Mechanisms of EUV Exposure: Internal Excitation and Electron Blur

EUV Symposium – June 16, 2016

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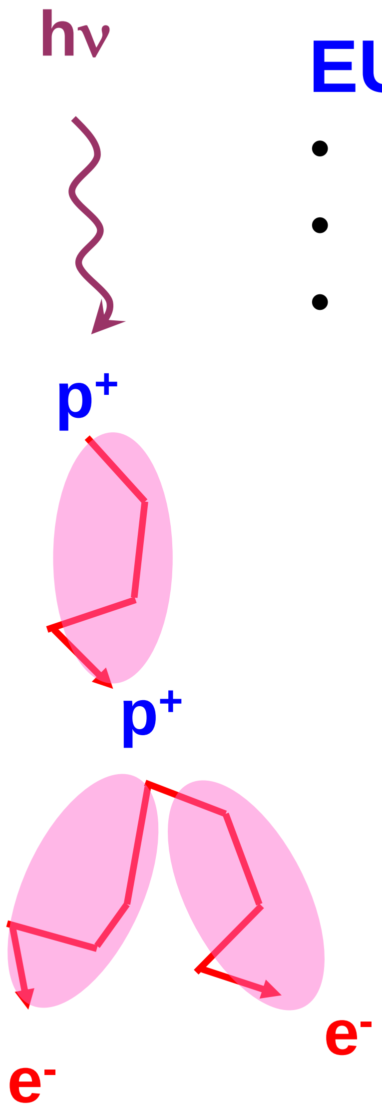
I. Introduction

II. Internal Excitation

III. Experiment/Modelling of Electron Blur

Goals and Motivation



EUV Photons:

- Create Electrons → Can Cause Reactions
- Create Holes → Can Cause Reactions
- Deposit Energy → Can Cause Reactions

What are the Mechanisms of These Reactions?

- For PAGs?
- For Metal-Containing Resists?

Understanding Should lead to Better Resists

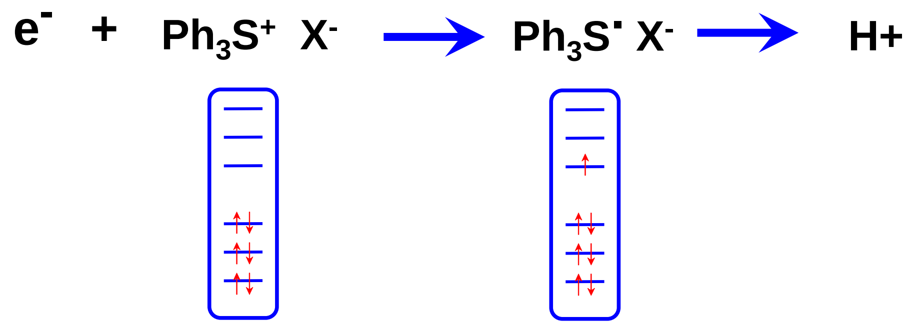
Fundamental Reactions between e-, hν and Matter:

Electron Trapping

Electron Trapped by PAG:

e- + PAG → H^+

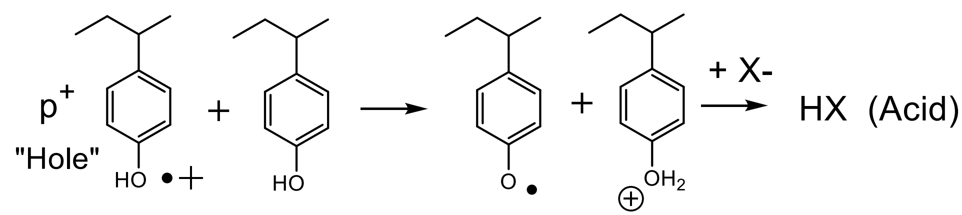
(ΔE = 2-3 eV)



Hole-Initiated Chemistry

(Kozawa Mechanism)

p^+ + Polymer → H^+

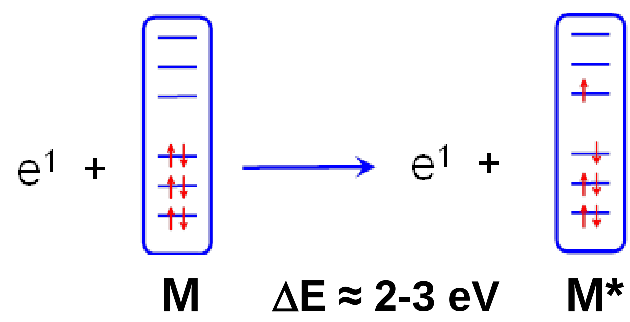


Internal Excitation

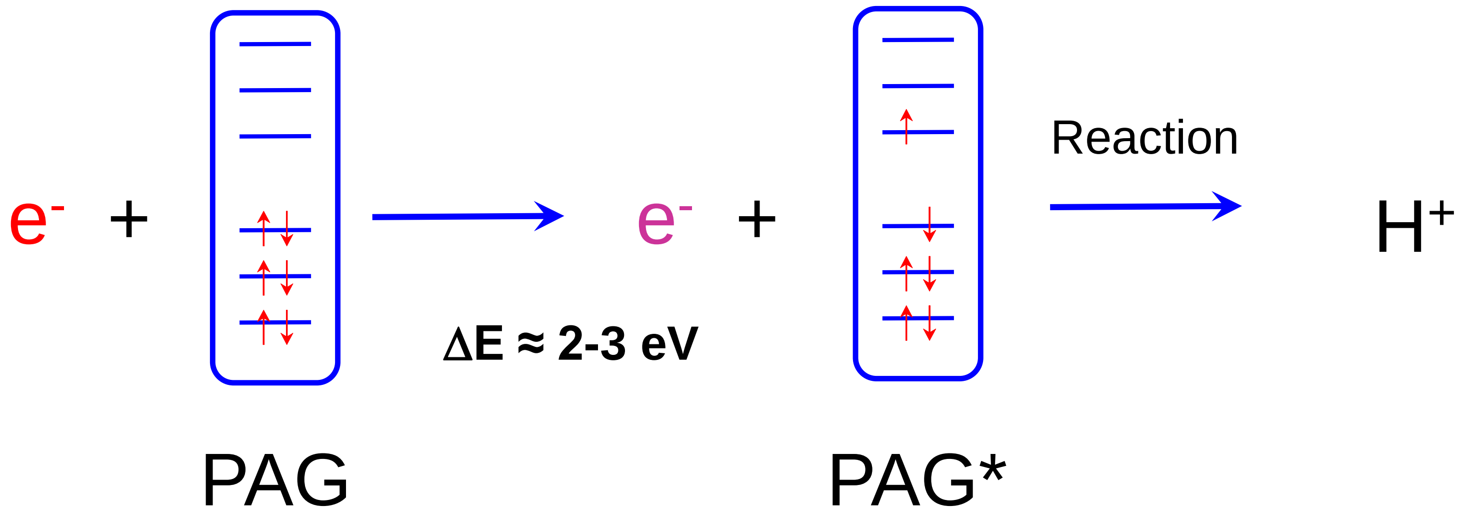
PAG is “Exposed” similar to photolysis.

e- + PAG → PAG* + e- → H^+

(ΔE = 2-3 eV)



II. Internal Excitation



Internal Excitation of PAG by Passing Electron:

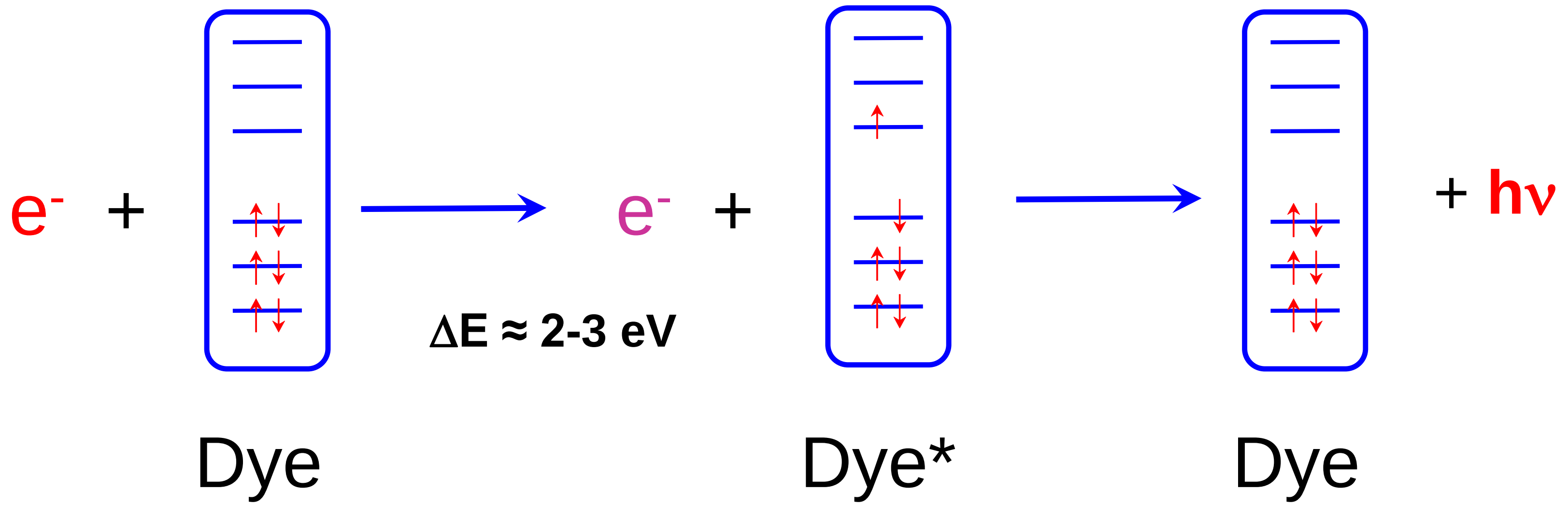
An electron could interact with a molecule to induce a HOMO/LUMO transition: analogous to photoexcitation.

One electron could "photolyze" several PAGs without being consumed.

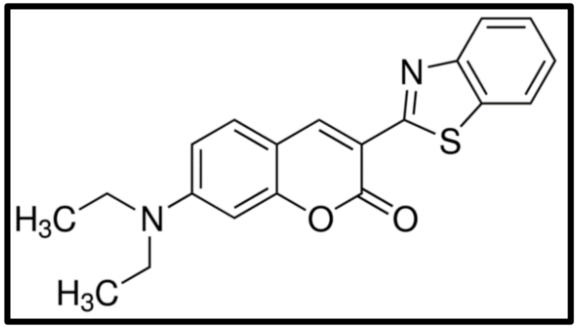
These energy loss mechanisms are known in the EELS Literature for simple structures.*

***Ritsko et al. JCP 1978; JCP 1979; Vilar et al. JESRP 2009; Vilar et al. *Langmuir* 2003, Liehr Phys Rev B 1986.**

Internal Excitation via Electron-Induced Fluorescence

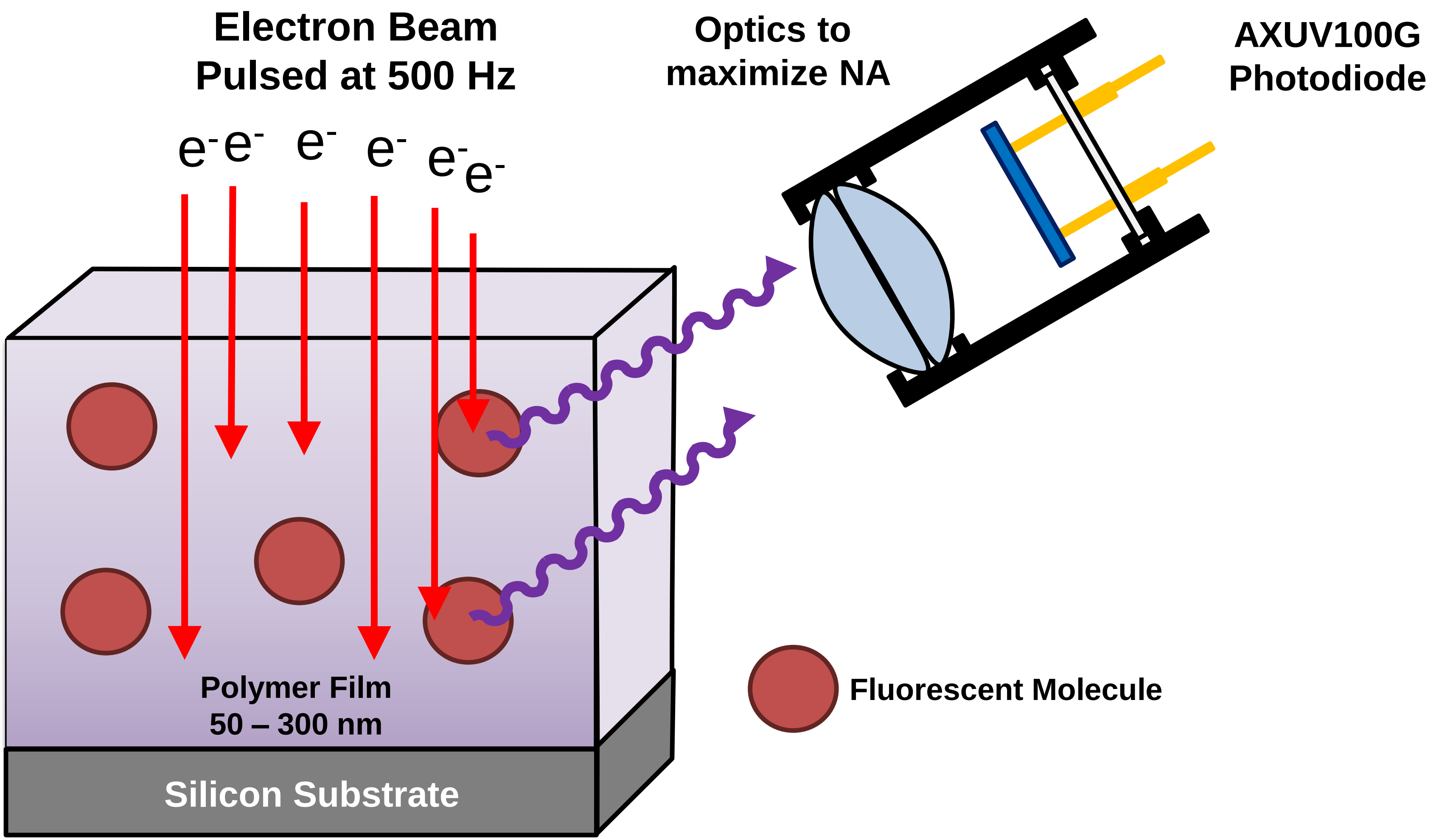


Can we demonstrate this mechanism using fluorescent dyes?

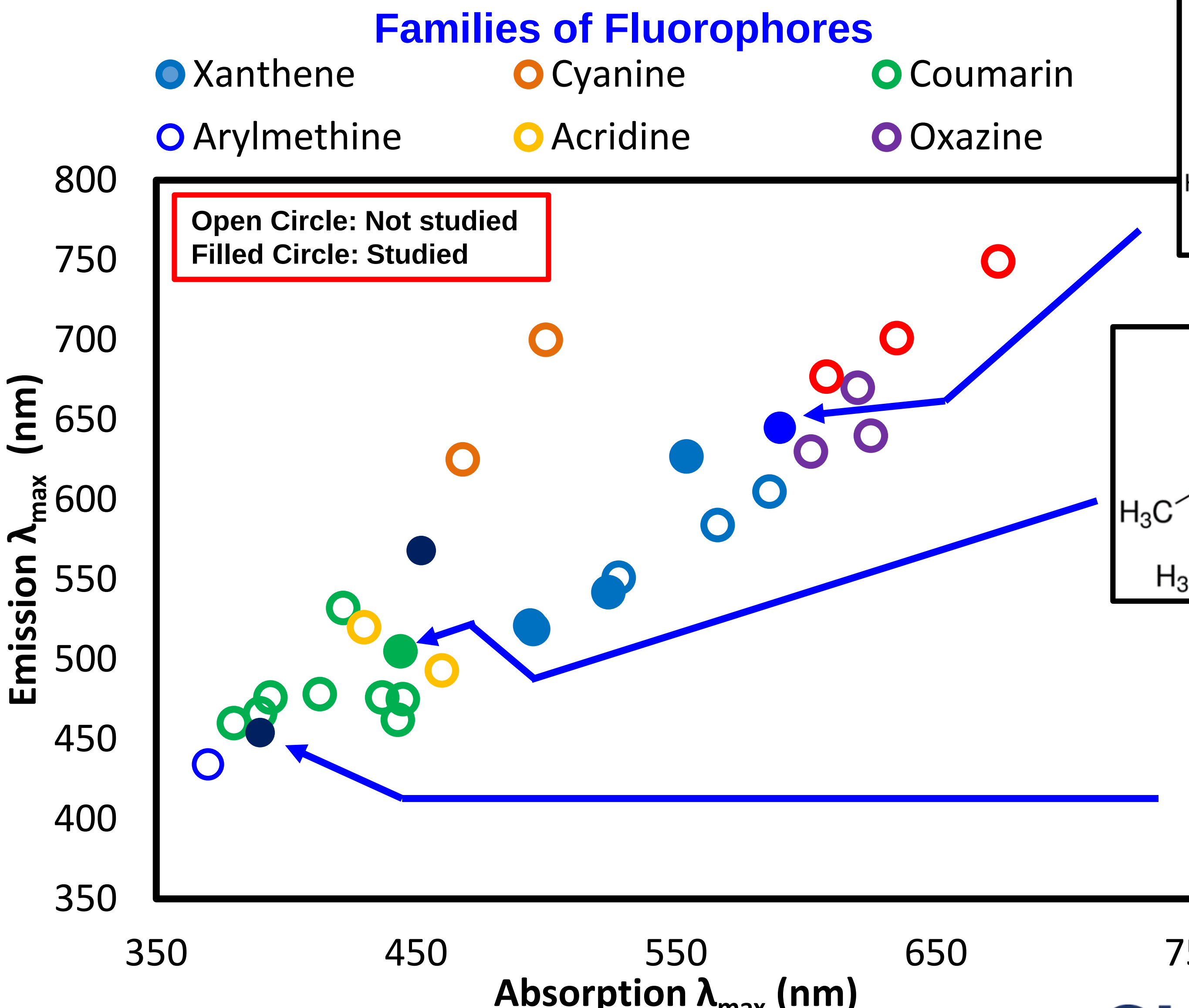


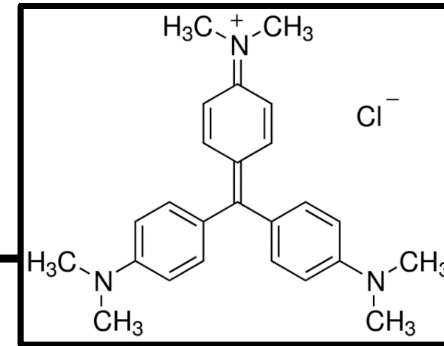
Coumarin 6
Fluorescent Dye

Experimental Schematic

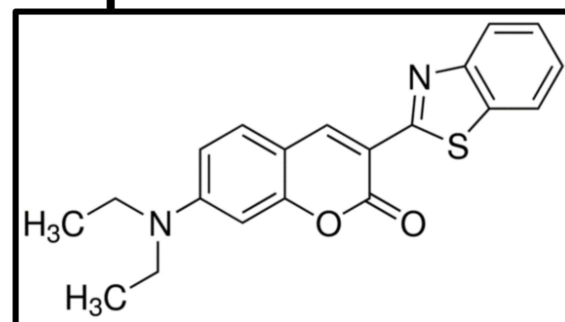


Fluorophores Studied

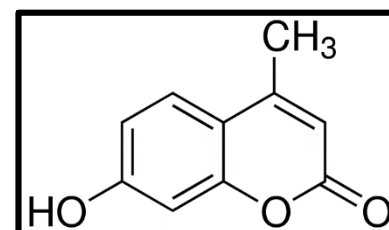




Crystal Violet

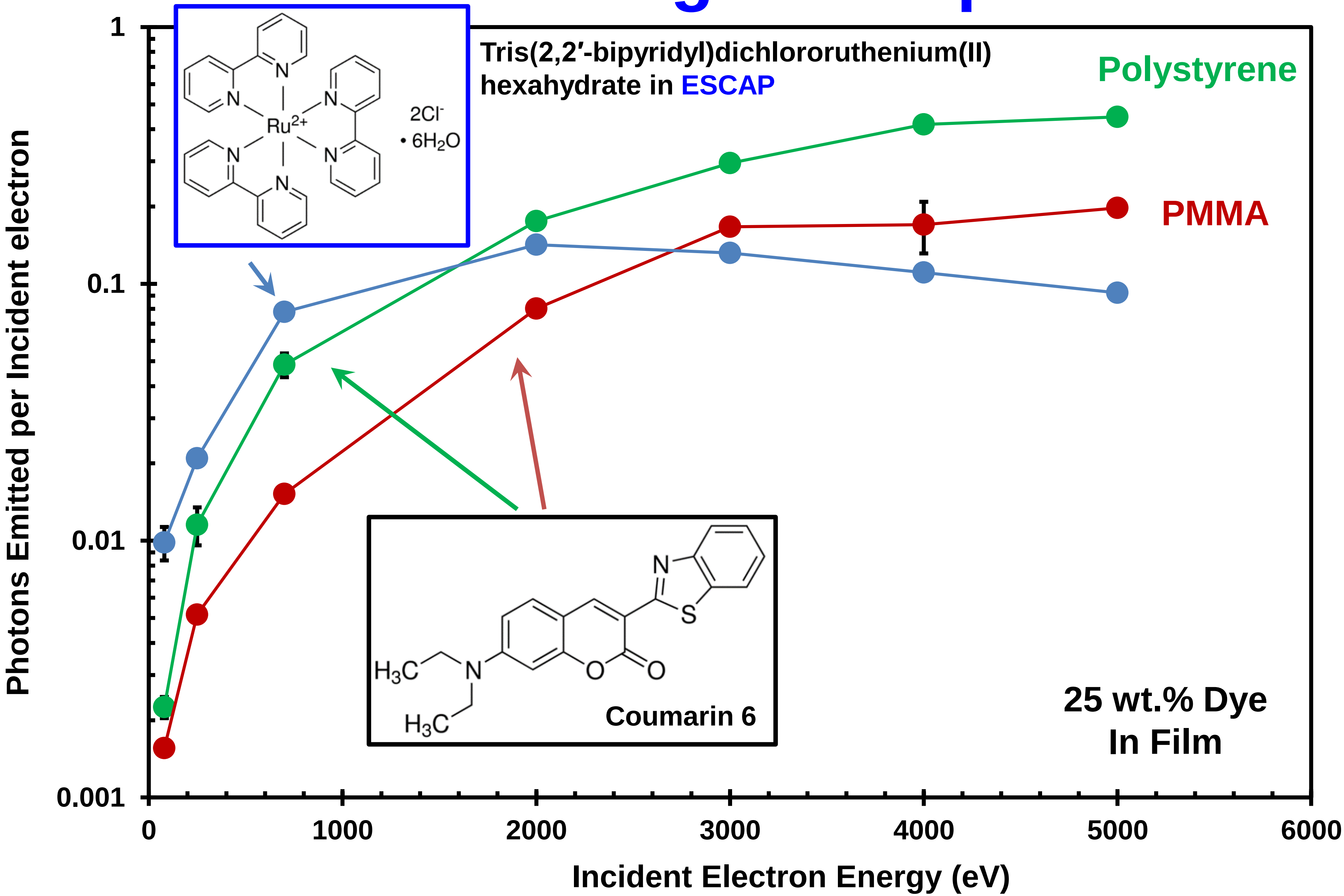


Coumarin 6



4-Methylumbelliferone

Best Performing Fluorophores



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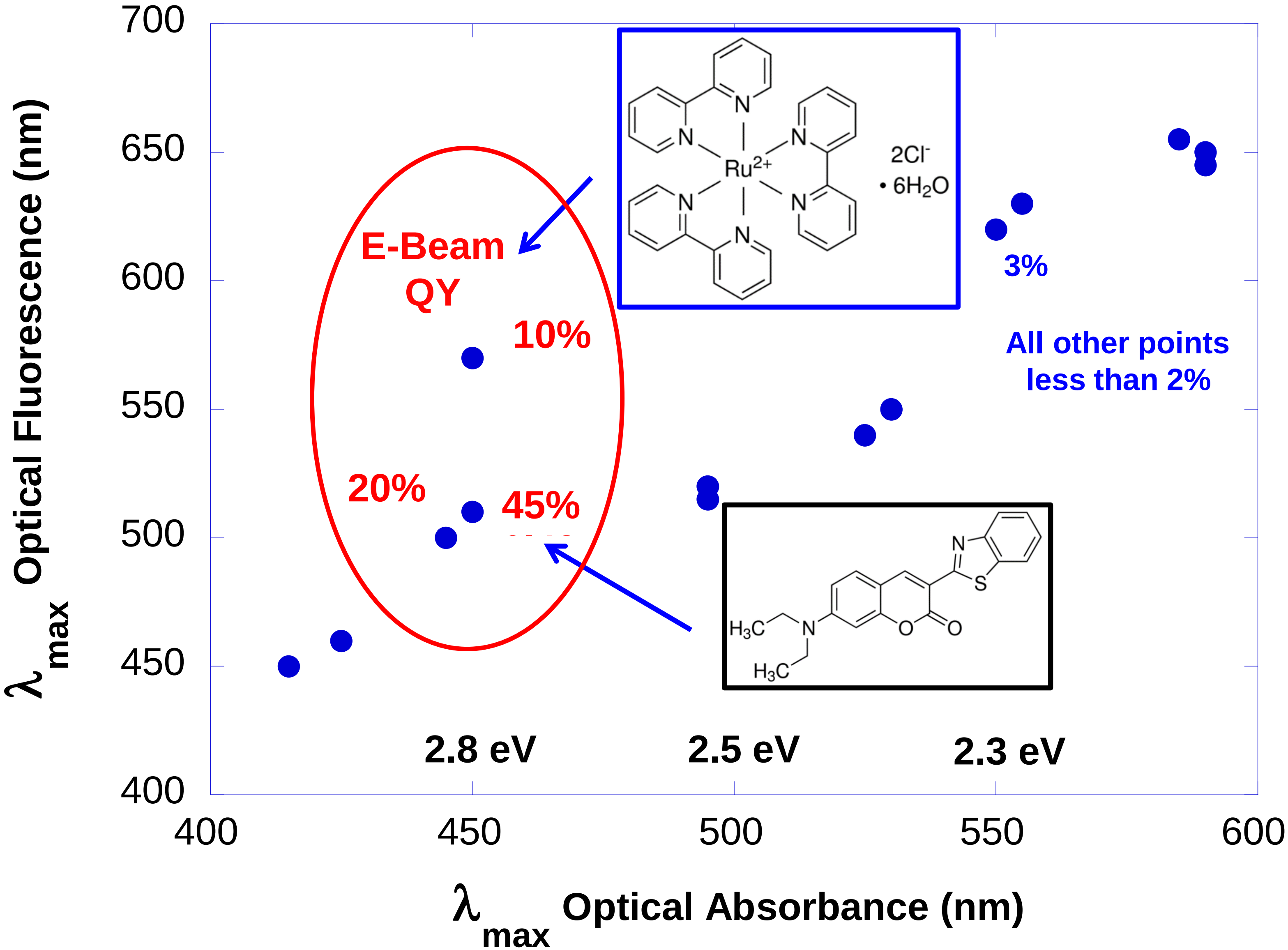
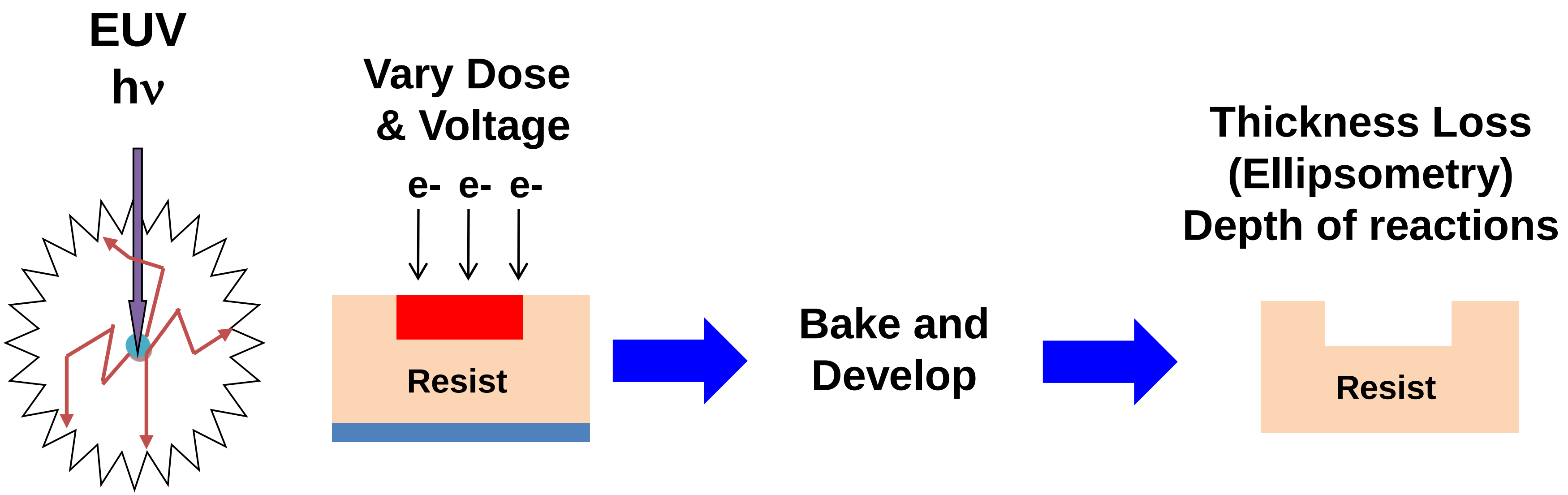
5000 eV E-Beam Fluorescence Maxima *vs.* Optical Fluorescence

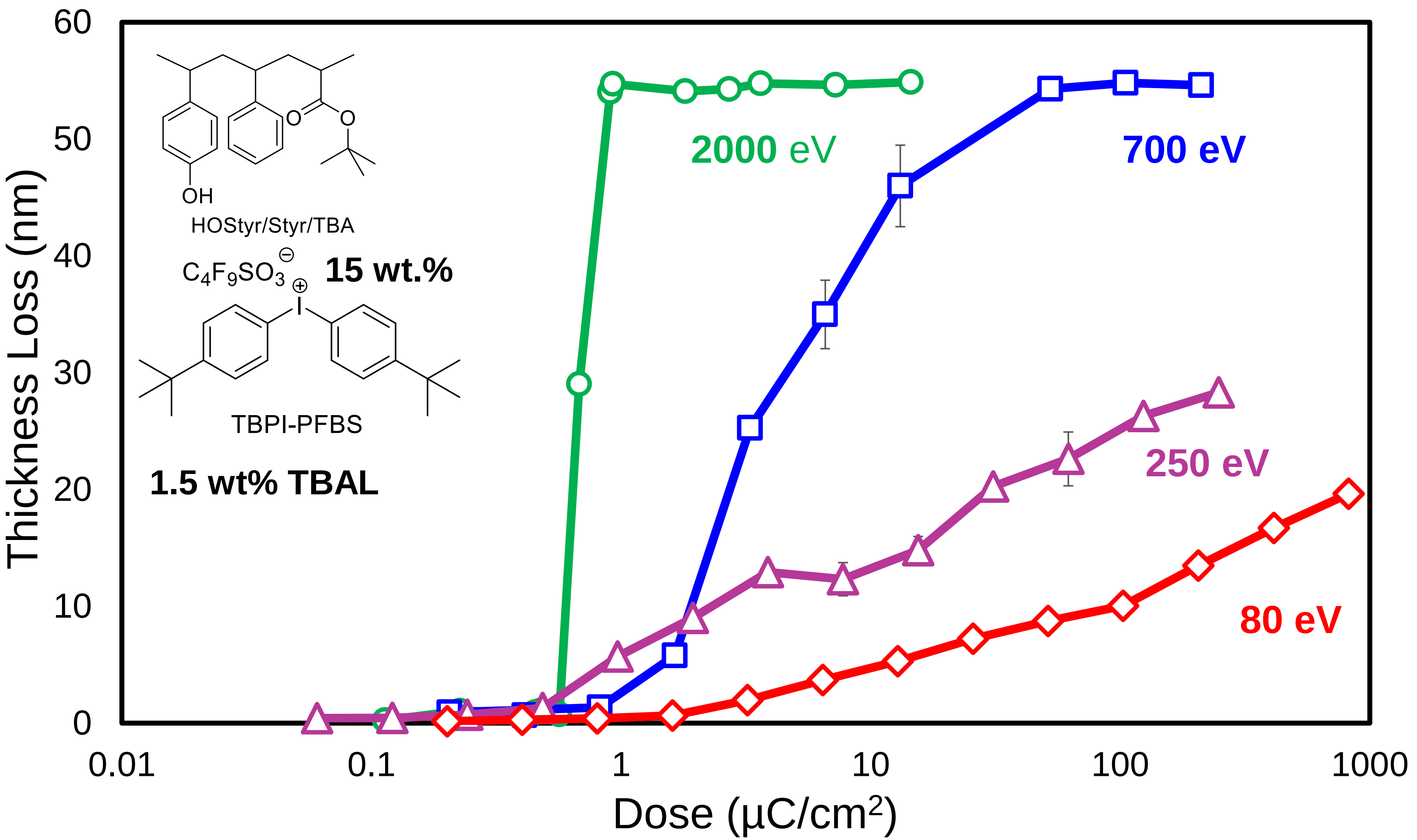


III. Experiment/Modelling of Electron Blur



Thickness Loss was measured as a function of e- energy and dose.

Thickness Loss of Open-Source Resist (OS2)



Comparison of Experiment with Monte Carlo Simulation using LESiS

(Low-energy Electron Scattering in Solids)

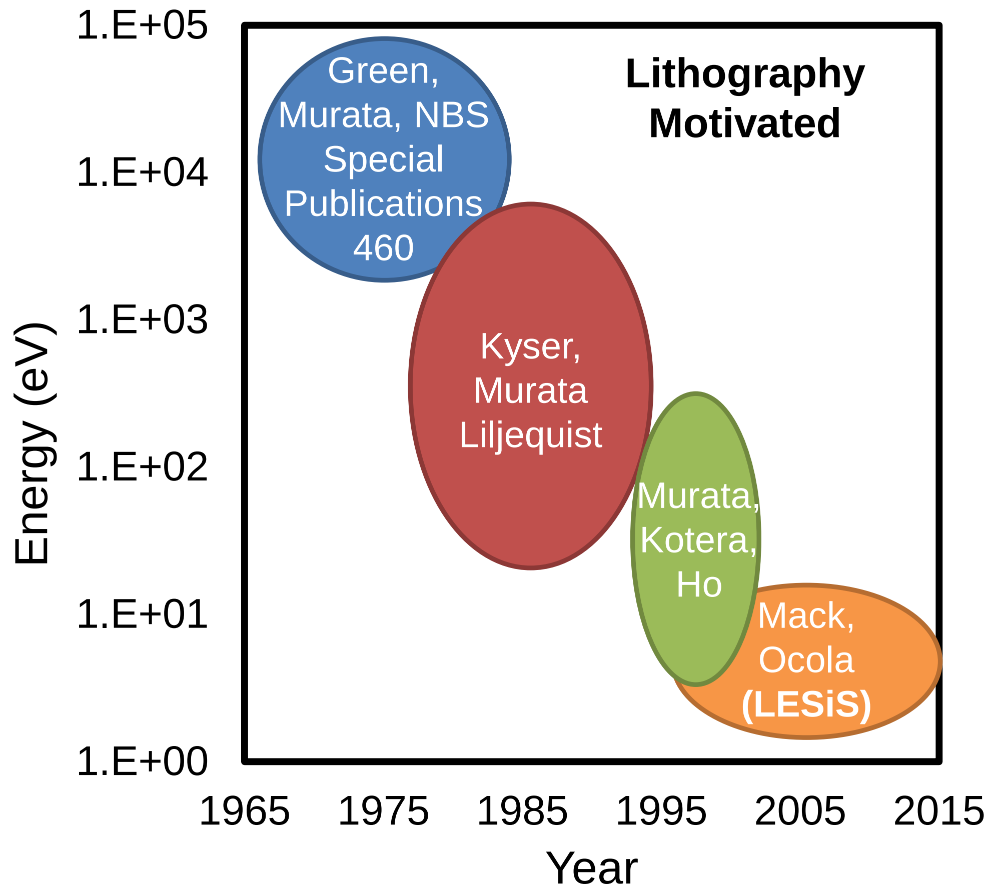
LESiS is a fully stochastic simulation program designed originally by Leo Ocola.

- Cross-sections are calculated in real time.
- Monte Carlo is implemented in real time.

LESiS can simulate exposures by electrons or photons.

LESiS outputs data for each scattering event

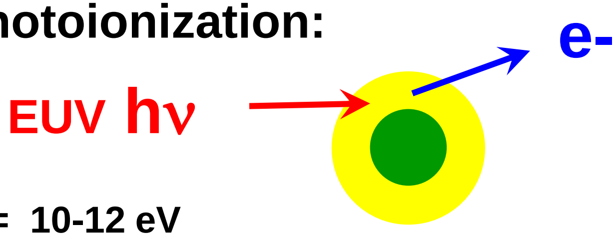
- Energy
- Trajectory
- Identity, location, and orbital of the involved atom



LESiS Model Follows these Events:

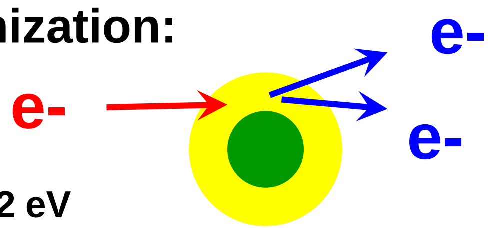
■ = Core Electrons
■ = Valence Electrons

(1) Photoionization:



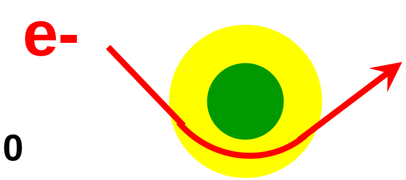
ΔE = 10-12 eV
Binding Energy

(2) Ionization:



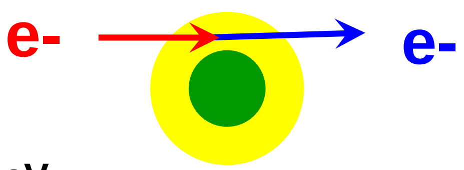
ΔE = 10-12 eV
Binding Energy

(3) Elastic Scattering:



ΔE = 0

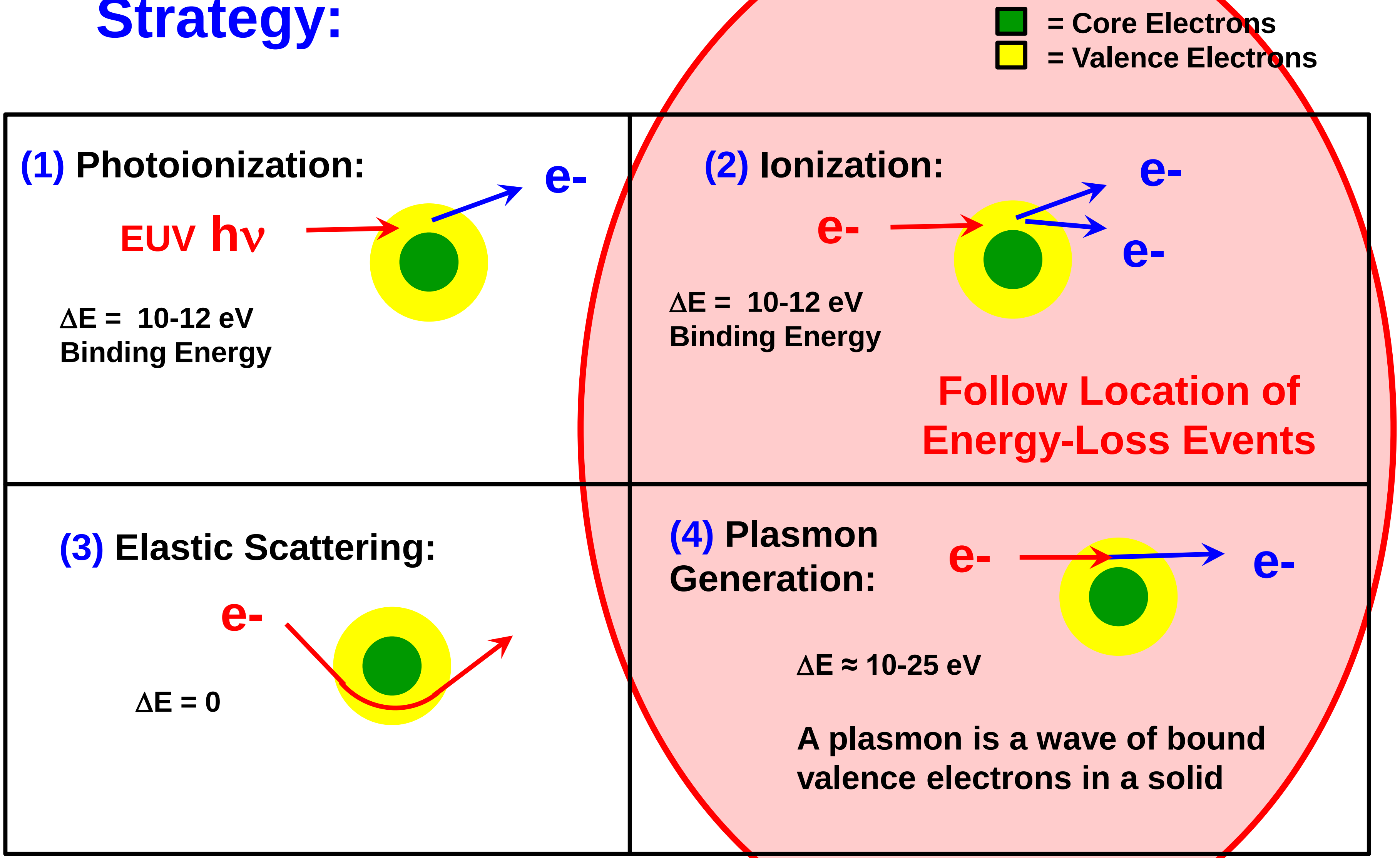
(4) Plasmon Generation:



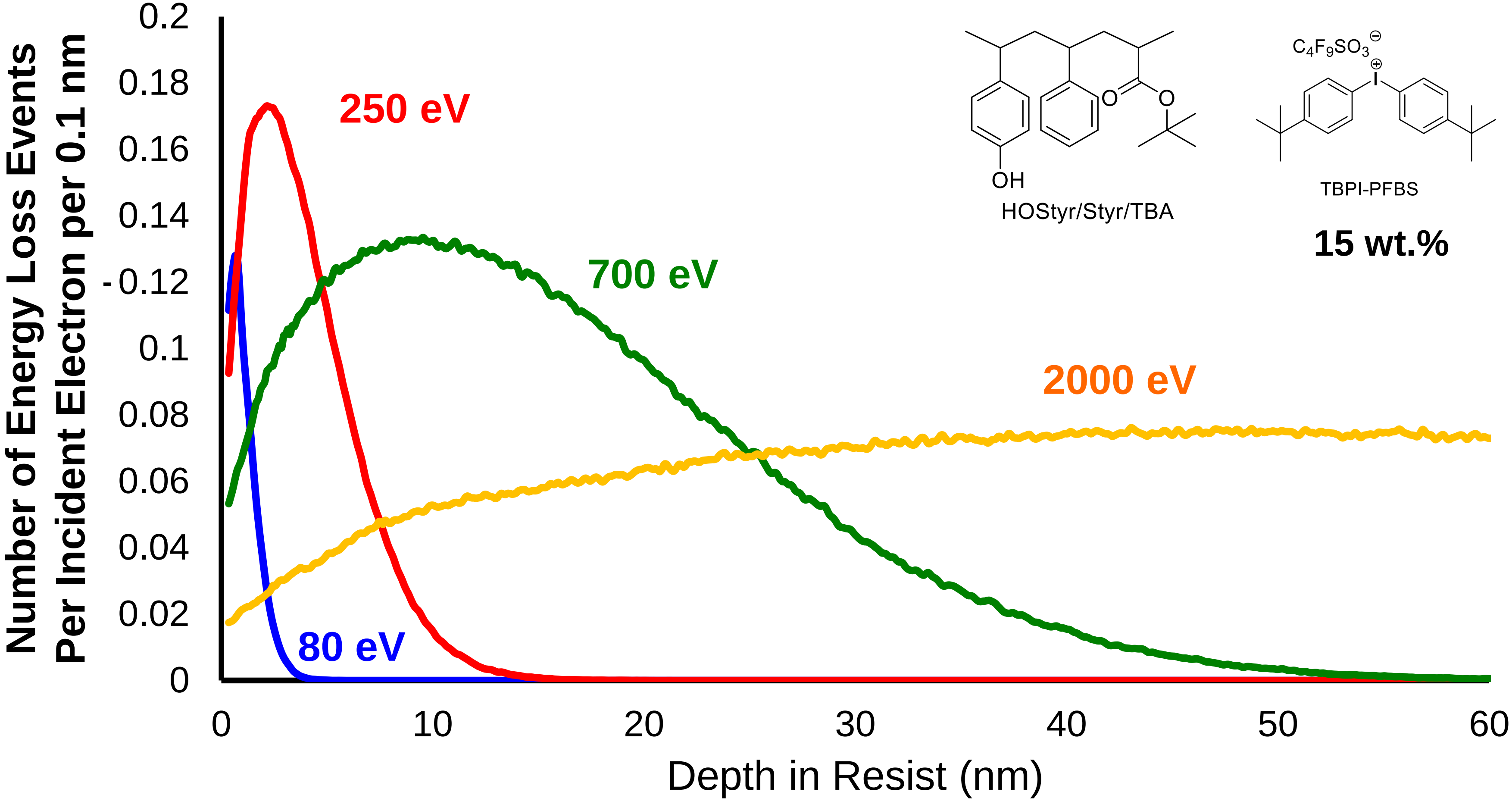
ΔE ≈ 10-25 eV

A plasmon is a wave of bound valence electrons in a solid

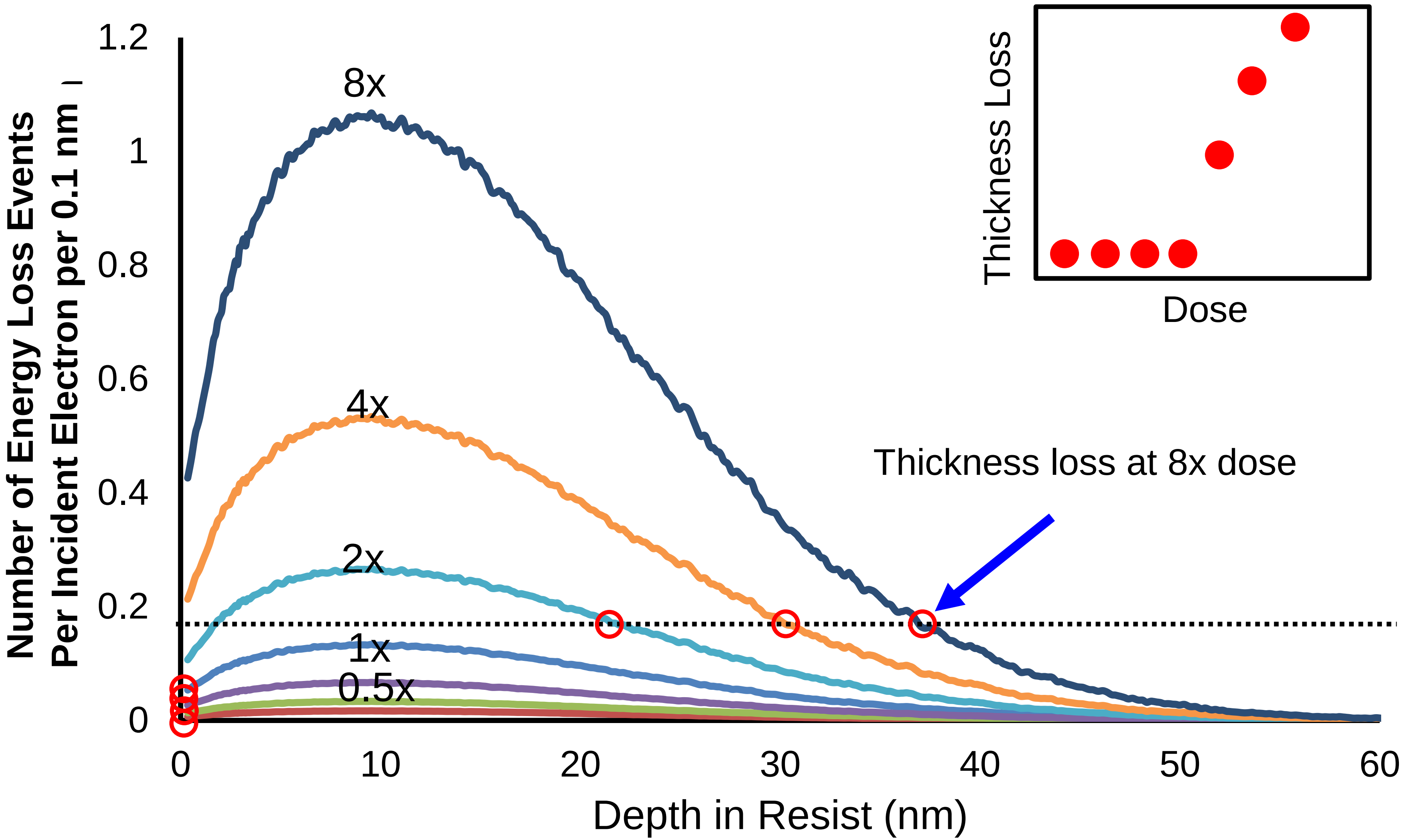
LESiS Model Strategy:



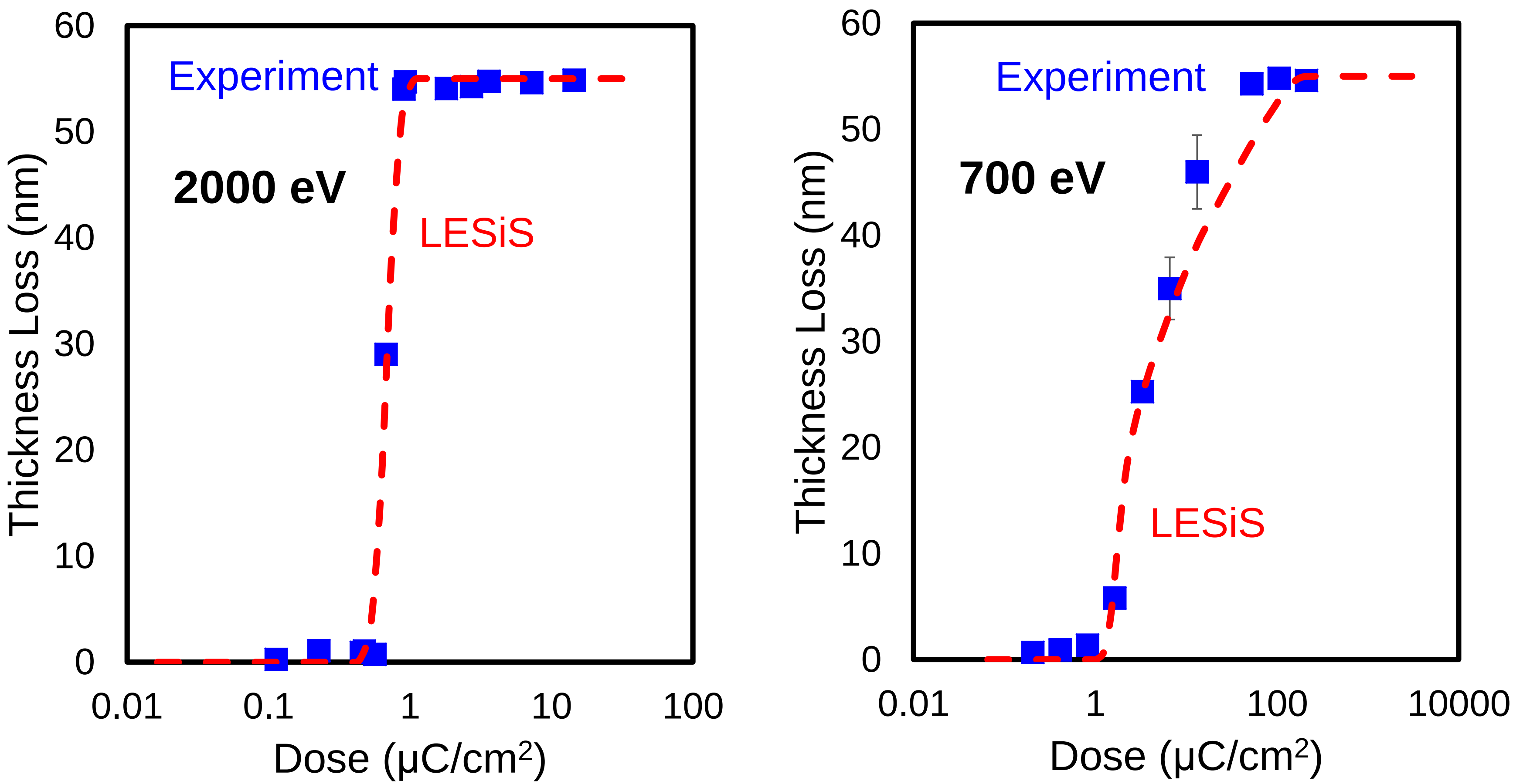
Energy Loss Events per e⁻ *vs.* Resist (OS2) Depth



Thickness Loss Simulation (OS2, 700 eV)

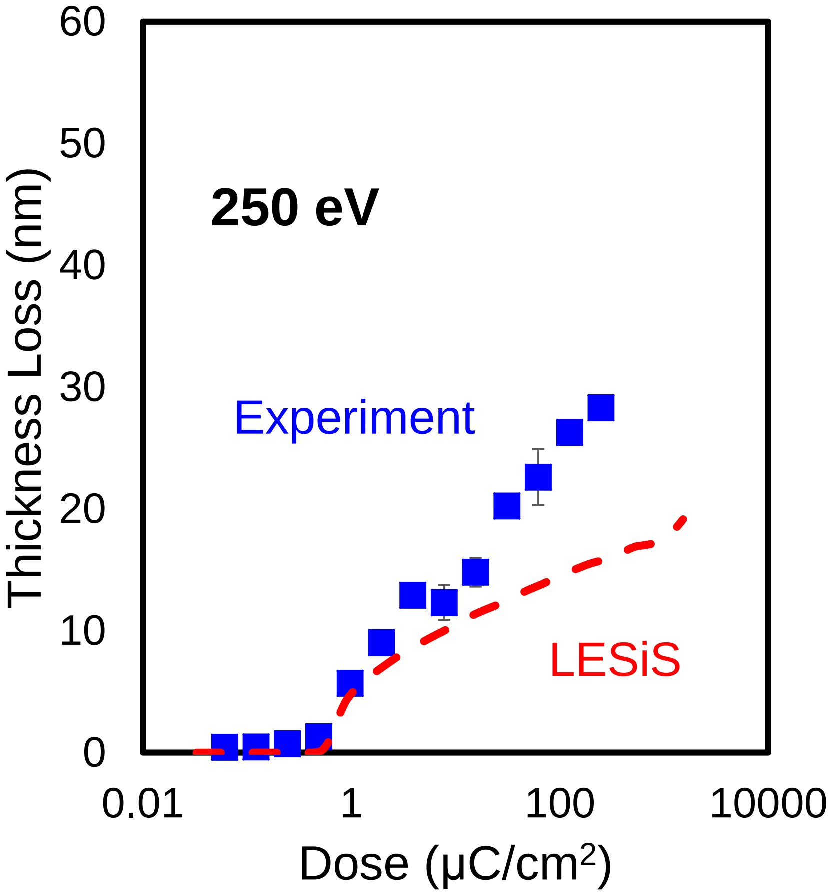


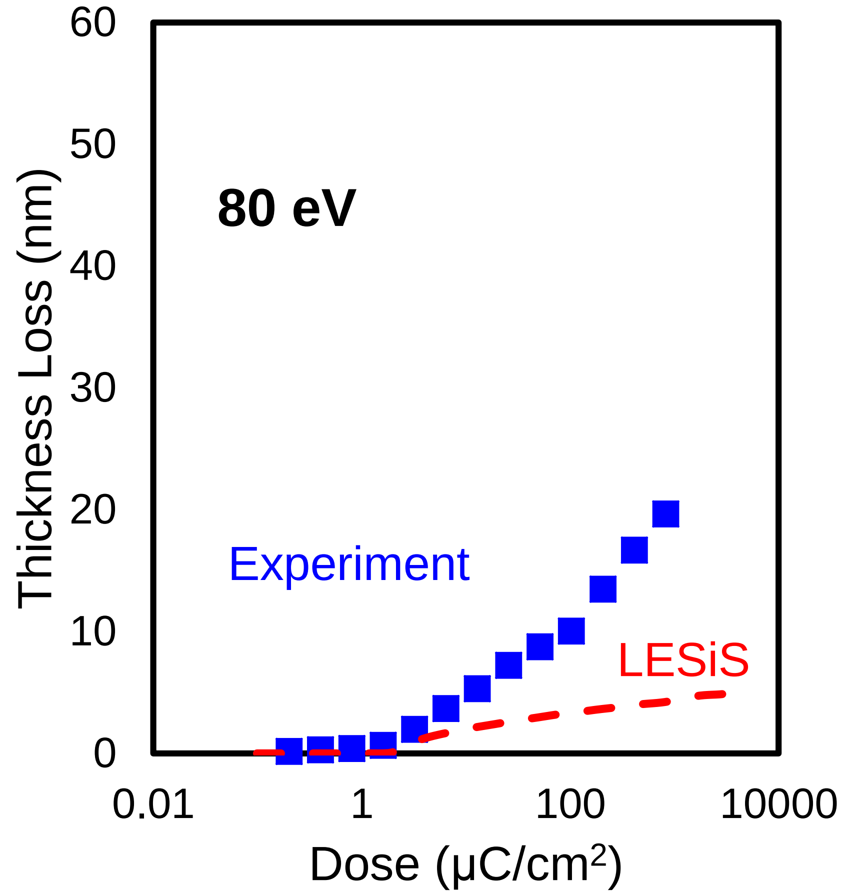
Thickness Loss Simulation Results (OS2)



Threshold set to match 700 eV simulation and experimental data

Thickness Loss Simulation Results (OS2)

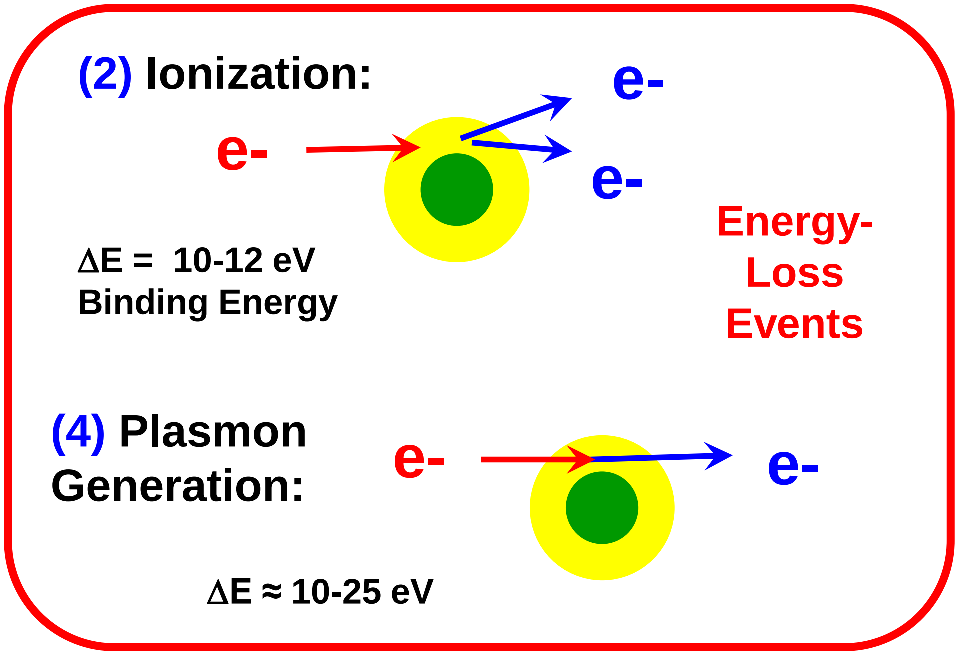


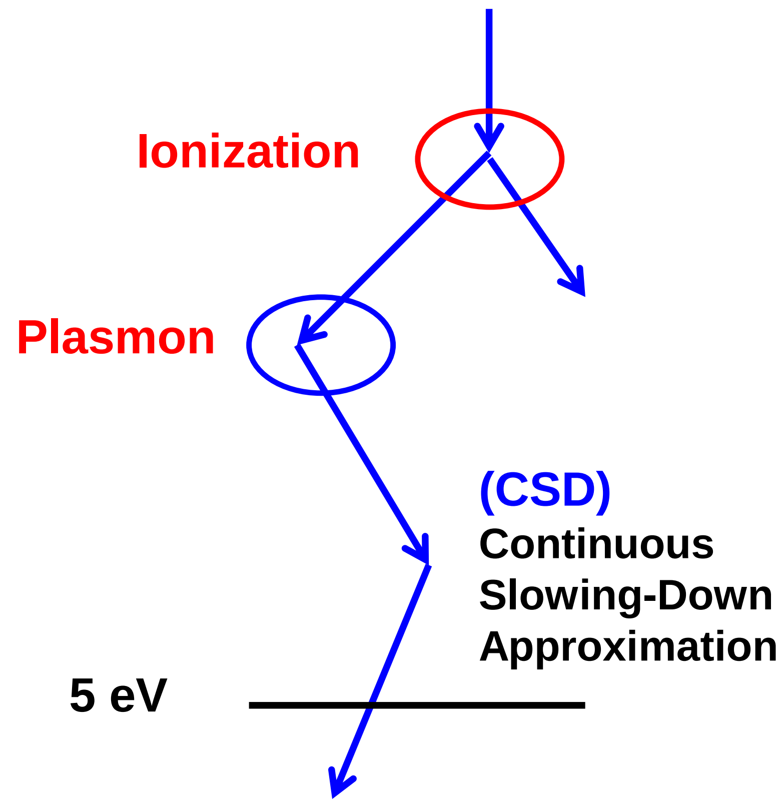


Currently, LESiS does not adequately model Very Low-Energy Electrons.

Threshold set to match 700 eV simulation and experimental data

Maybe these Energy Loss Events Don't Properly Model Chemical Reactions





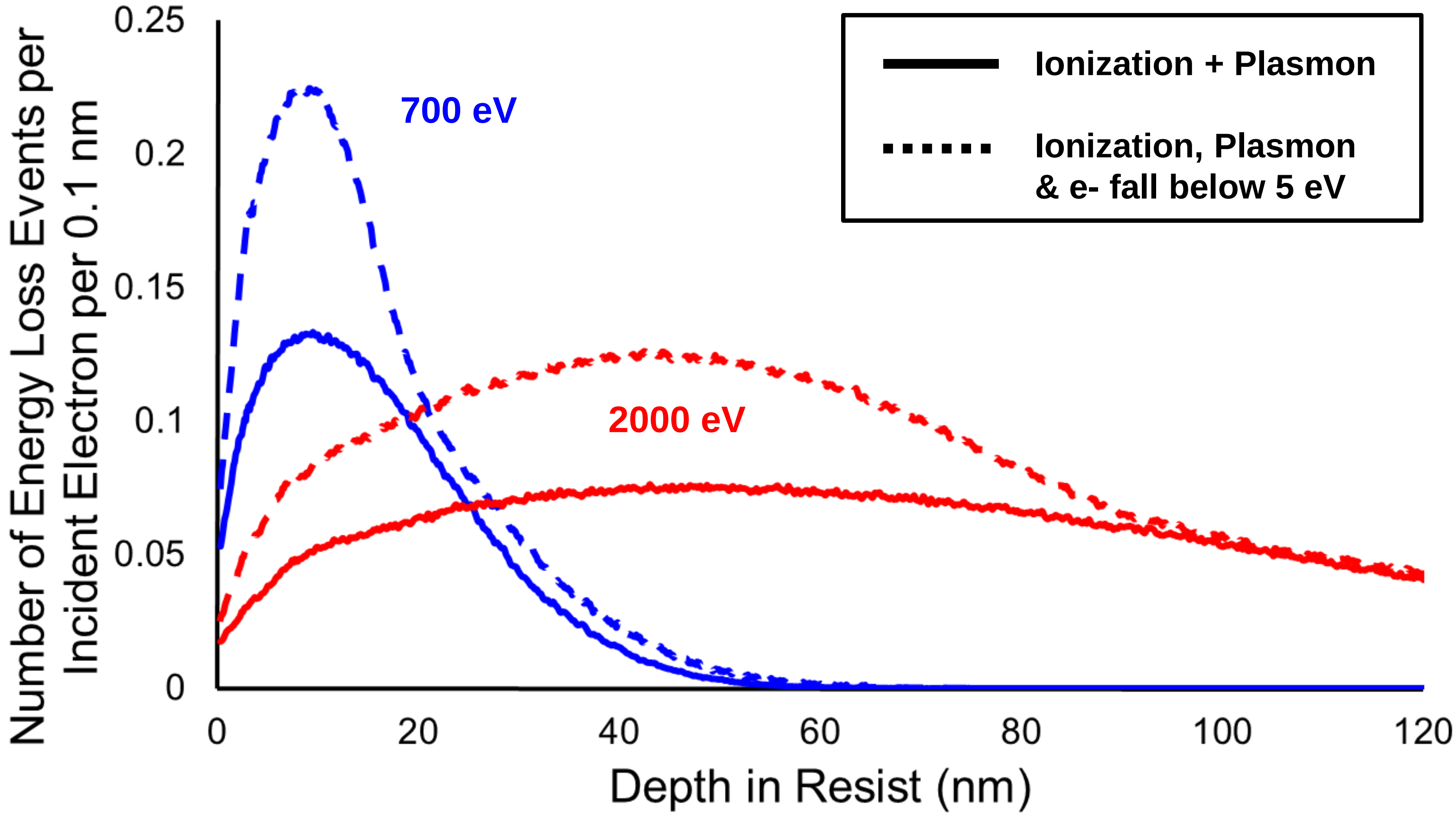
Electron Trapping

e- + PAG → H^+

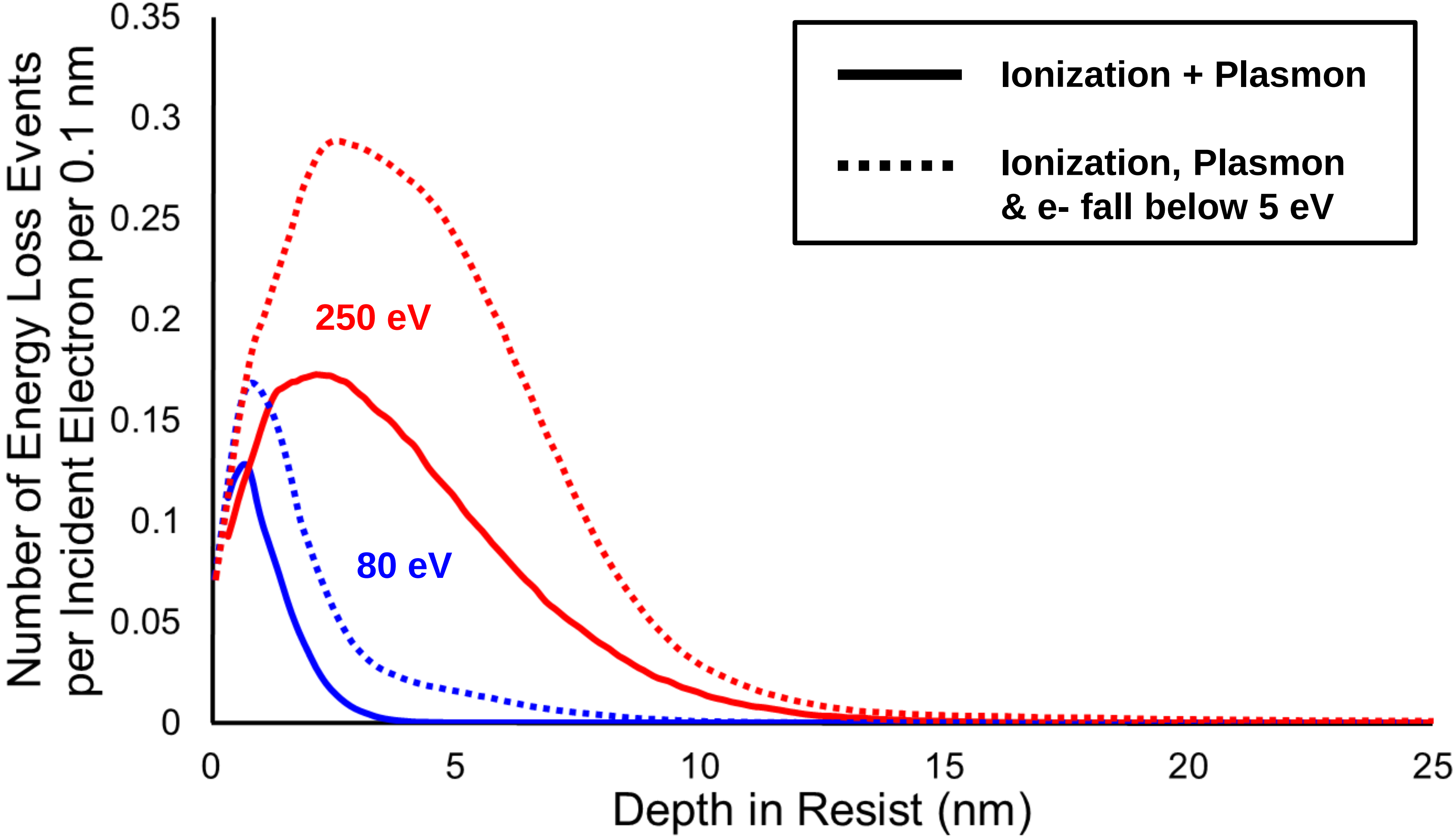
(ΔE = 2-3 eV)

Count when Electrons "Fall below 5 eV"

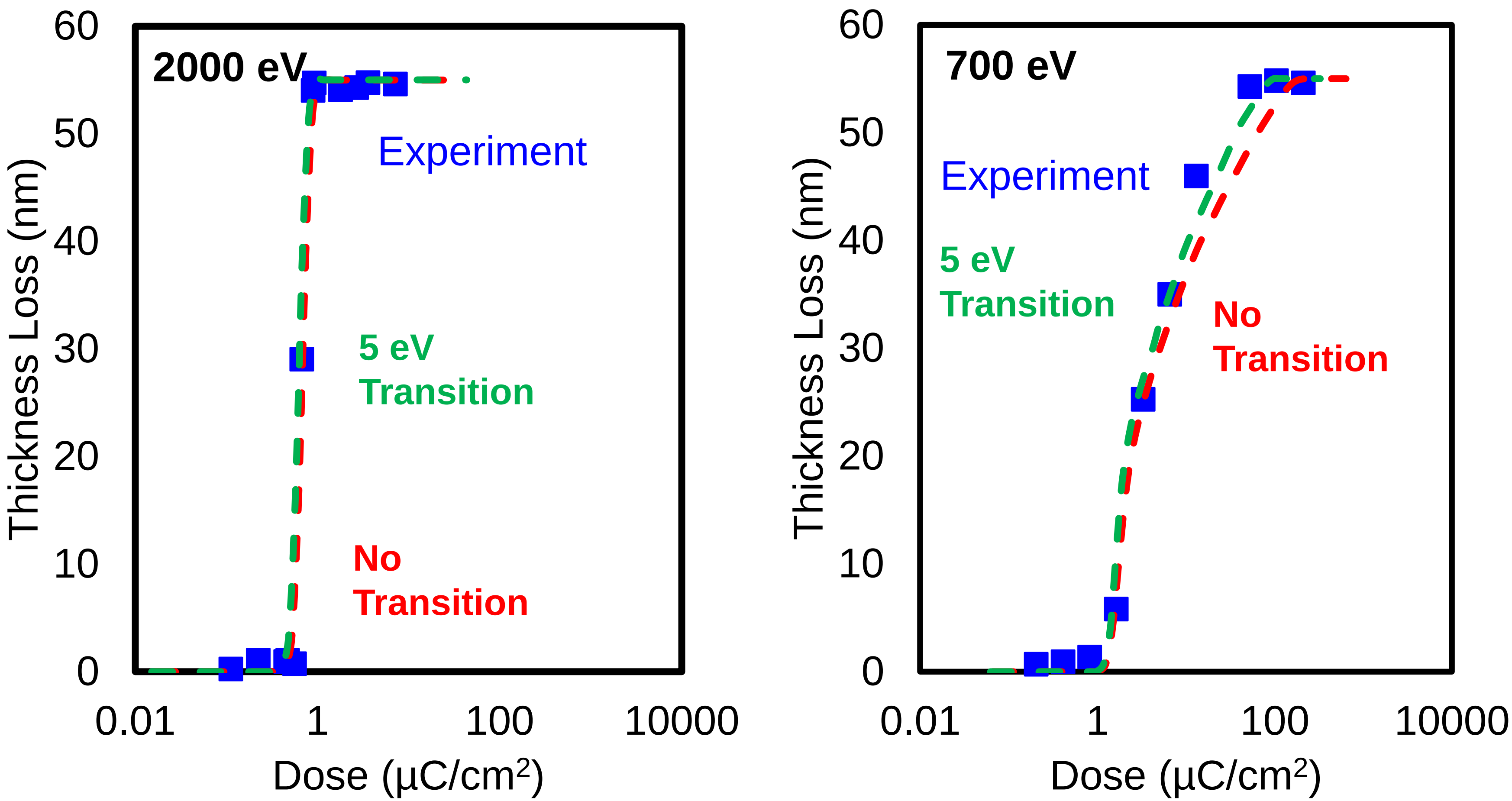
Energy Loss Events per e⁻ *vs.* Resist (OS2) Depth



Energy Loss Events per e⁻ *vs.* Resist (OS2) Depth

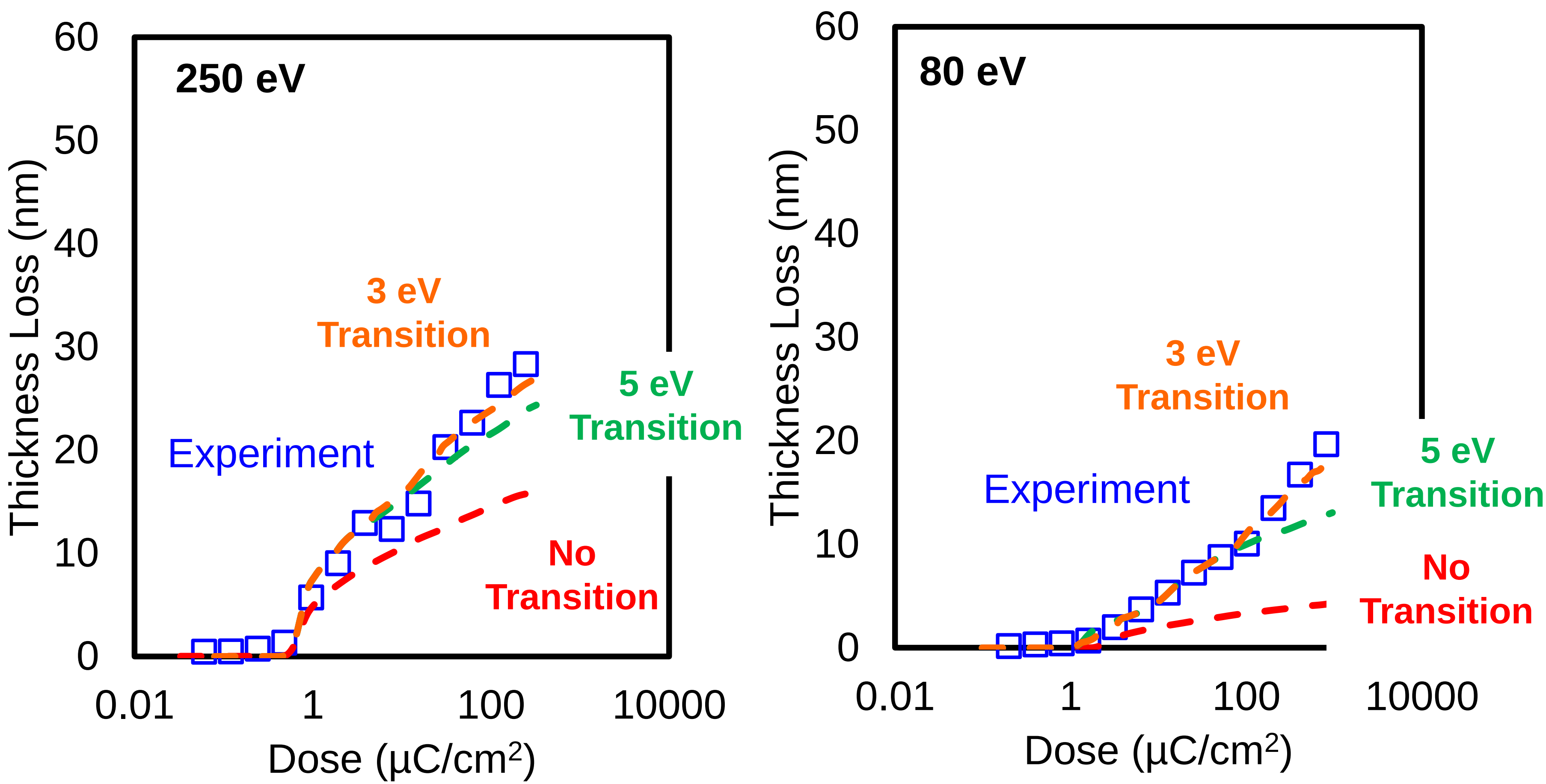


Thickness Loss Simulation Results (OS2)



Threshold set to match 700 eV simulation and experimental data

Thickness Loss Simulation Results (OS2)



A better model when 3 or 5 eV transitions are included.

Threshold set to match 700 eV simulation and experimental data

Conclusions

Internal Excitation

- Demonstrated that secondary electrons can create excited states through internal excitation.
- Two dyes have significantly greater internal excitation quantum yields and very similar optical absorption maxima (450 nm/2.8 eV).
- However, the electron cross-sections for internal excitation by 80 eV electrons is low (~1%) for the best dyes. Key discoveries are required before this mechanism can be useful.

Thickness Loss/Electron Blur

- The best agreement between model and experiment is achieved when the reactivity of very low energy electrons (~3 eV) are included.
- This mechanism could improve sensitivity as a trade-off to electron blur.

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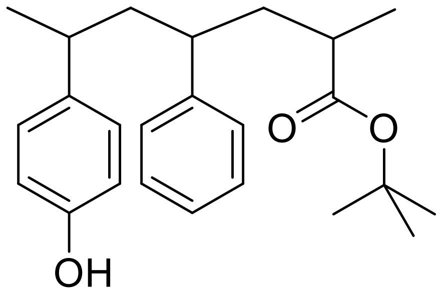
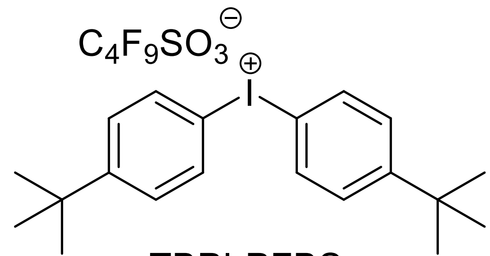
Appendix

Open-Source Photoresist: OS2

For most of our work, we use an Open Source Chemically Amplified Resist, Called OS2.*

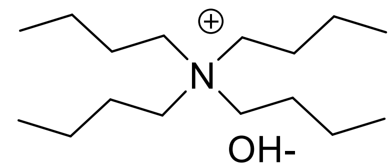


PHS/Sty/TBA
65/20/15 mol %



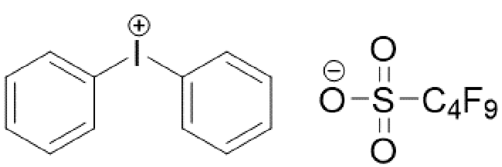
TBPI-PFBS

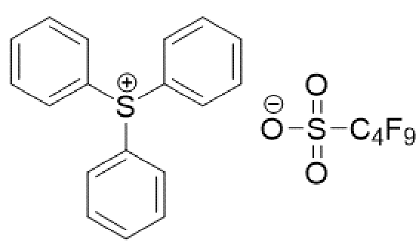
15 wt.%

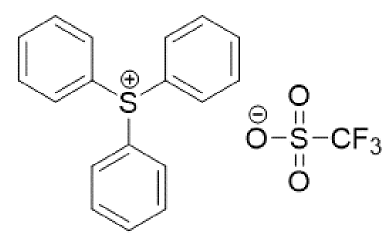


1.5 wt% TBAL

In some cases, we replace the PAG with equal weight (15 wt%) of these Photoacid Generators (PAGs):







*Higgins, Brainard et al.
JJAP *50*, 036504, **2011**