RLS Trade-Off: Questions about Molecular Size and Quantum Yield

Robert Brainard and Craig Higgins

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Outline

I. Introduction

II. Effect of Molecular Weight

III. Quantum Yield

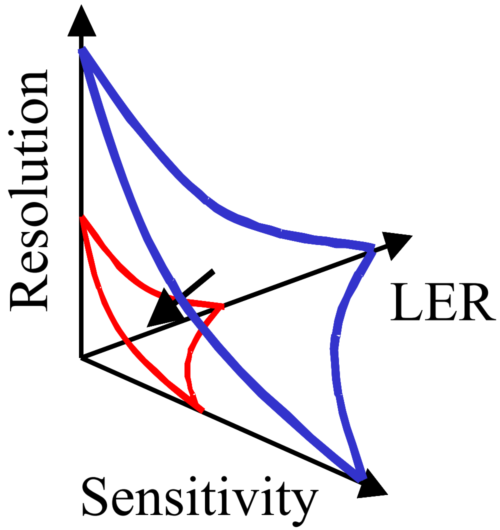
IV. Ultra High PAG Resists

V. Conclusions and Questions

RLS Trade-Off[1]

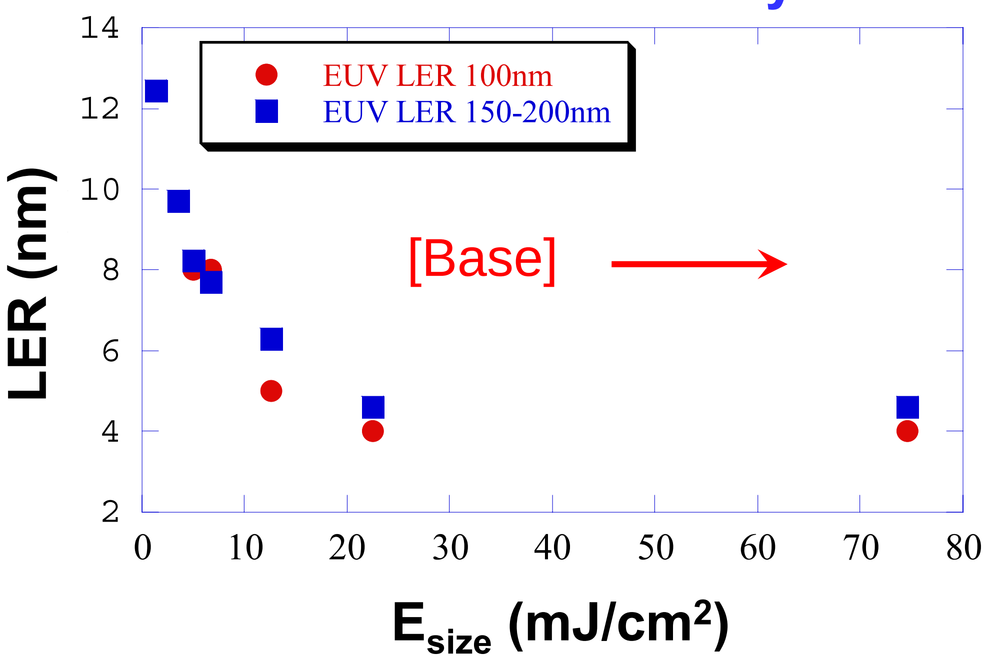
New materials/approaches are needed to "break-through" to new performance surfaces:

- Reduction in Polymer Molecular Weight
- Increasing Quantum Yield



Surfaces defined by Z-Parameter or K_{LUP}

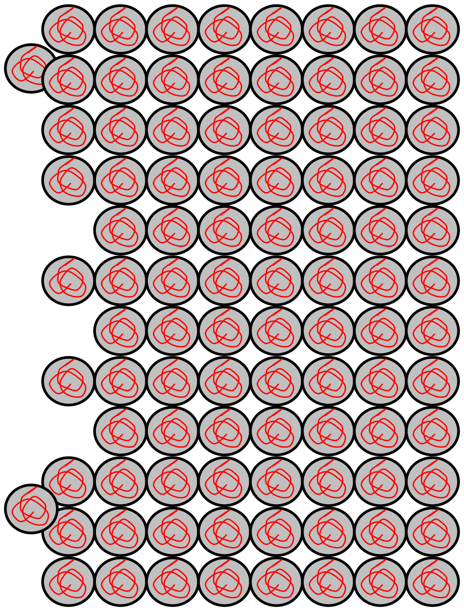
EUV-2D Base Study



(1) Brainard, DARPA Review 2002

II. Effect of Molecular Weight

Can we reduce LER by decreasing the size of the polymer?



In this conference:

61% of the papers
about new resist materials
are about Molecular Glasses

Polymer Radius of Gyration

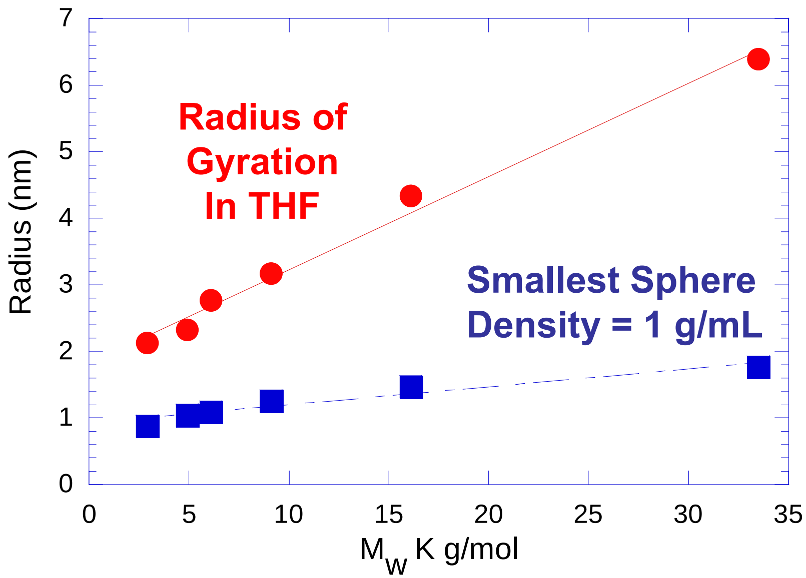
R_g = 3-4 nm
Diameter = 6-8 nm

II. Effect of Polymer M_w on LER:
EUV-2D using 0.088 NA in 2003[2]

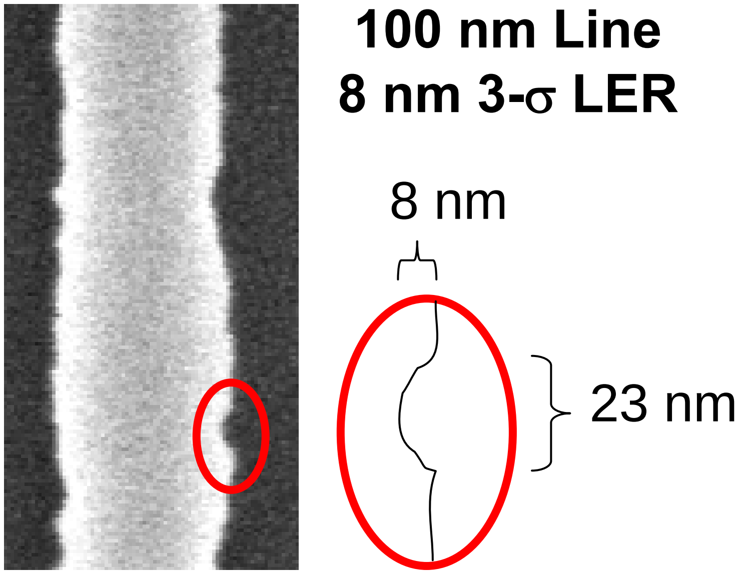
6 New Polymers M_w = 3-33 Kg/mol

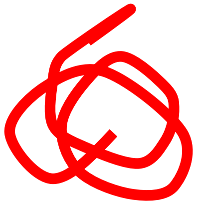
Changes in M_w will alter dissolution properties:

Vary [PAG] and [base]

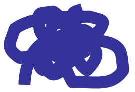


100 nm Line
8 nm 3-σ LER





R_g = 2-6 nm
Diameter = 4-12 nm

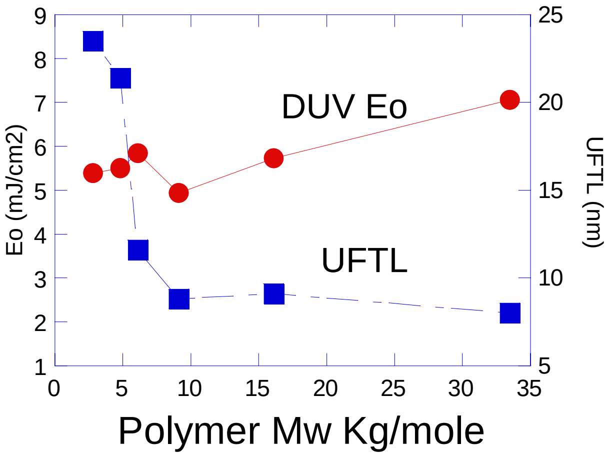


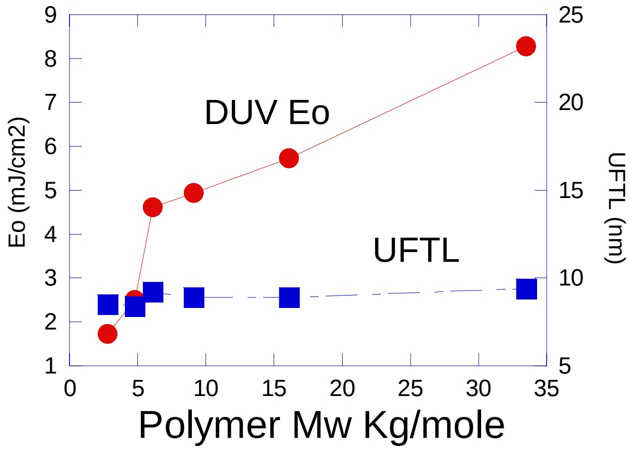
R = 0.9-1.8 nm
Diameter = 1.8-3.6 nm

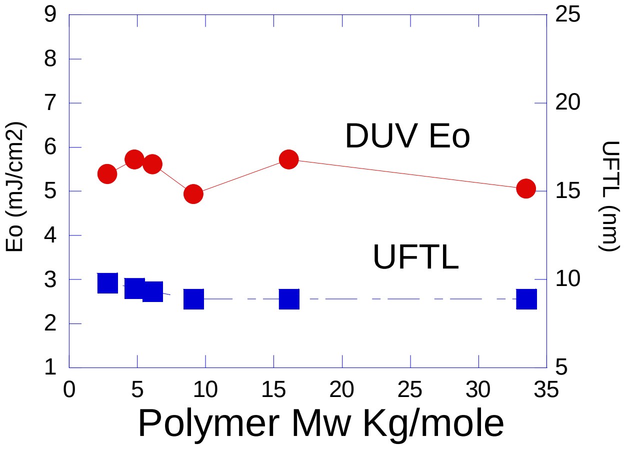
(2) Cutler & Brainard, SPIE 2003

[PAG] and [Base] Variations over Wide Polymer M_w Range

Round 1	Round 2	Round 3
6 Mws Changing UFTLs	6 Mws, 6 [PAG] Constant UFTL Changing Eo	6 Mws 6 [PAG], 6 [Base] Constant UFTL, Eo







UFTL =
Unexposed Film Thickness Loss or Dark Loss

M_W has no effect on LER

Round 1

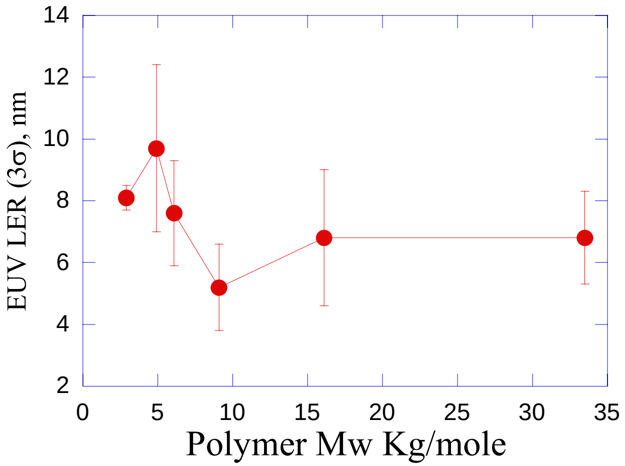
6 Mws
Changing UFTLs

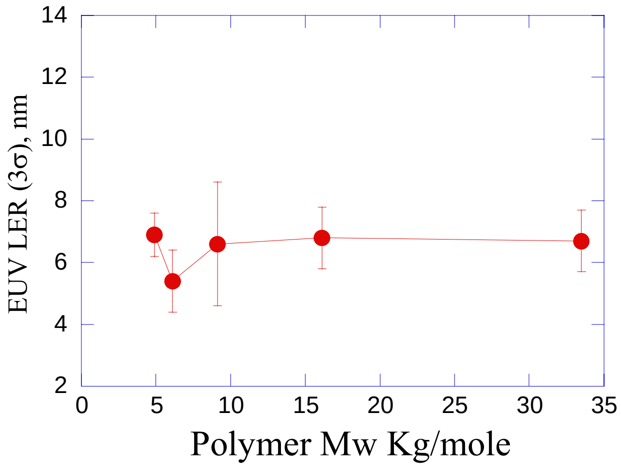
Round 2

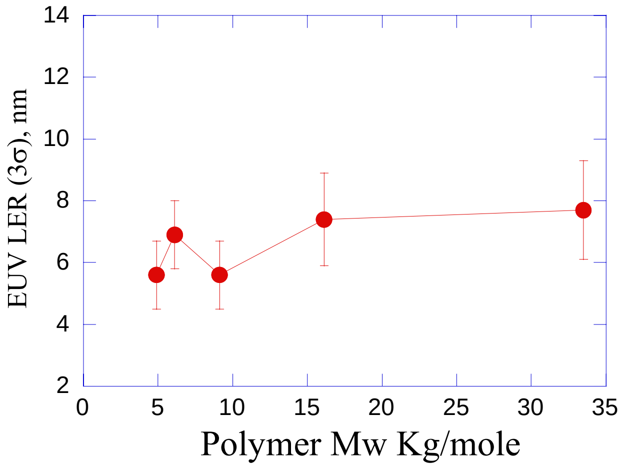
6 Mws, 6 [PAG]
Constant UFTL
Changing Eo

Round 3

6 Mws
6 [PAG], 6 [Base]
Constant UFTL, Eo





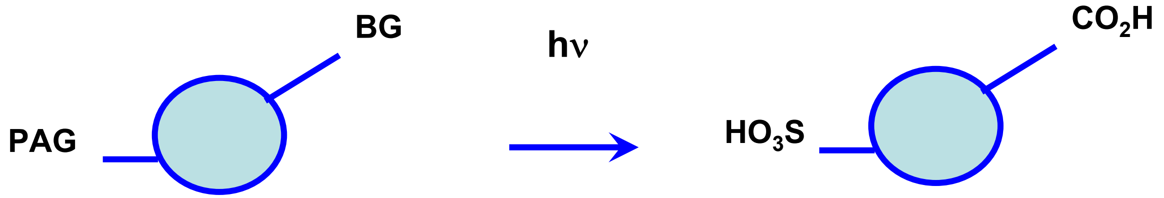


LER is *UNAFFECTED* by an order of magnitude change in polymer M_w when UFTL is held constant.

II. Molecular Glasses (MG)

Start Small

Stay Small



1) (My observation) Positive Molecular Glasses *DO NOT* show improved LER, unless they are fairly slow.

2) Negative resists look good → Because of polymer formation?

3) Champion resists appear to result from polymeric resists.

Questions about the role of Molecular Size:

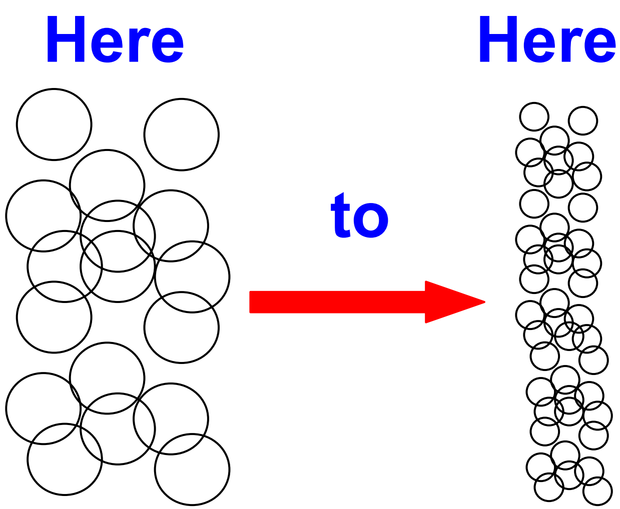
(1) Our polymer Mw work was performed in 2003 at 0.088 NA. Should it be repeated at 0.3 NA and/or IL?

(2) Should Molecular Glass Resists be included in a systematic study against polymeric resists?

3) Why do negative MG resists appear to give good LER/Sensitivity? Must polymers be involved for top performance?

III. Can we Beat RLS by Increasing Film Quantum Yield?

We propose that higher quantum yield will allow us to go from…



…with no penalty to sensitivity.

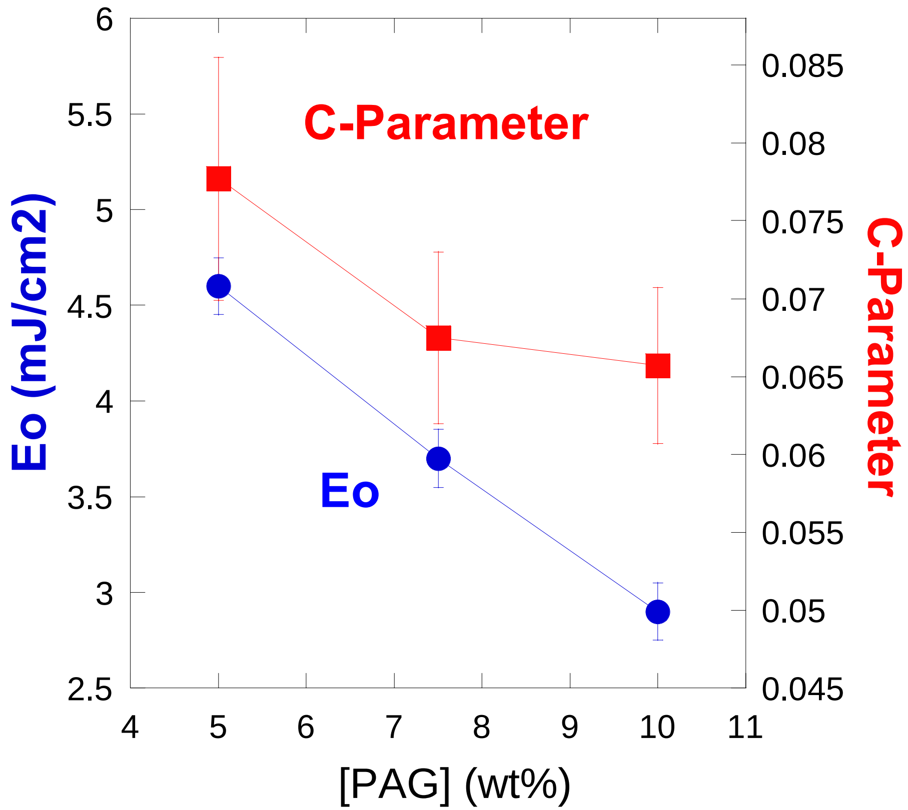
Gregg Gallatin:[3]

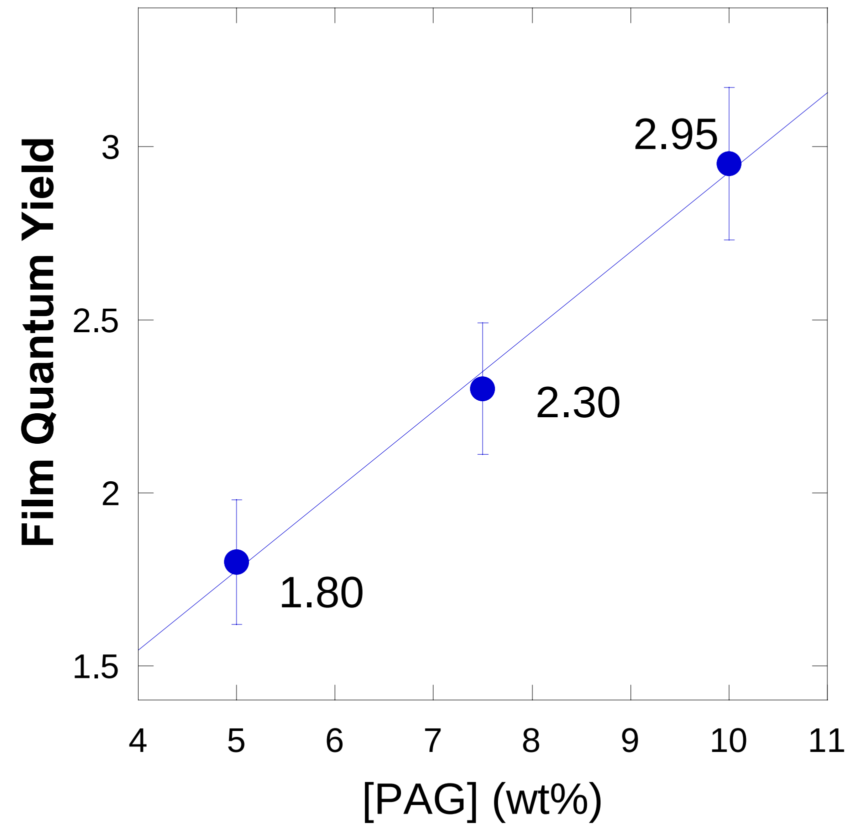
Increased quantum yield can break the RLS tradeoff

$$LER \propto \frac{1}{\sqrt{\alpha\, Q\, E\, R^{3}}}$$

$$\text{Film Quantum Yield} = \frac{\text{Number of Acids Generated in the Film}}{\text{Number of Photons Absorbed in the Film}}$$

Quantum Yield Increases with PAG Concentration





Used Szmanda Base-Titration Method

 # Acids Generated $= [PAG](1 - e^{(-CE)})(6.02 \times 10^{23})$

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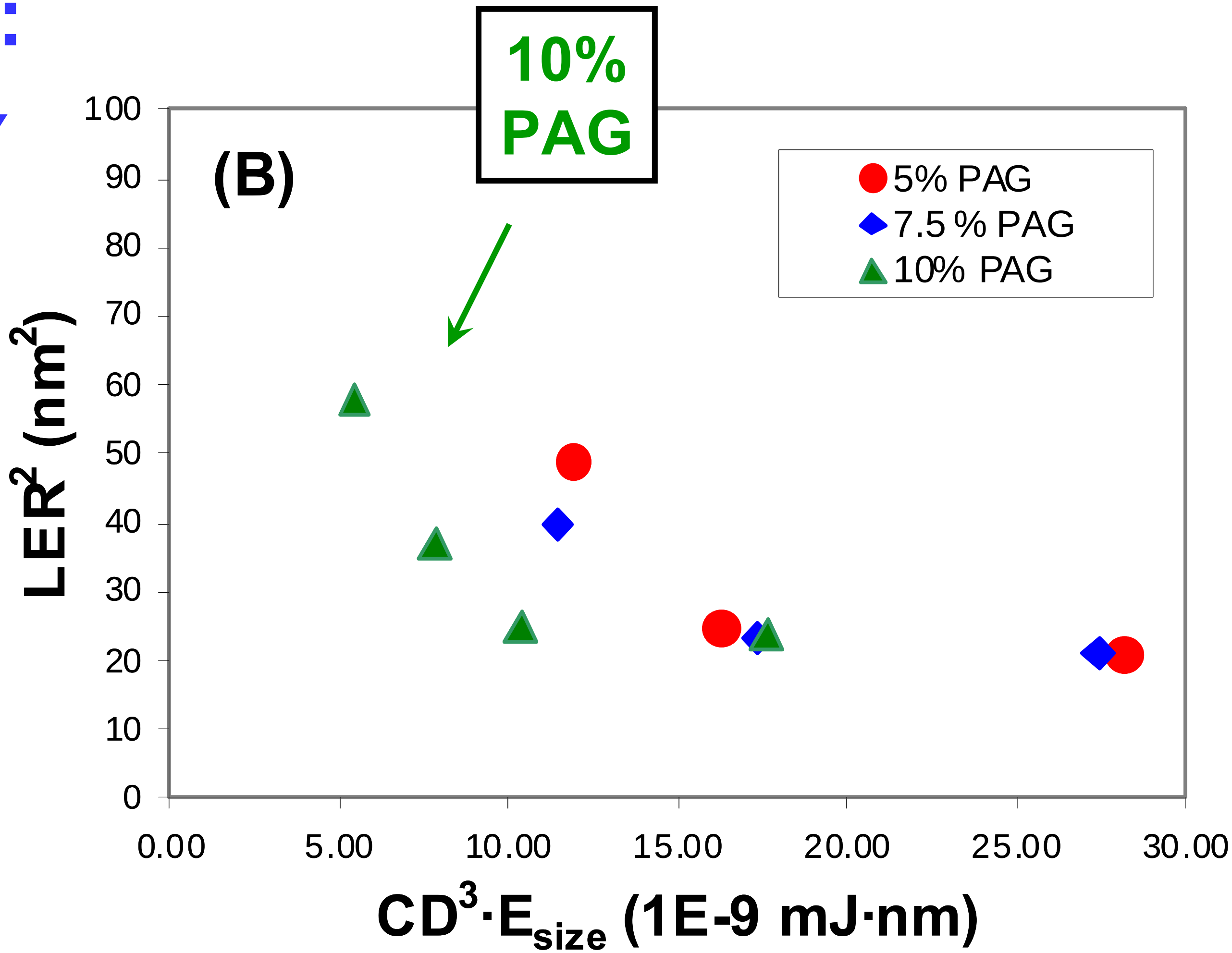
State University of New York

Higher [PAG]:

- **Higher FQY**
- **Lower Z[3,4]**



(3) Gallatin, EUV 2007 Symposium

(4) Wallow, Higgins and Brainard, SPIE 2008

How far can we push [PAG]?

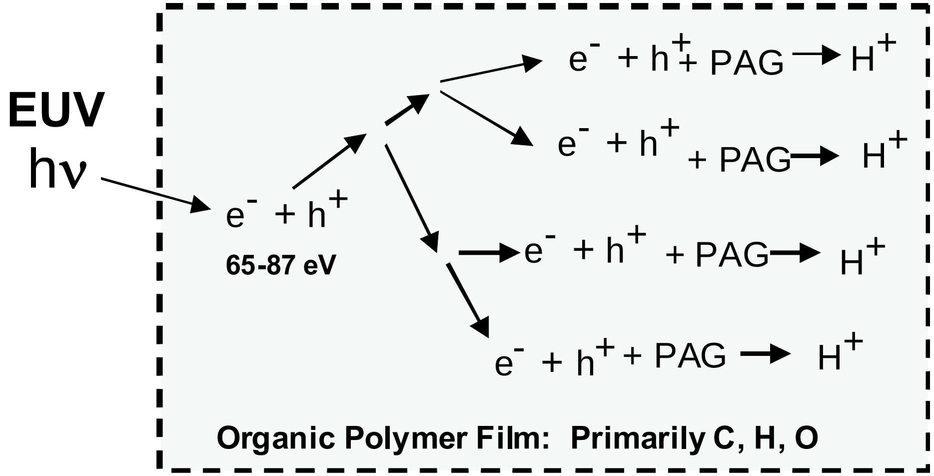
IV. Ultra High PAG Resists

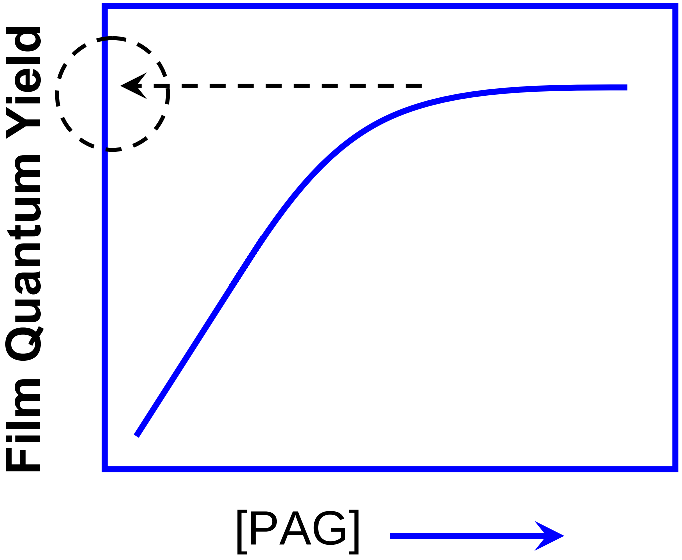
Question #1: How high can we make FQY?

Question #2: Do we improve RLS?

Question #3: Can we determine how many photoelectrons are made?

PAG + e^- → H^+

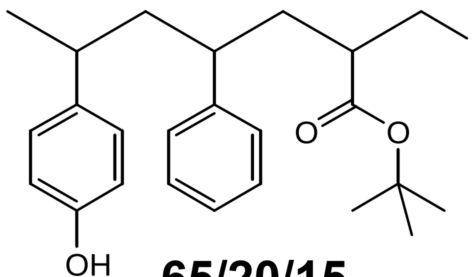




IV. High PAG Resist Platforms for FQY and Imaging RLS Study

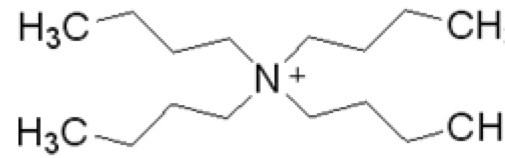
Resist Formulations

Polymer



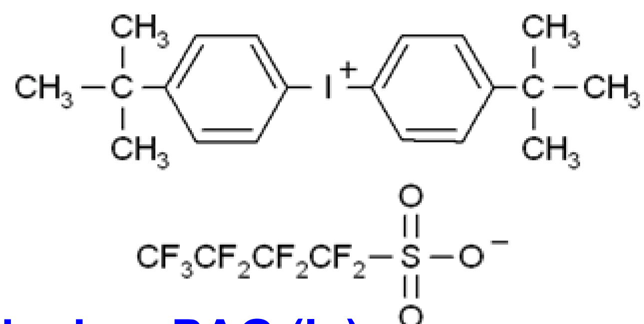
65/20/15

Base
TBAH

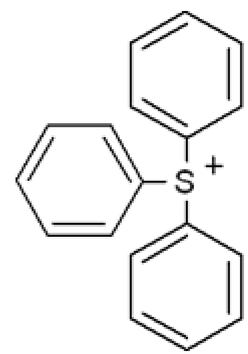


OH^-

Photoacid Generator (PAG)



Iodonium PAG (I+)
DTBI-PFBS

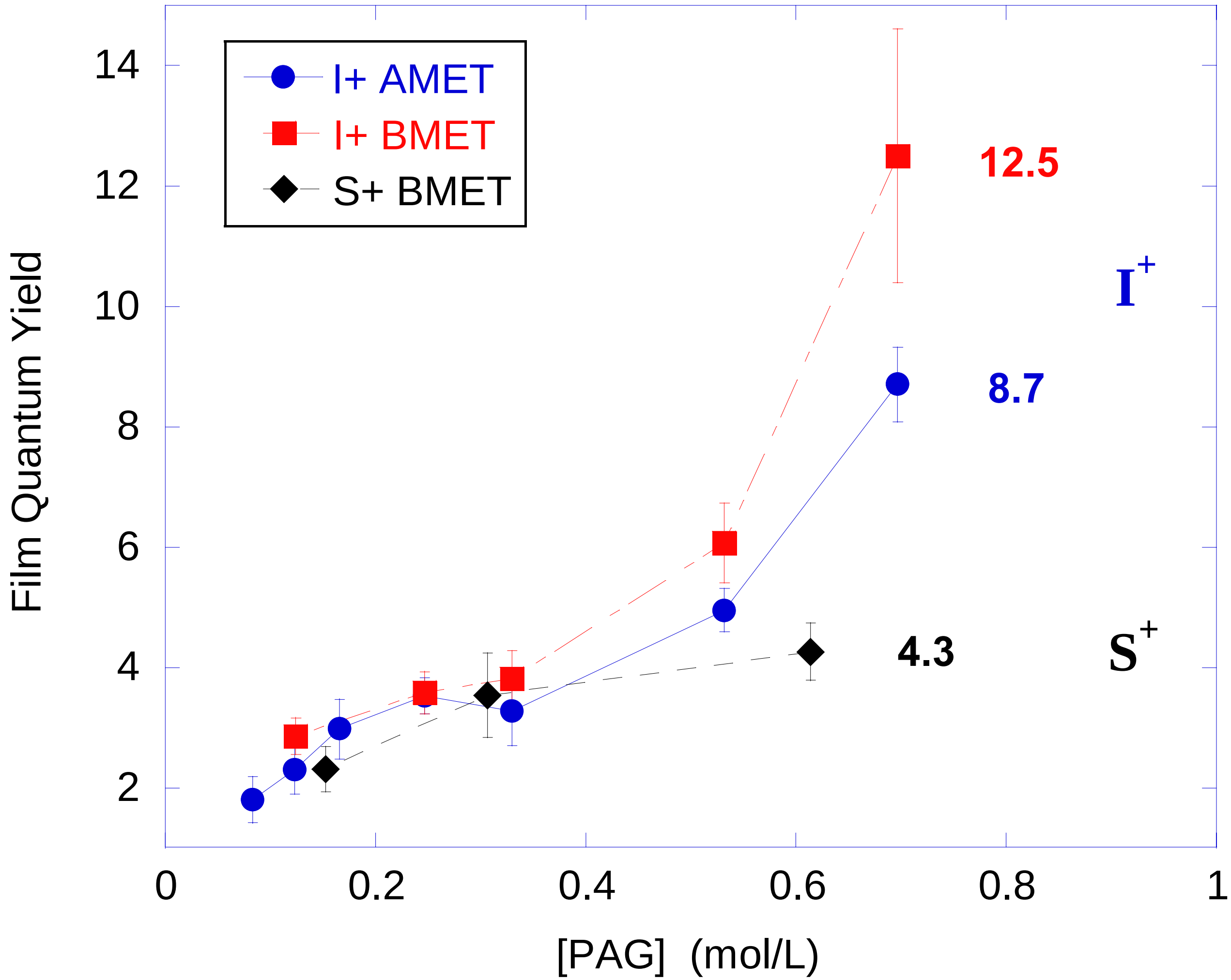


$CF_3CF_2CF_2CF_2SO_3^-$

Sulfonium PAG (S+)
TPS-PFBS

(5) Hassanein, Higgins, Thackeray, Brainard et al SPIE (2008)

Film Quantum Yields *vs.* [PAG]

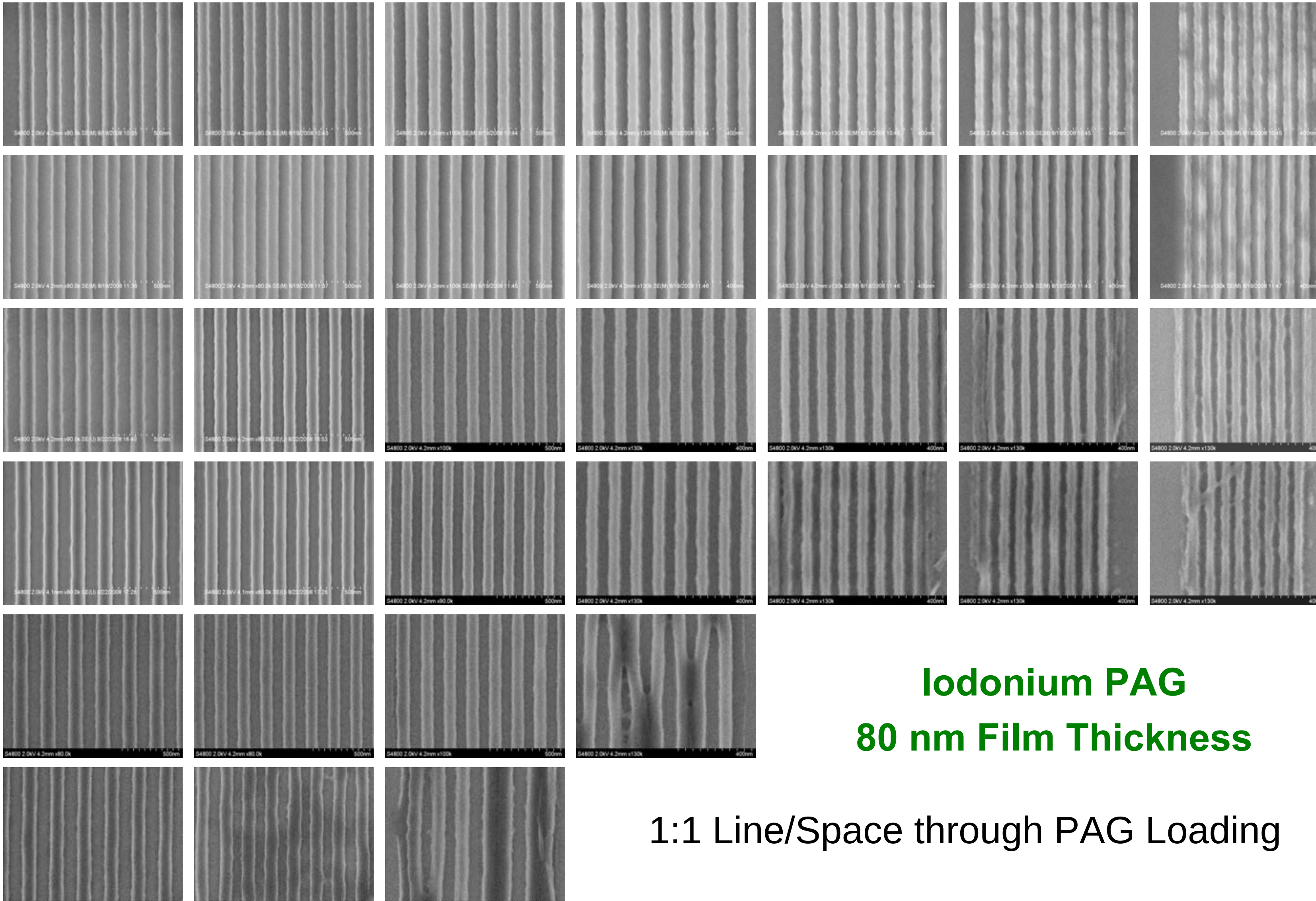


I^+ FQY =
~10 H^+ / EUV hν

S^+ FQY =
~4 H^+ / EUV hν

(6) **Brainard, Higgins et al.**, Journal of Photopolymer Science and Tech. (2008)

Resolution of Ultra-High PAG Resists

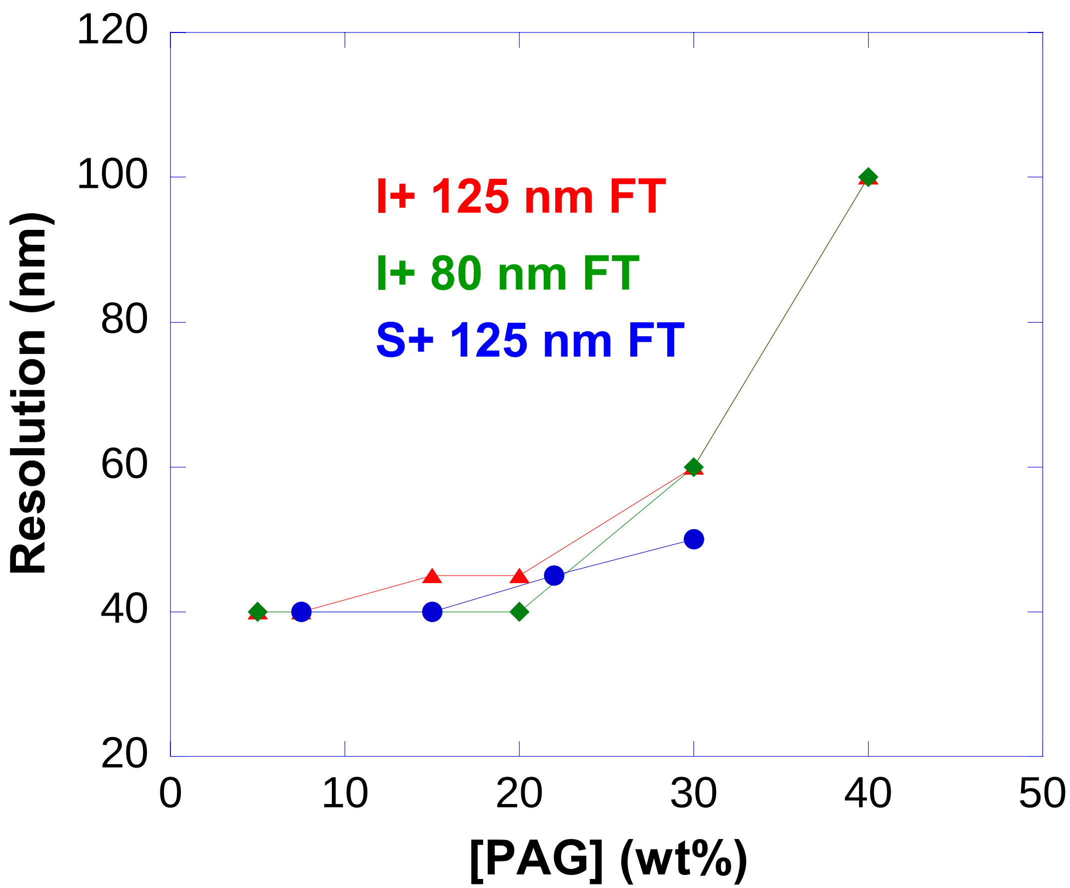


Iodonium PAG

80 nm Film Thickness

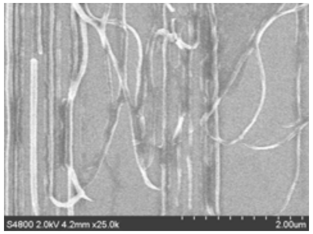
1:1 Line/Space through PAG Loading

Resolution of Ultra-High PAG Resists

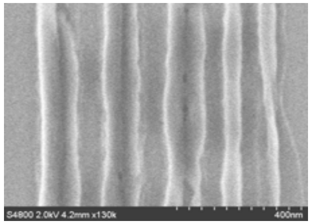


Patterning Issues at Very High PAG Loadings:

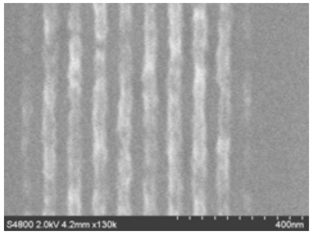
I+ 125 nm FT:
- Adhesion Failure



I+ 80 nm FT:
- Pattern Collapse

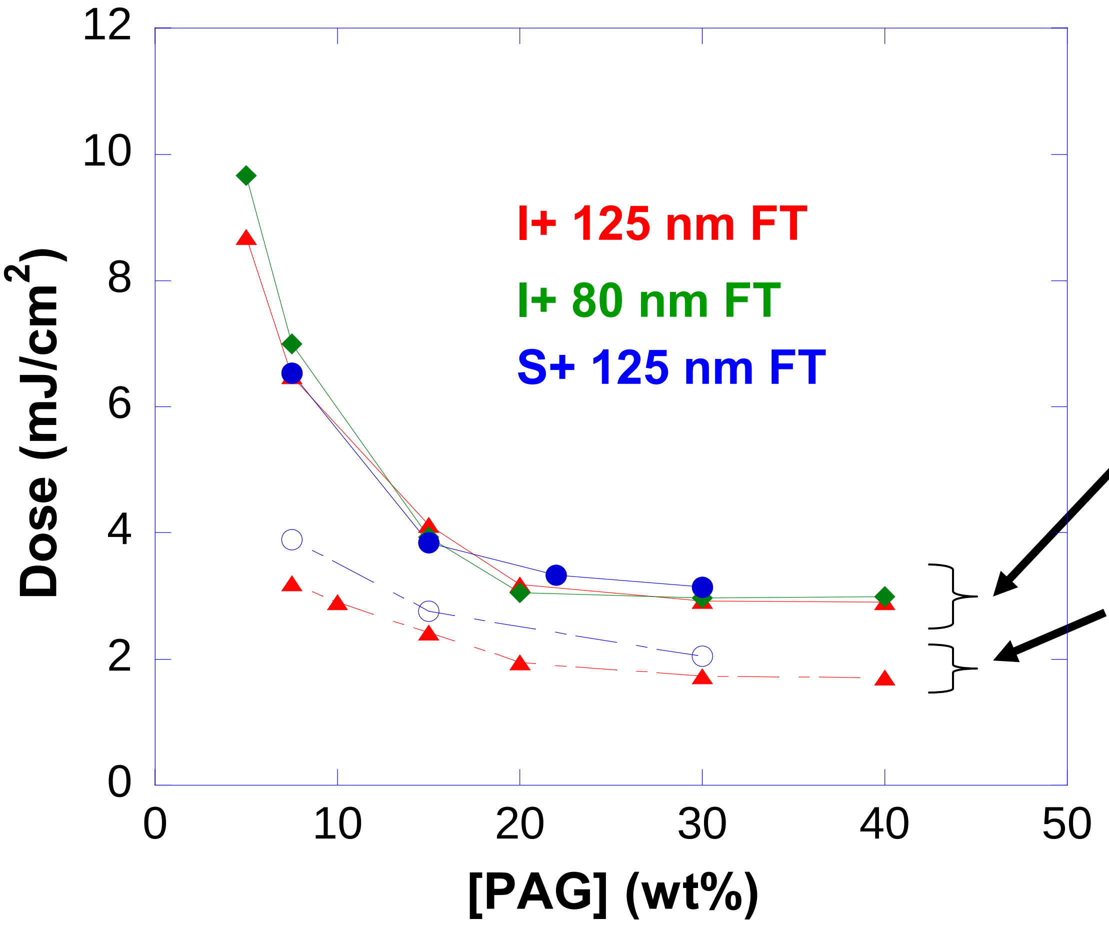


S+ 125 nm FT:
- Top Loss



Resolution is consistent, then degrades at > 20% PAG

Sensitivity of Ultra-High PAG Resists



Esize (100 nm L/S) Data:

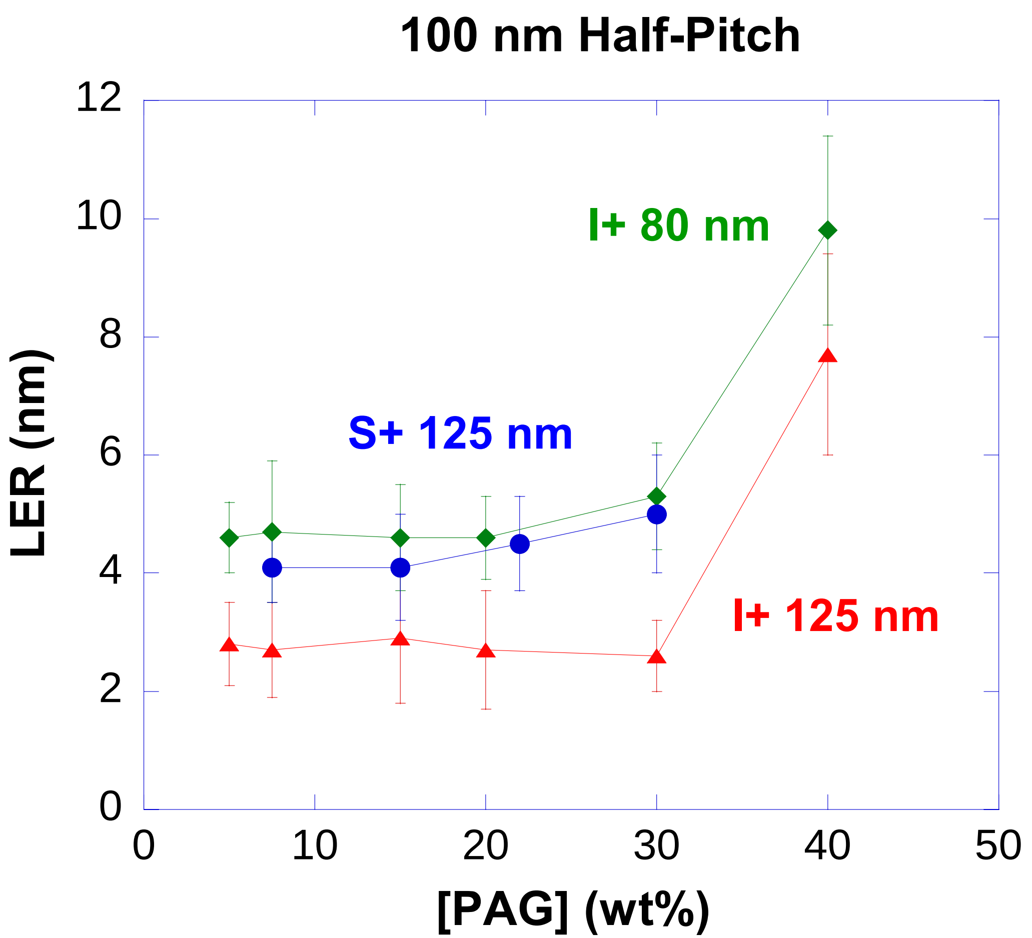
- Saturated at 15-20% PAG

Eo Data:

- Saturated at 15-20% PAG

All data obtained from BMET

LER of Ultra-High PAG Resists

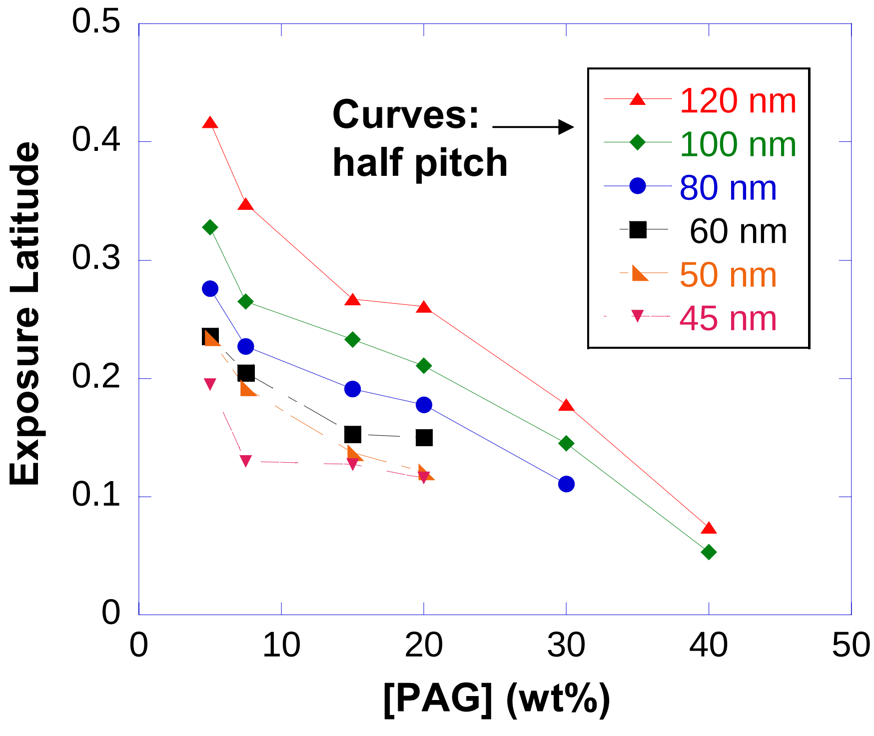


LER is consistent, then degrades > 30-40 wt% PAG

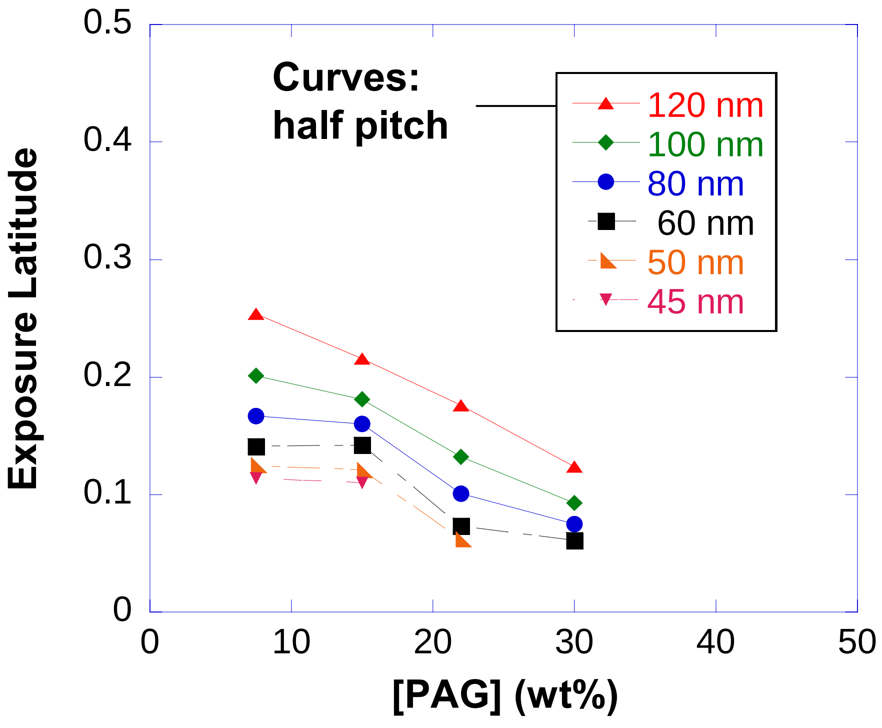
Exposure Latitude, Acid Diffusion and K_{LUP}

Exposure Latitude *decreases* with [PAG]

Iodonium PAG

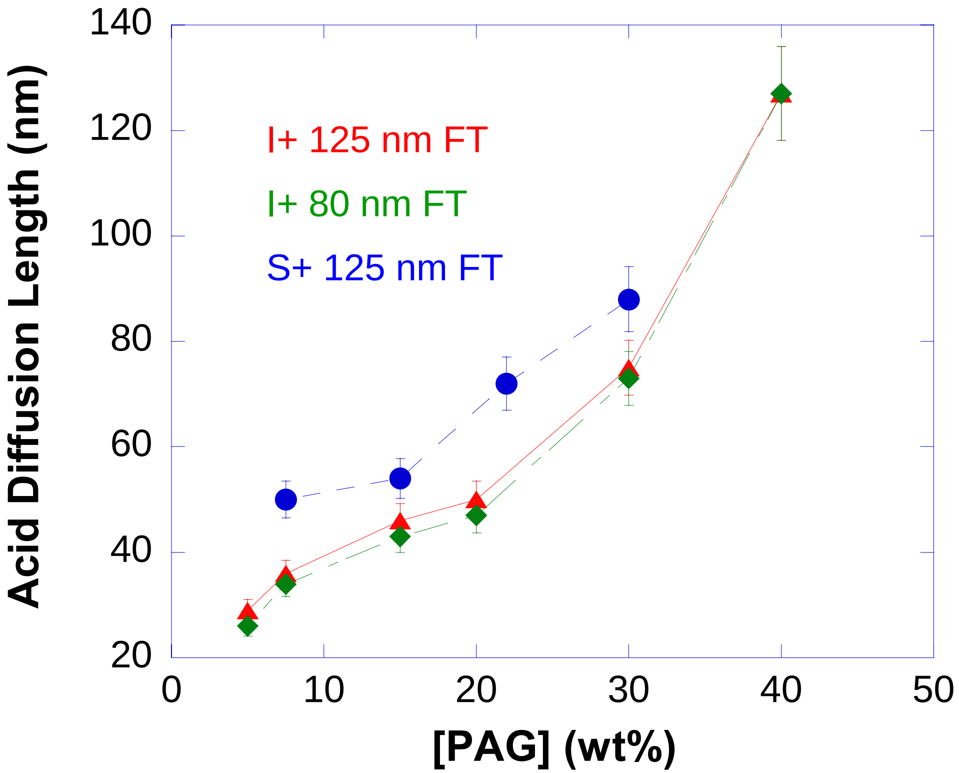


Sulfonium PAG



All Data at 125 nm Film Thickness

Acid Diffusion *Increases* with [PAG]



Acid diffusion was determined from exposure latitude using the following method:[7]

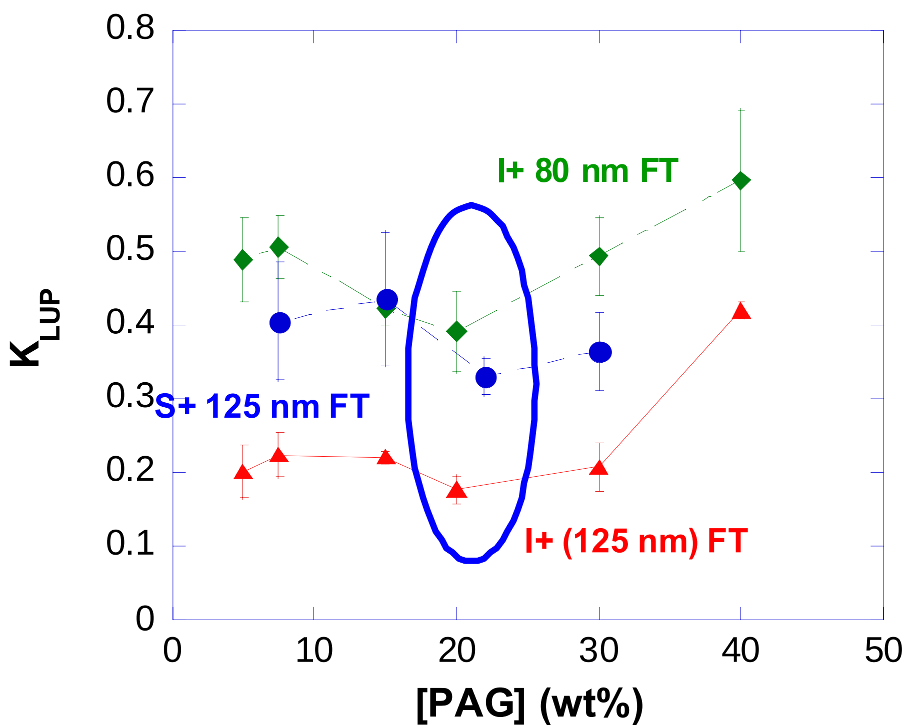
$$MTF_{DIFF} \propto \frac{EL}{NILS}$$

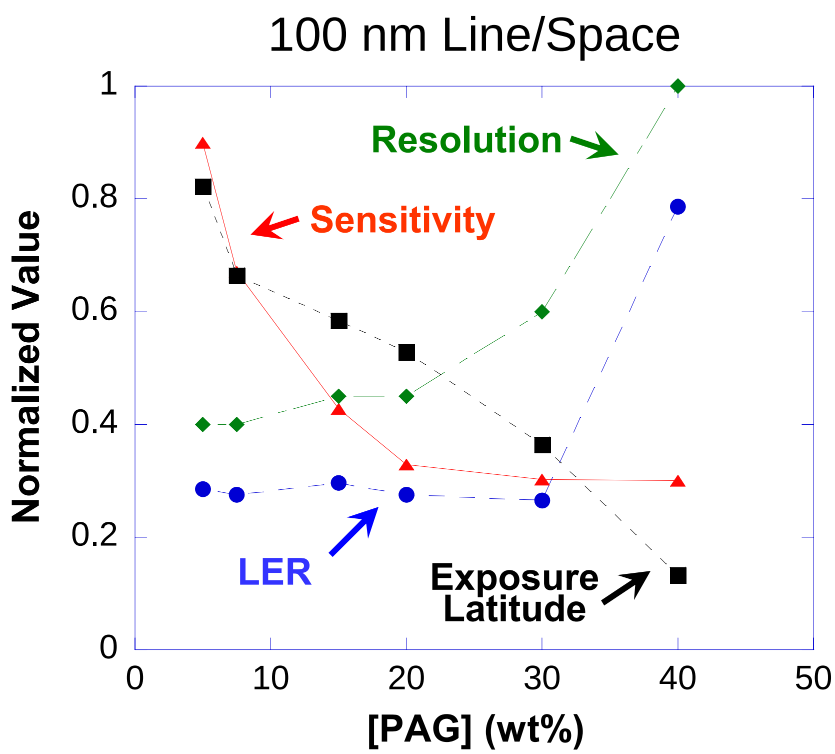
$$MTF_{diff} = \frac{1 - \exp\left(-2\pi^2 \left(\frac{L_D}{p} \right)^2 \right)}{2\pi^2 \left(\frac{L_D}{p} \right)^2}$$

Why does L_D increase for increasing PAG?

(7) Van Steenwinckel, Lammers, Koehler, Brainard, and Trefonas JVST (2005)

Ultra-High PAG Resist Performance: K_{LUP}





Best performance is at ~20% PAG:

Sensitivity Gains are Cancelled by Acid Diffusion Increases

V. Conclusions and Additional Questions

LER and Resolution Appear to be Flat with [PAG], but then degrades at > 30% PAG.

Sensitivity improves, but then flattens out.

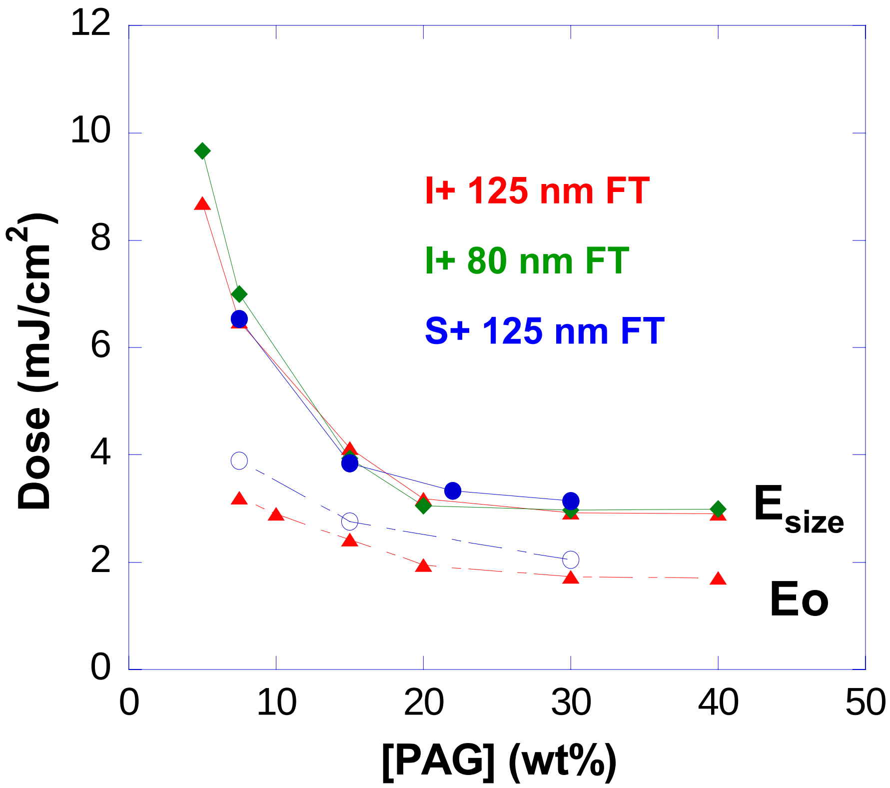
EL decreases/ diffusion increases with [PAG]

The KLUP analysis shows that the sensitivity gains are cancelled by the increased diffusion.

Why do the improvements in sensitivity stop?

Style borrowed from Chris Anderson

Why do the improvements in sensitivity stop?



a) Base is being overwhelmed

b) Used all available electrons (but why the high FQY for I+?)

c) Not enough deblocking groups

Why does diffusion increase with [PAG]?

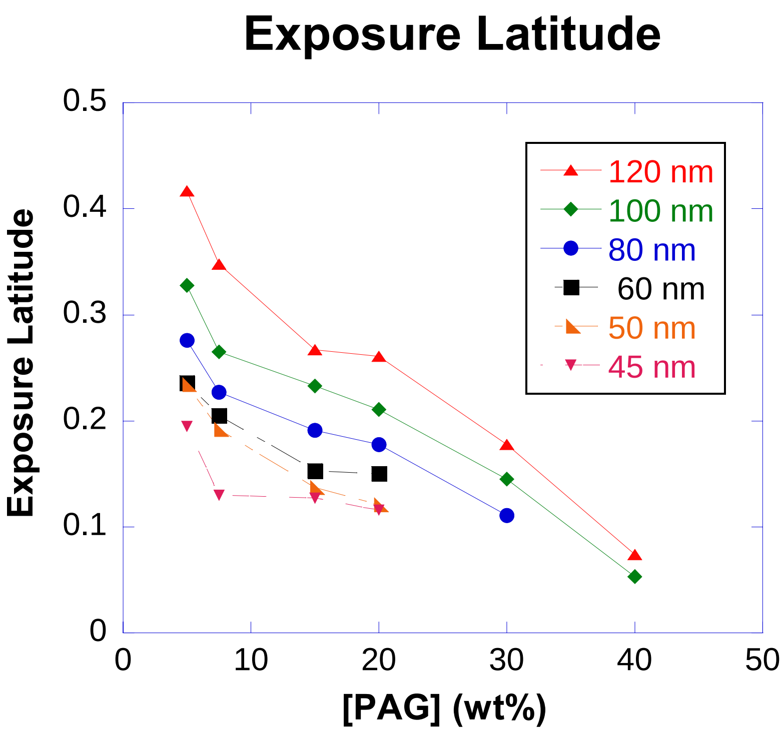
Why does diffusion increase with [PAG]?

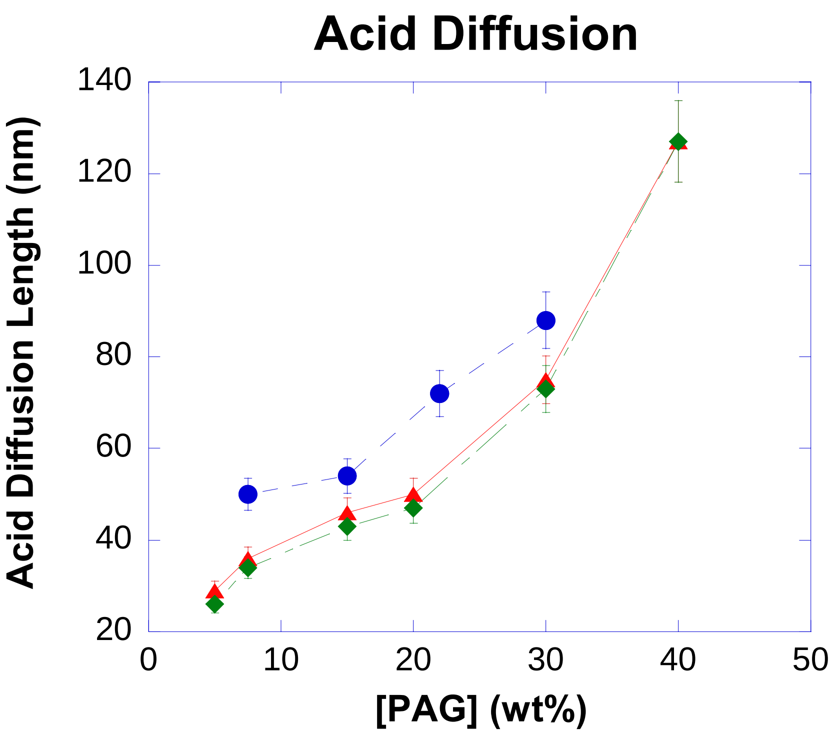
a) Film T_g may change

b) Acid solubility parameter may change

c) More free volume for acid to diffuse

d) Base is being overwhelmed





V. Planned and Possible Future Work

1) Verify Film Quantum Yield Results

(SEMATECH Funded – In Collaboration with G. Denbeaux)

a) Use direct method for determining optical density

b) Use acid sensitive dye to directly measure acid generation

2) Test Low Diffusion Material and Processes

a) Lower PEB temperature

Increased generated acids no longer need to diffuse as far

b) Increase TBA deblocking group in polymer

[TBA] may be limiting deblocking rate in high [PAG]

Optimize surface for better adhesion

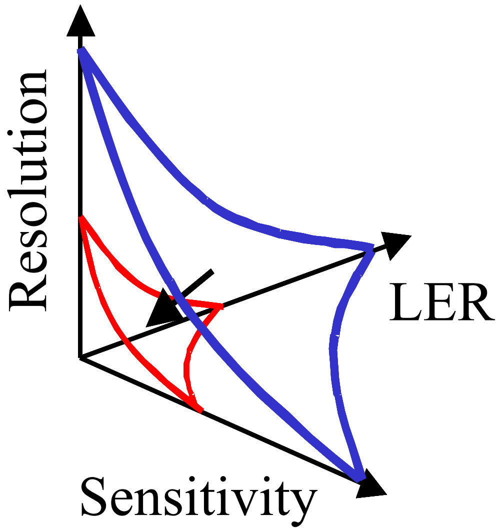
Will Smaller Molecules give better LER?

V. Possible Future Work

3) Side-by-side comparison of polymeric and MG resists using:

- 10 X range in Polymer Mw
- Best MG available
- High Resolution tools (BMET 0.3 NA, PSI IL)
- Apples-to-Apples comparison (K_{LUP} or Z Parameter)

Break-Through Strategies: An Editorial



Surfaces defined by Z-Parameter or K_{LUP}

Higher Absorption

Molecular Glass (Pos)

Molecular Glass (Neg)

Higher Quantum Yield

High E_{RED} PAGs

Ultra-High PAG

Anisotropic Diffusion

Acknowledgements

CNSE:

Craig Higgins

Srividya Revuru

Alin Antohe

Greg Denbeaux

Richard Matyi

Rohm and Haas:

Jay Machevich

Charlotte Cutler

Jim Thackeray

Peter Trefonas

Kathleen Spear

Applied Math Solutions:
Gregg Gallatin

SEMATECH:

Jacque Georger

Kim Dean

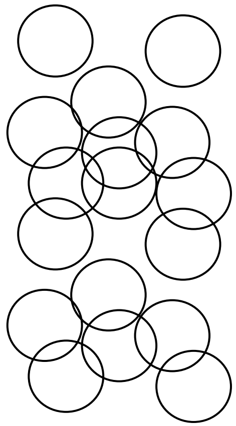
Andrea Wüest

Berkeley:

Patrick Naulleau

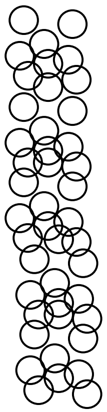
Chris Anderson

Future Work



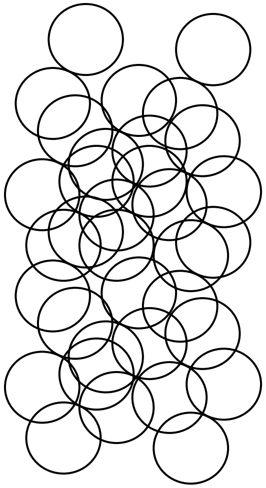
We propose that higher quantum yield will allow us to improve resolution, LER…

…with no penalty to sensitivity.



This Work

- Increased the # of Acids
- Saturated Sensitivity Improvement
- Used Constant Process

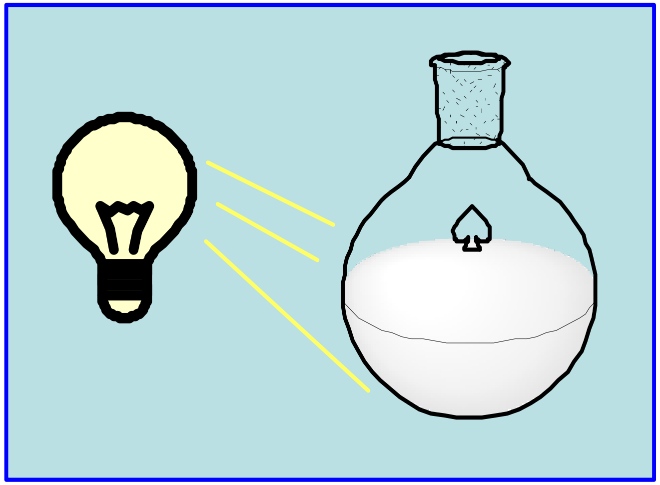


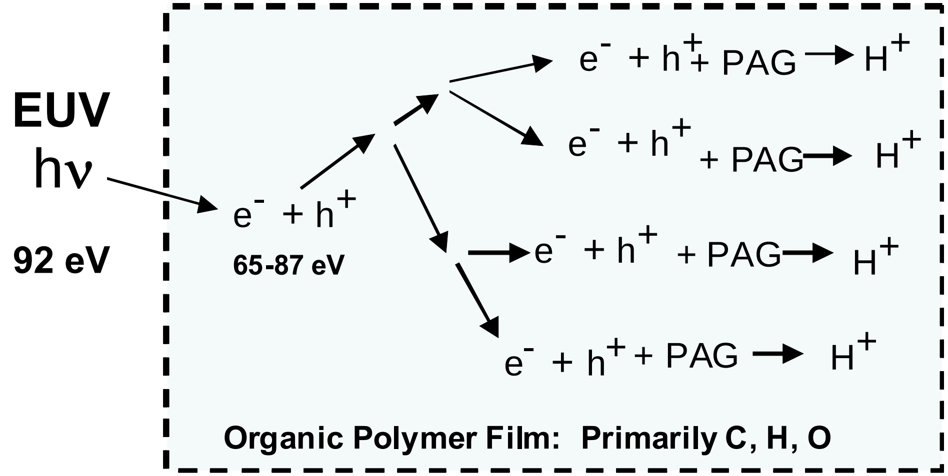
Future Work:

Increased generated acids no longer need to diffuse as far

What is Film Quantum Yield?

Traditional Quantum Yield *vs.* Film Quantum Yield





Experiments are done in transparent solvents

Light is primarily absorbed by single molecules

QY < 1

Light is absorbed by everything in the film.

Multiple electrons are made.

FQY of Acid > 1

$$\text{Quantum Yield} \equiv \frac{\text{Moles of Product}}{\text{Moles of Photons Absorbed}}$$

$$\text{Film Quantum Yield} \equiv \frac{\text{Moles of Acids Generated in the Film}}{\text{Moles of Photons Absorbed by the Film}}$$