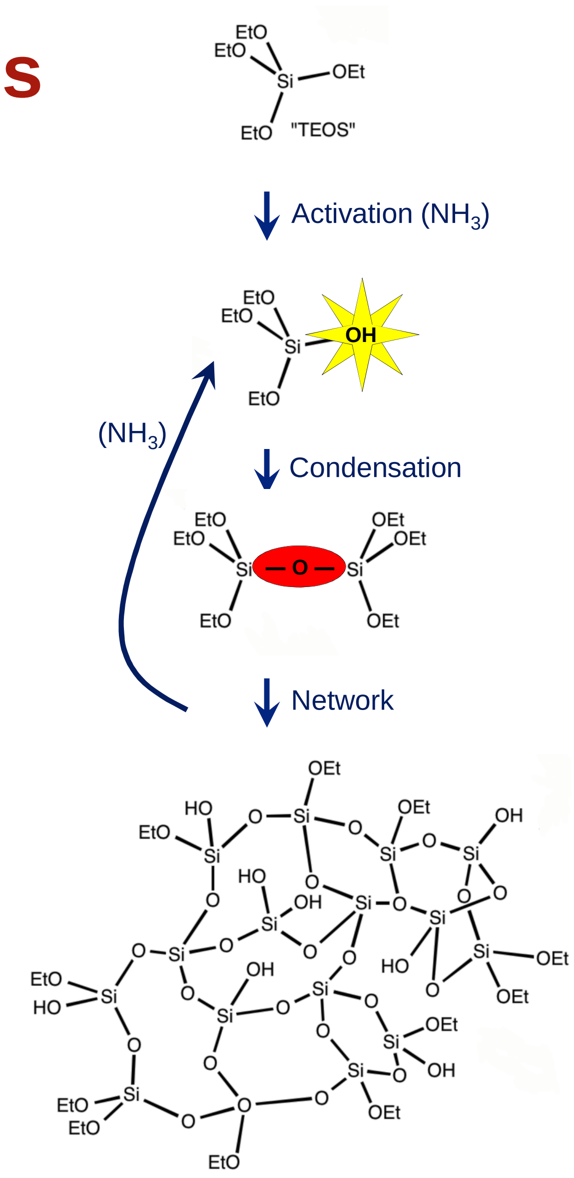
- Basic approach :
  - Minimalist description of chemistry and physics
  - Follow progression of radiation and condensation chemistry
- Resist building block notation
  - Core molecule / framework / cluster / nanoparticle
  - Multiple **radiation-sensitive ligands L** per core
  - Condensation of **active site A** formed upon ligand radiolysis leads to **Oxo-Network** formation

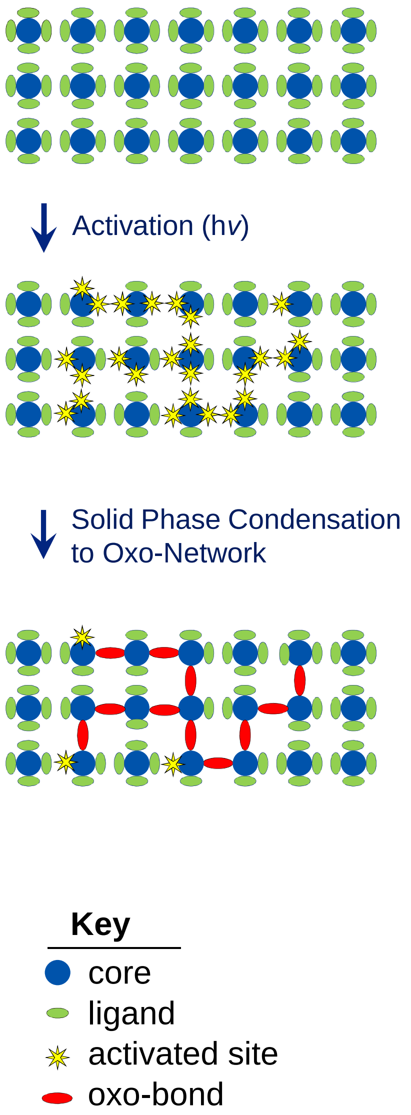


Analogue of Sol-Gel Process

- **Characteristics of sol-gel chemistry:**
  - Site activation by catalyst
  - Simultaneous condensation and further activation
  - Complex mixture of intermediate species
  - Polymerization proceeds toward oxo-network formation

- **MOx imaging model:**
  - Site activation by radiation chemistry
  - Solid phase condensation of neighboring cores
  - Complex mixture of intermediate species
  - Polymerization proceeds toward oxo-network formation





Overview of Modeling Process

A Molecular-Scale Description

- 3D array of individual molecules
- Track individual events
- Statistical effects accounted for

Model Inputs:

- Molecular volume
- Number of radiation-sensitive ligands per core
- EUV absorption coefficient
- "Quantum yield":
  - Definition: ***number of ligands fragmented per photon absorbed***
  - In model, use the number of electrons generated per photon as a proxy
- "Radiochemical blur length":
  - Definition: ***distance scale over which chemical change may occur from point of photon absorption***
  - In model, use "electron blur" length as a proxy
- Film thickness
- Exposure dose

1. Calculate EUV light absorption

↓ 3D spatial distribution of photon absorption

2. Calculate secondary electron generation

↓ 3D spatial distribution of generated electrons

3. Calculate photoproduct distribution

↓ 3D spatial distributions of each photoproduct

4. Calculate condensation reactions

↓ 3D spatial distribution of oxo-bonds formed

5. Analyze condensation product

↓ 3D topology of oxo-network

6. Imaging properties

Step 1 - EUV Absorption

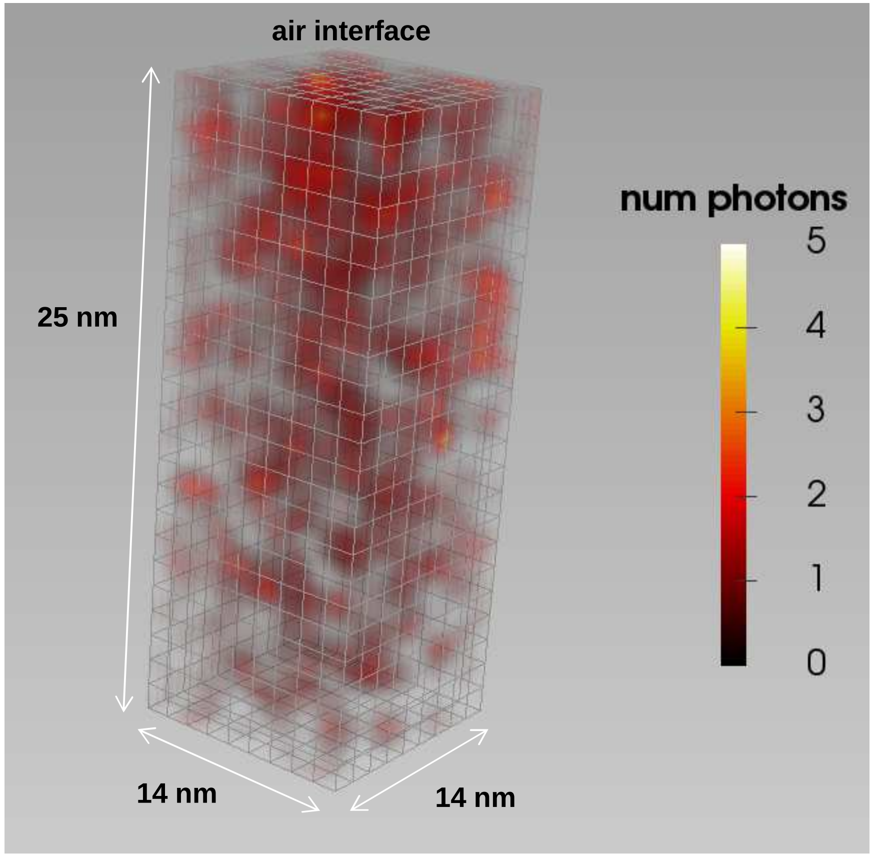
Example

- molecular volume 2.3 nm^3
- 15 mJ/cm^2 flood exposure
- 1928 impinging photons, 662 absorbed

A stochastic implementation of Beer’s Law

Protocol:

- Divide film surface into sub-areas
- Distribute impinging photons onto surface
- Distribute photons in sublayers according to probabilities



Step 2 - Secondary Electron Generation

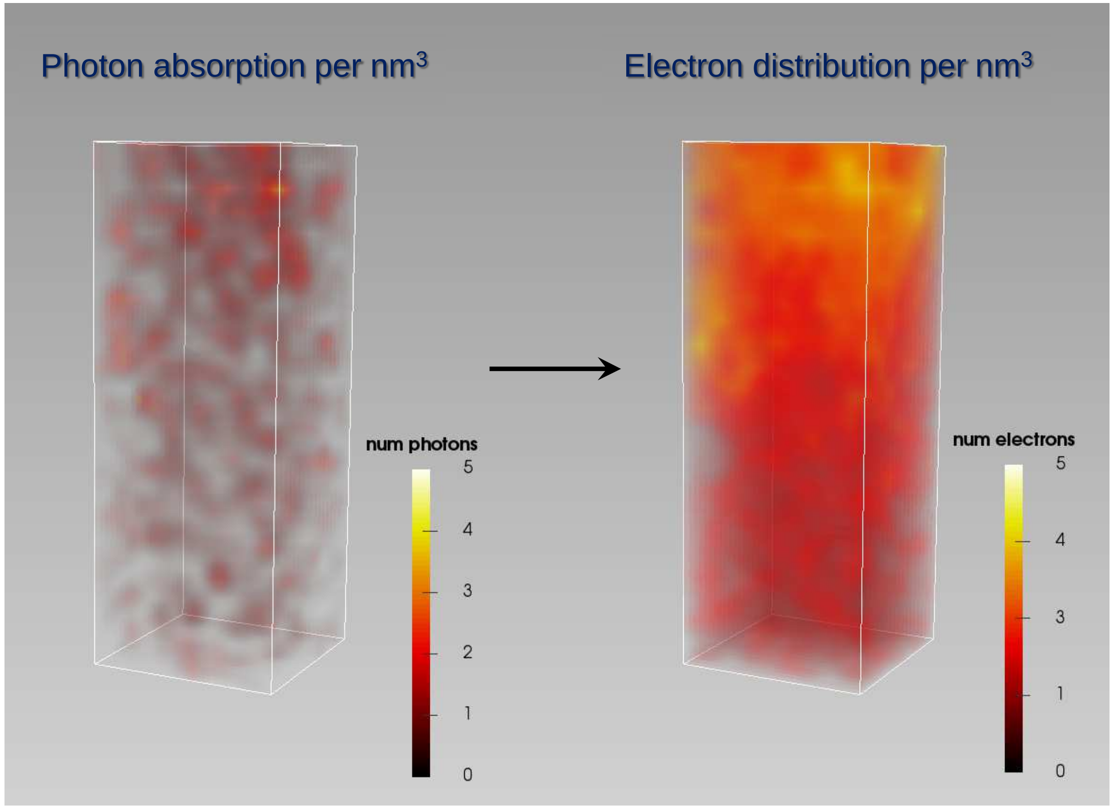
Apply experimentally derived electron yield and blur length to photon absorption distribution

Example

- molecular volume 2.3 nm^3
- 15 mJ/cm^2 flood exposure
- avg 8 electrons per photon
- 1.4 nm electron blur length

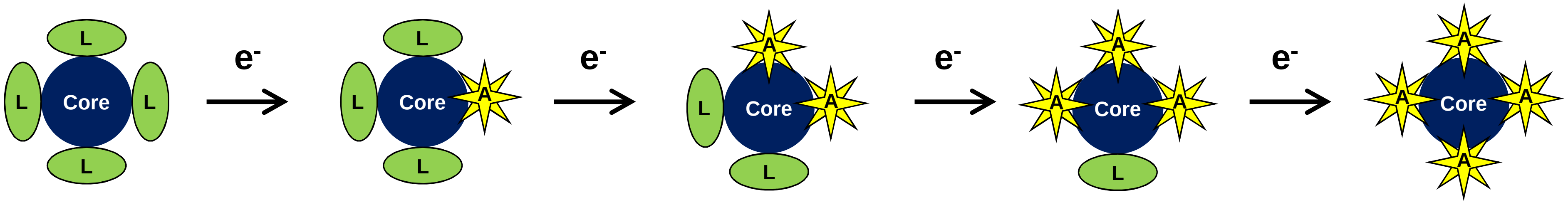
Protocol:

- Each photon generates on average ***n*** electrons
- Allow electrons to stochastically “diffuse” from point of photon absorption
- Terminate electron diffusion when average diffusion distance = blur length



Step 3 – Primary Photoproduct Distribution

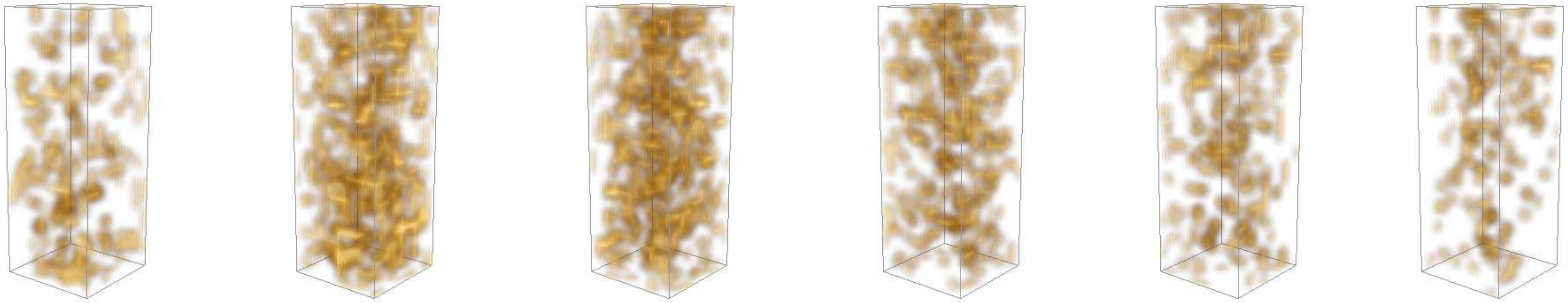
- Allow electron distribution to interact with resist material
- Assumptions:
  - Each ligand is chemically equivalent
  - Reactivity is unaffected by degree of decomposition
- A complex product mix results: e.g., for a tetra-substituted core



- Photoproduct distribution is a function of dose

An Example Photoproduct Spatial Distribution

Hypothetical MOx resist with 12 radiation-sensitive ligands per core, EUV flood exposure 15 mJ/cm^2 dose



0 active sites

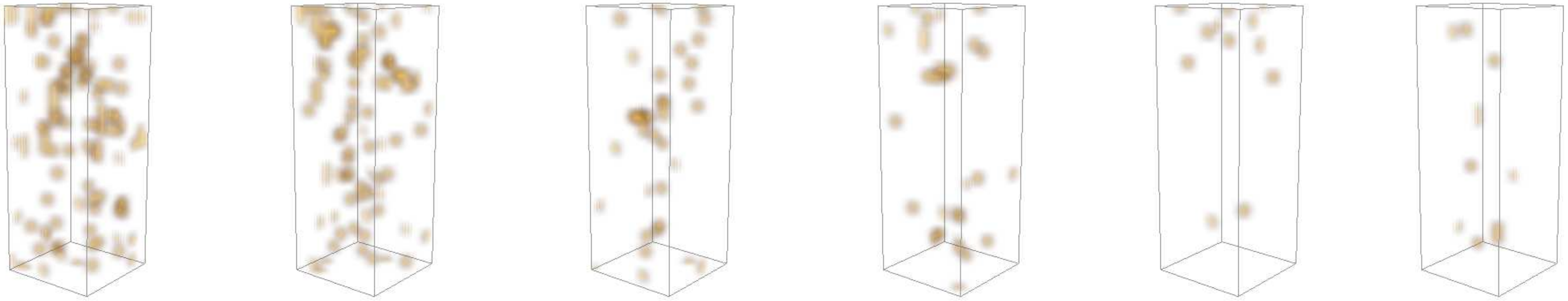
1 active site

2 active sites

3 active sites

4 active sites

5 active sites



6 active sites

7 active sites

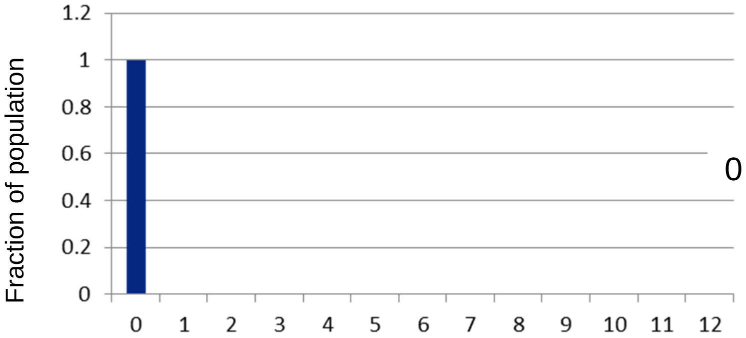
8 active sites

9 active sites

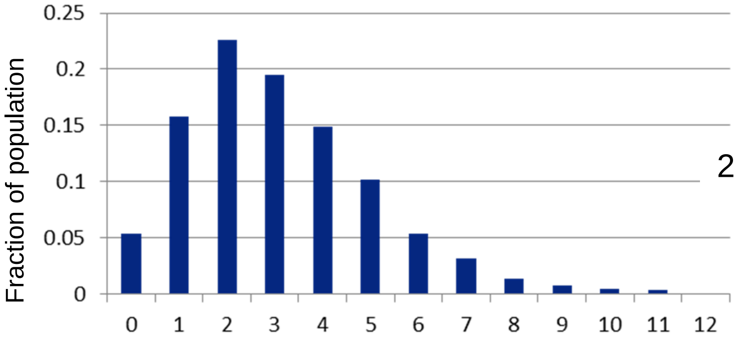
10 active sites

11 active sites

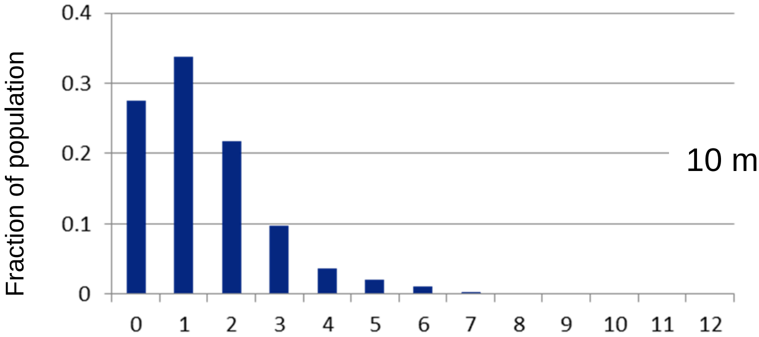
Photoproduct Distribution Depends on Dose



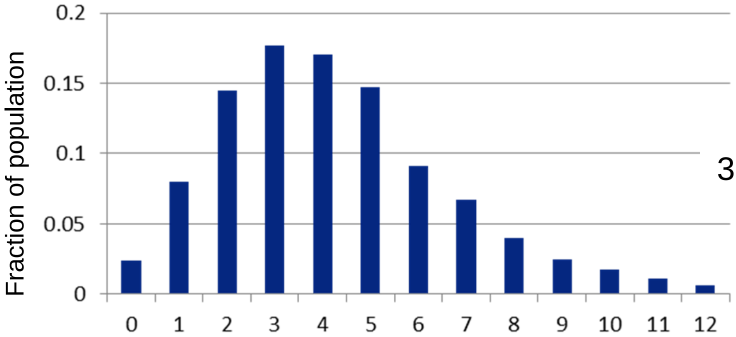
0 mJ/cm^2



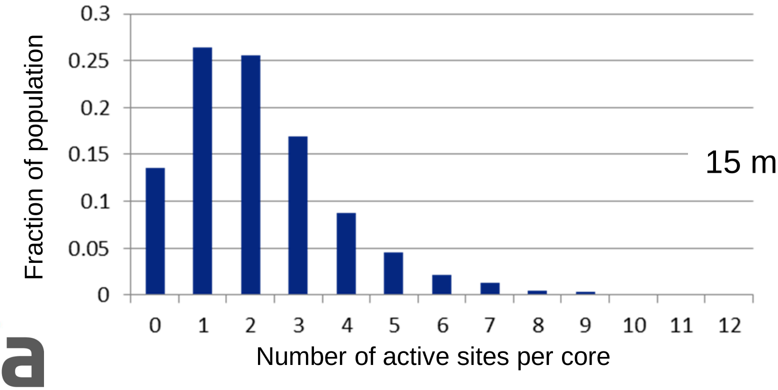
20 mJ/cm^2



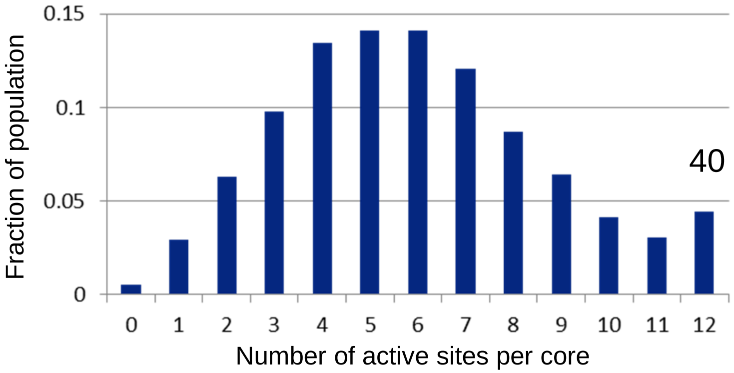
10 mJ/cm^2



30 mJ/cm^2



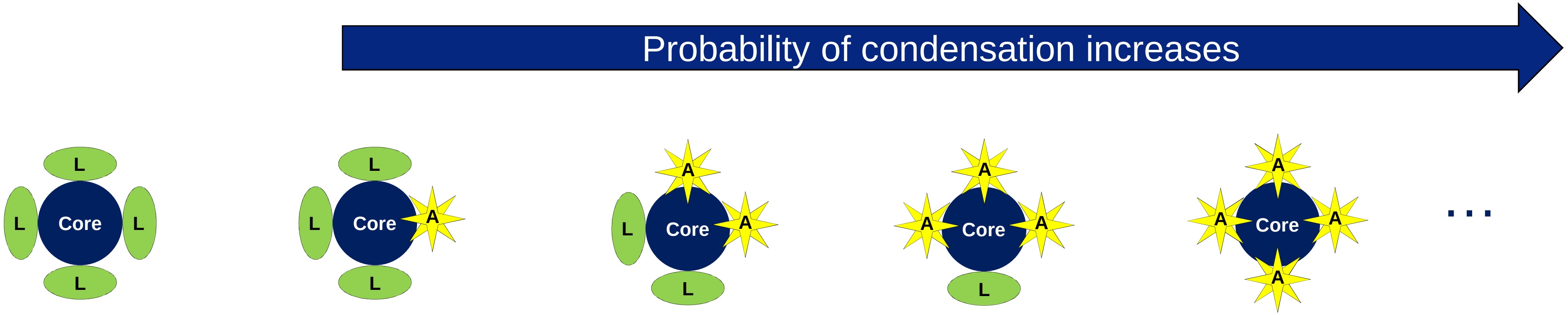
15 mJ/cm^2



40 mJ/cm^2

Impact of Photoproduct Distribution

Role of photoproduct in condensation depends on structure:


Probability of condensation increases

- Inert

- Terminates chain

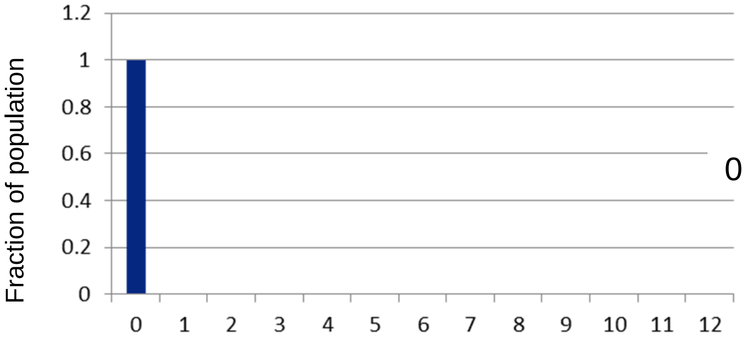
- Extends chain

- Extends chain
- Branch point

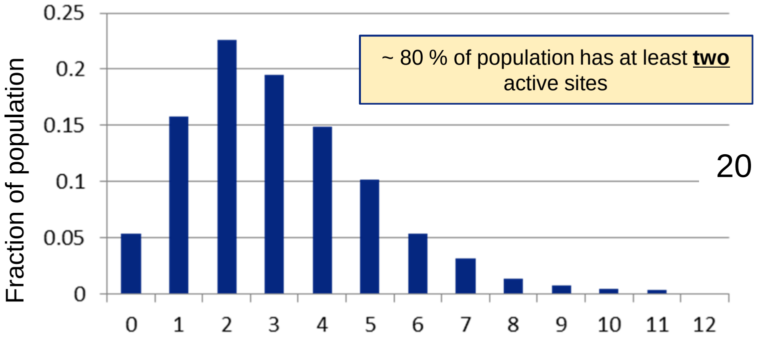
- Extends chain
- Branch point
- Crosslink point

Supports oxo-network formation

Photoproduct Distribution Depends on Dose

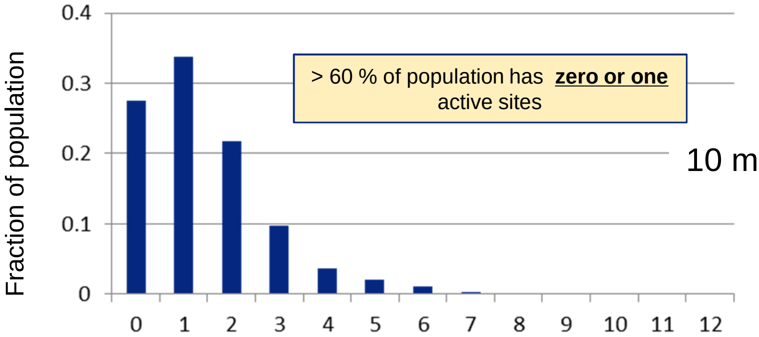


0 mJ/cm^2



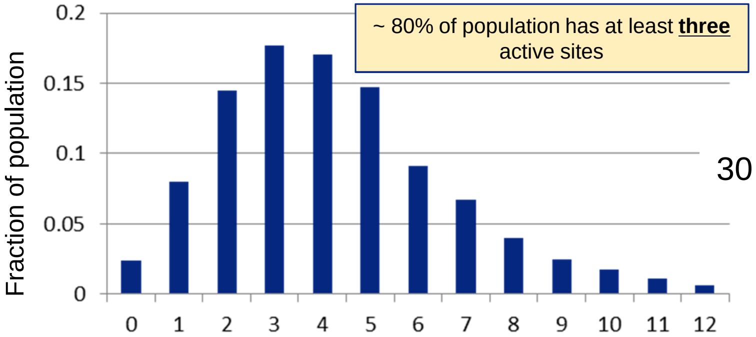
~ 80 % of population has at least **two** active sites

20 mJ/cm^2



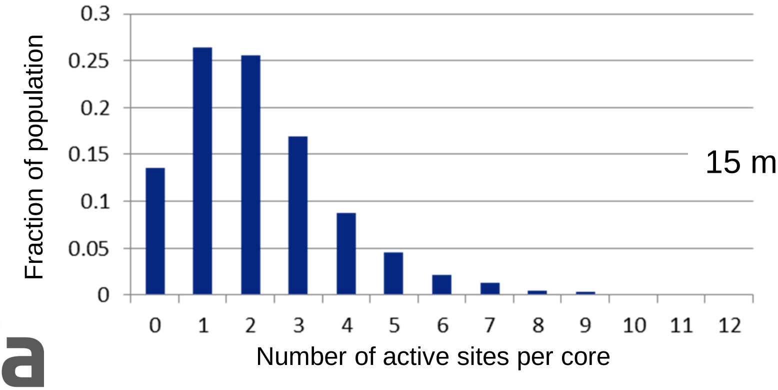
> 60 % of population has **zero or one** active sites

10 mJ/cm^2

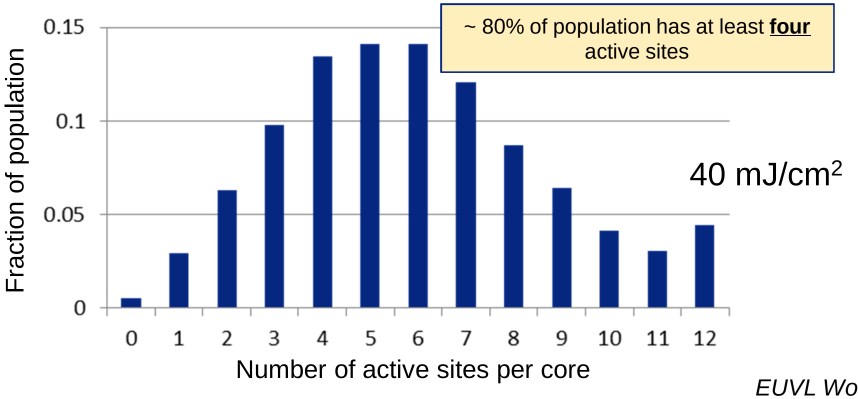


~ 80% of population has at least **three** active sites

30 mJ/cm^2



15 mJ/cm^2

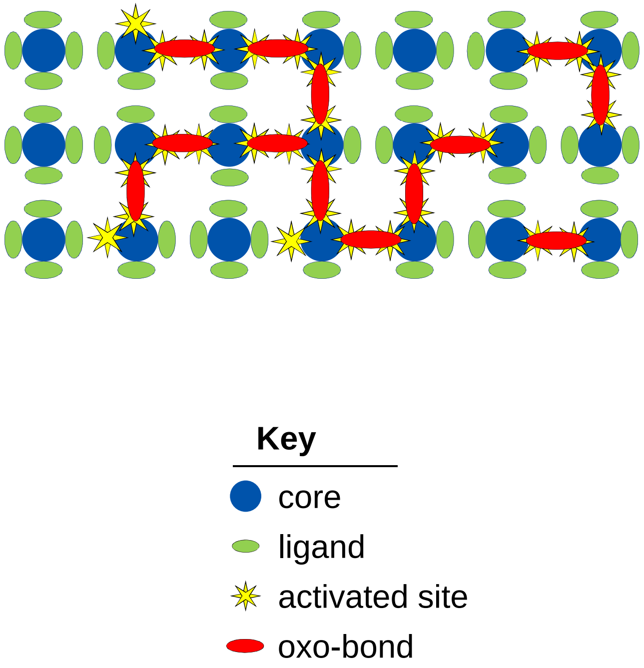


~ 80% of population has at least **four** active sites

40 mJ/cm^2

Step 4 – Condensation of Primary Photoproducts

- Calculate the evolution of oxo-networks
  - Each core starts with a set number of active sites
  - Condensation only if core and neighbor both have an active site
  - Condensation forms one oxo-bond and consumes two active sites

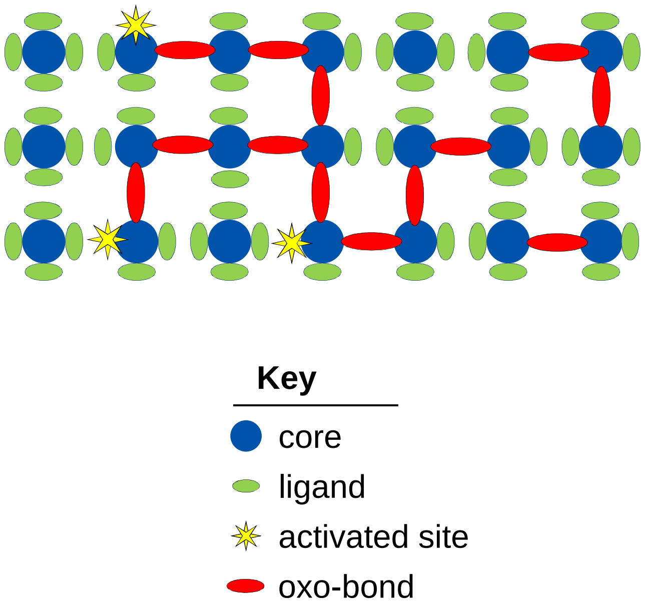


- Protocol:
  a) Initialize with photoproduct distribution
  b) Select a core
  c) Core and neighbor both have active sites?
    i. Form oxo-bond
    ii. Subtract active sites
  d) Repeat (b) and (c) until probability of reaction is zero

Result: Population of oxo-network polymers

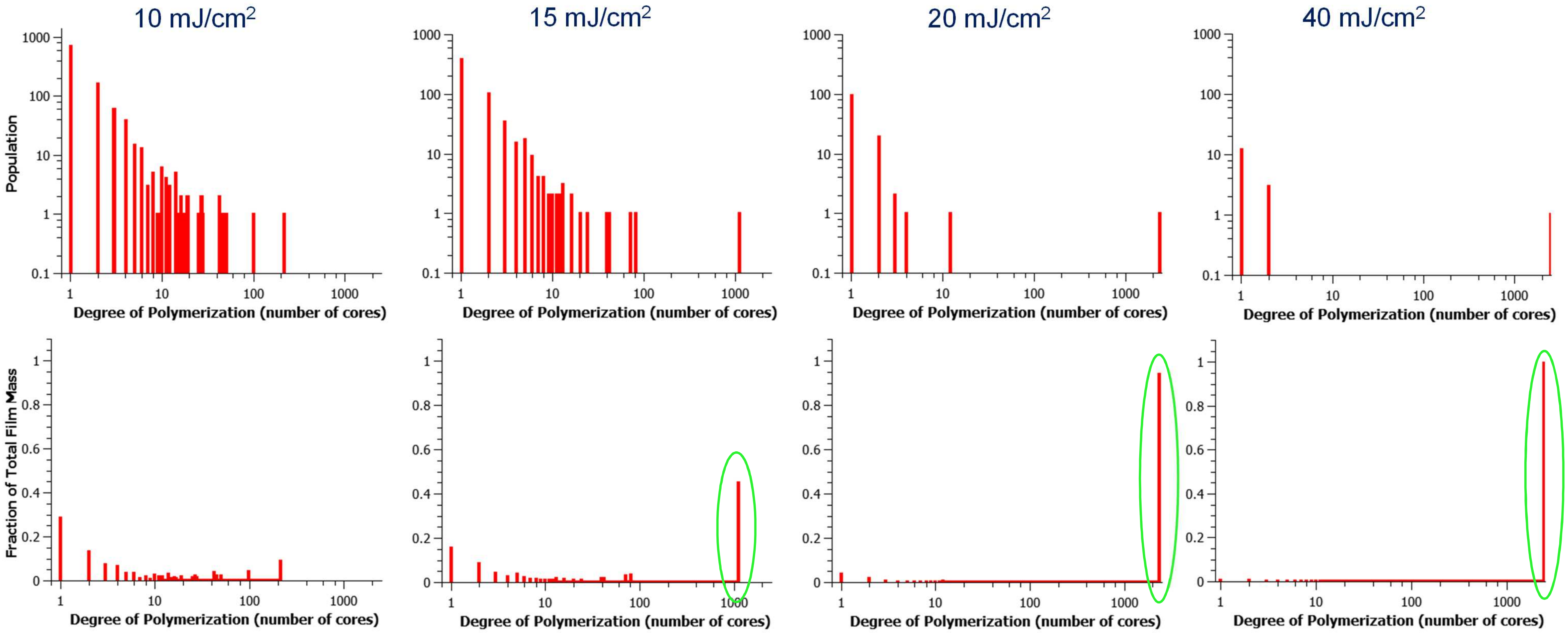
Step 5 – Analyze Topology of Condensation Products

- Protocol:
  a) Scan through array of cores looking for bonds
  b) If a core is bonded to any of its neighbors
    1. Check each bonded neighbor to see if it is bonded to its neighbors
    2. Recursively following the bonding including branches and crosslinks
  c) Continue scan until every core has been visited



Result: 3D map and population distribution of oxo-network polymers

Condensation Product Distribution vs Dose



Degree
of
polymerization

Film
mass
distribution

Degree
of
crosslinking

Gaussian Mean
0.88 bonds per core

1.47 bonds per core

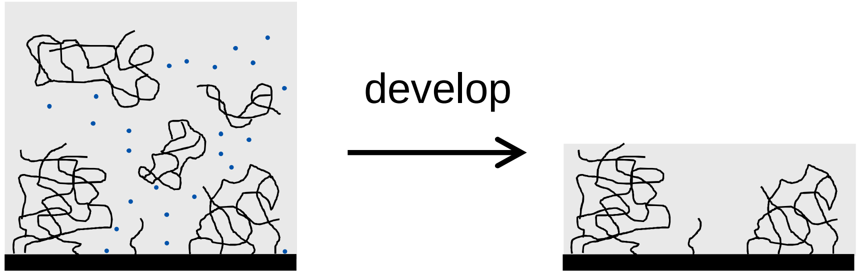
2.58 bonds per core

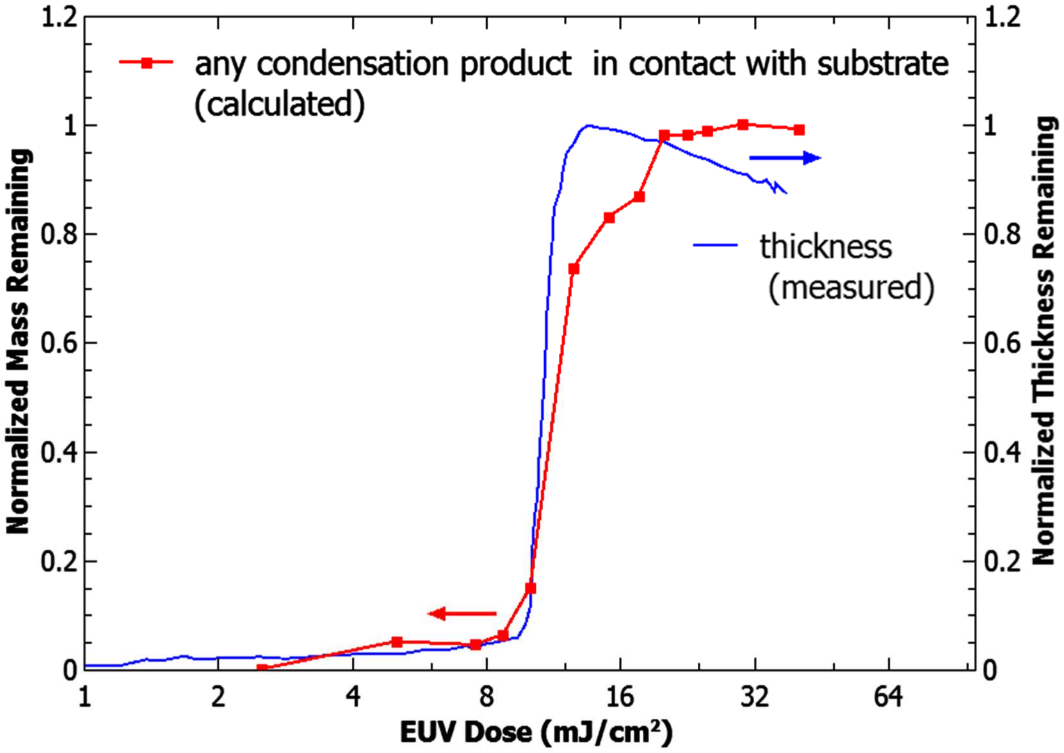
3.57 bonds per core

Calculate Resist Contrast for a Real Resist

Inpria experimental MOx resist system

1. Estimate quantum yield and blur length from experimental data
2. Use model to calculate condensation products vs dose
3. Apply binary dissolution process
    - Only condensation products in direct contact with the substrate are insoluble

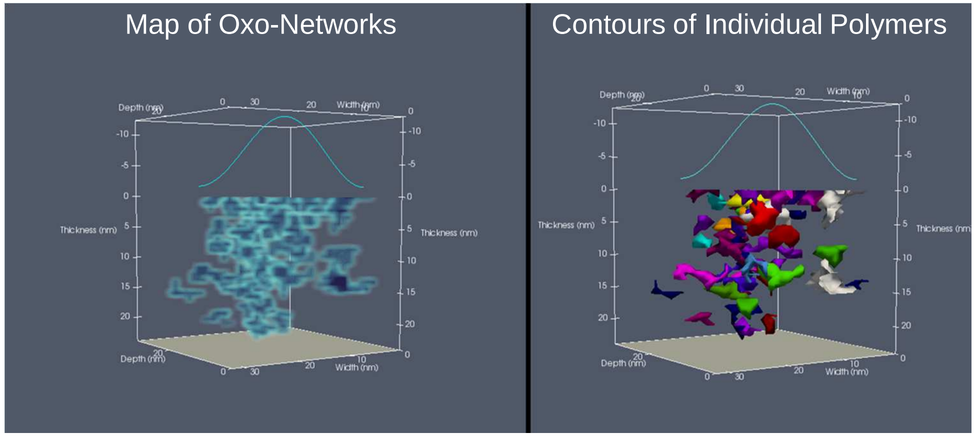




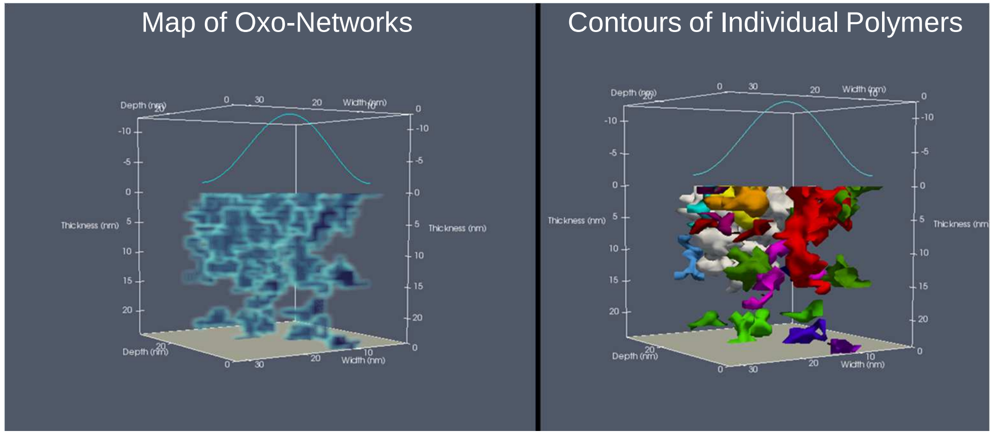
Imaging - Chemical Latent Images

NXE 3300, Dipole illumination, 16 nm line/32 nm pitch

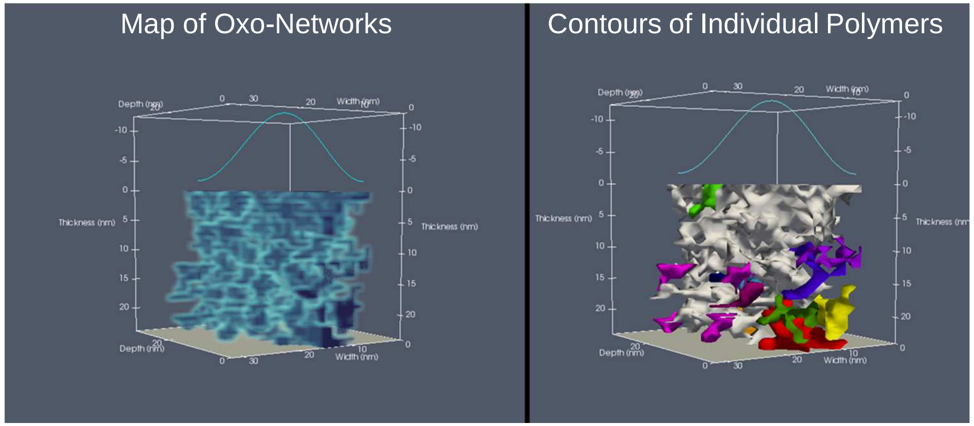
10 mJ/cm^2



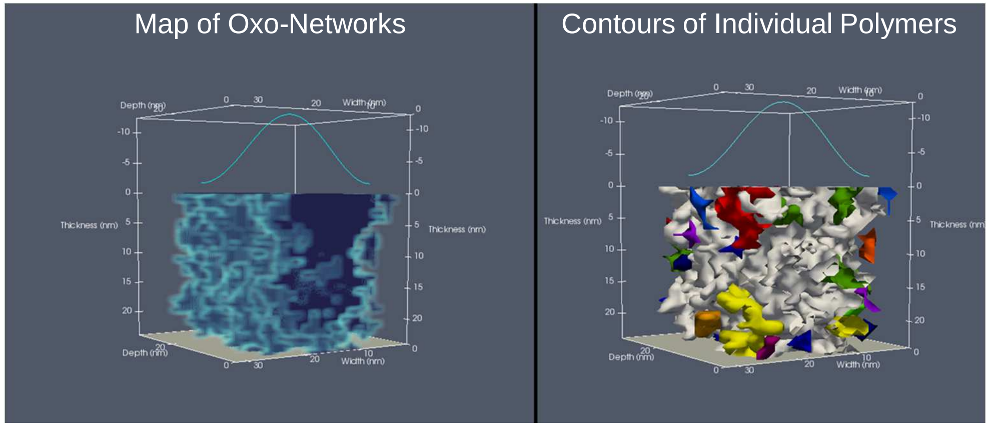
15 mJ/cm^2



20 mJ/cm^2



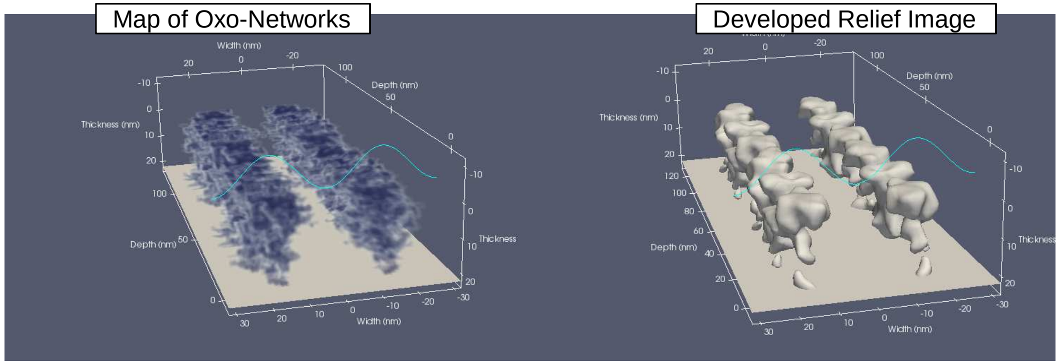
30 mJ/cm^2



Calculated Line-Space Images

NXE 3300, Dipole illumination, 16 nm line/32 nm pitch

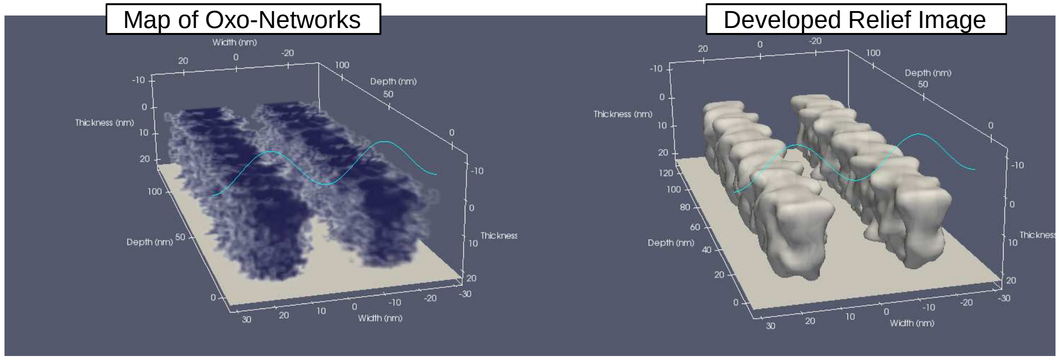
20 mJ/cm^2



Map of Oxo-Networks

Developed Relief Image

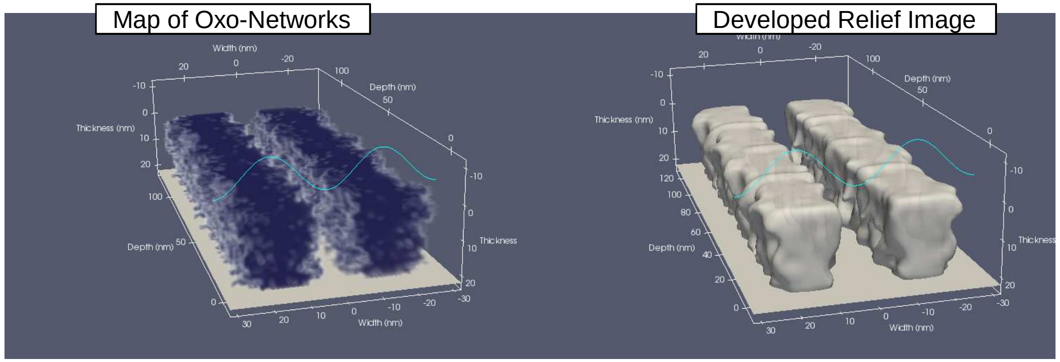
30 mJ/cm^2



Map of Oxo-Networks

Developed Relief Image

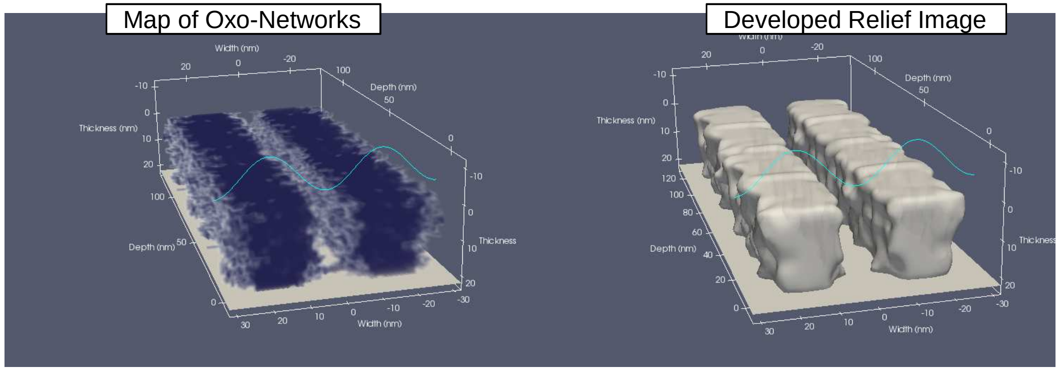
40 mJ/cm^2



Map of Oxo-Networks

Developed Relief Image

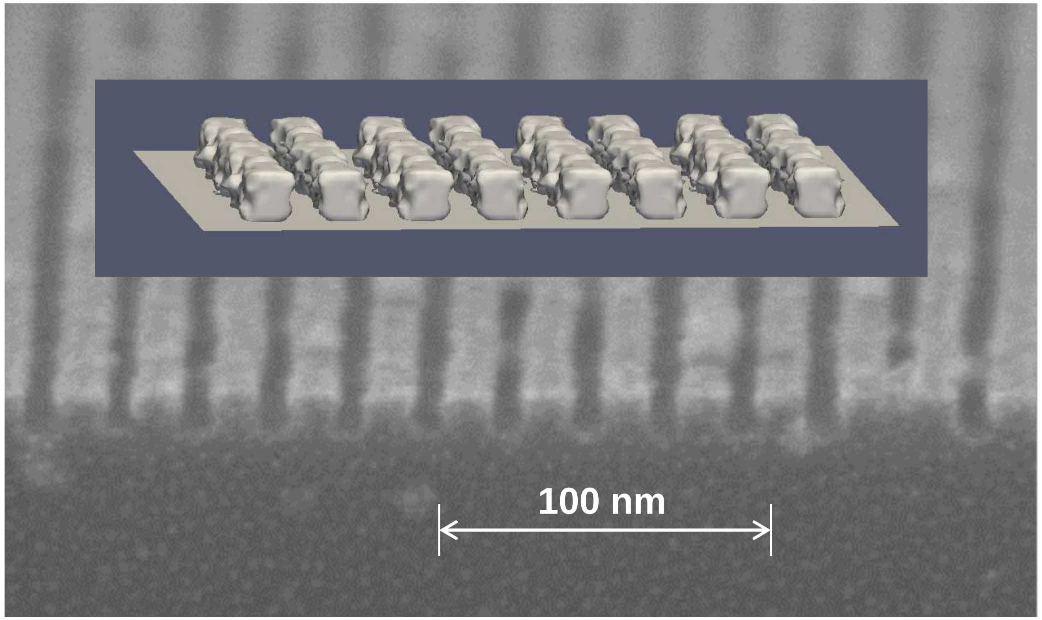
50 mJ/cm^2



Map of Oxo-Networks

Developed Relief Image

Calculated vs Experimental Image : 24 nm pitch



Imaged using EUV-IL tool
(Paul Scherrer Institut)

Summary

Simple chemical description of MOx resist

- Photo-induced condensation of **multifunctional** cluster
- EUV exposure chemistry data from **Inpria MOx resist** test vehicles
- General **stochastic simulation** process

Quantitative link between photochemistry and imaging

- Contrast originates from non-linear **oxo-network** formation
- **Lithographic predictions** consistent with experimental observations
- Potentially applicable to **many resist systems**