ROHM AND HAAS ELECTRONIC MATERIALS

Is It Shot Noise or Is It Chemistry?

Chuck Szmanda

Why Are We Talking About Shot Noise? Consider 1 mJ/cm^2

193 nm	**13.4 nm**	**193 nm**	**13.4 nm**
Photons/cm^2	Photons/cm^2	Photons/nm^2	Photons/nm^2
9.7e14	6.8e13	9.7	0.68

- So DN/N is potentially significant relative the number of incident photons.
- This could be a catastrophe…
- …but the story doesn't end here.

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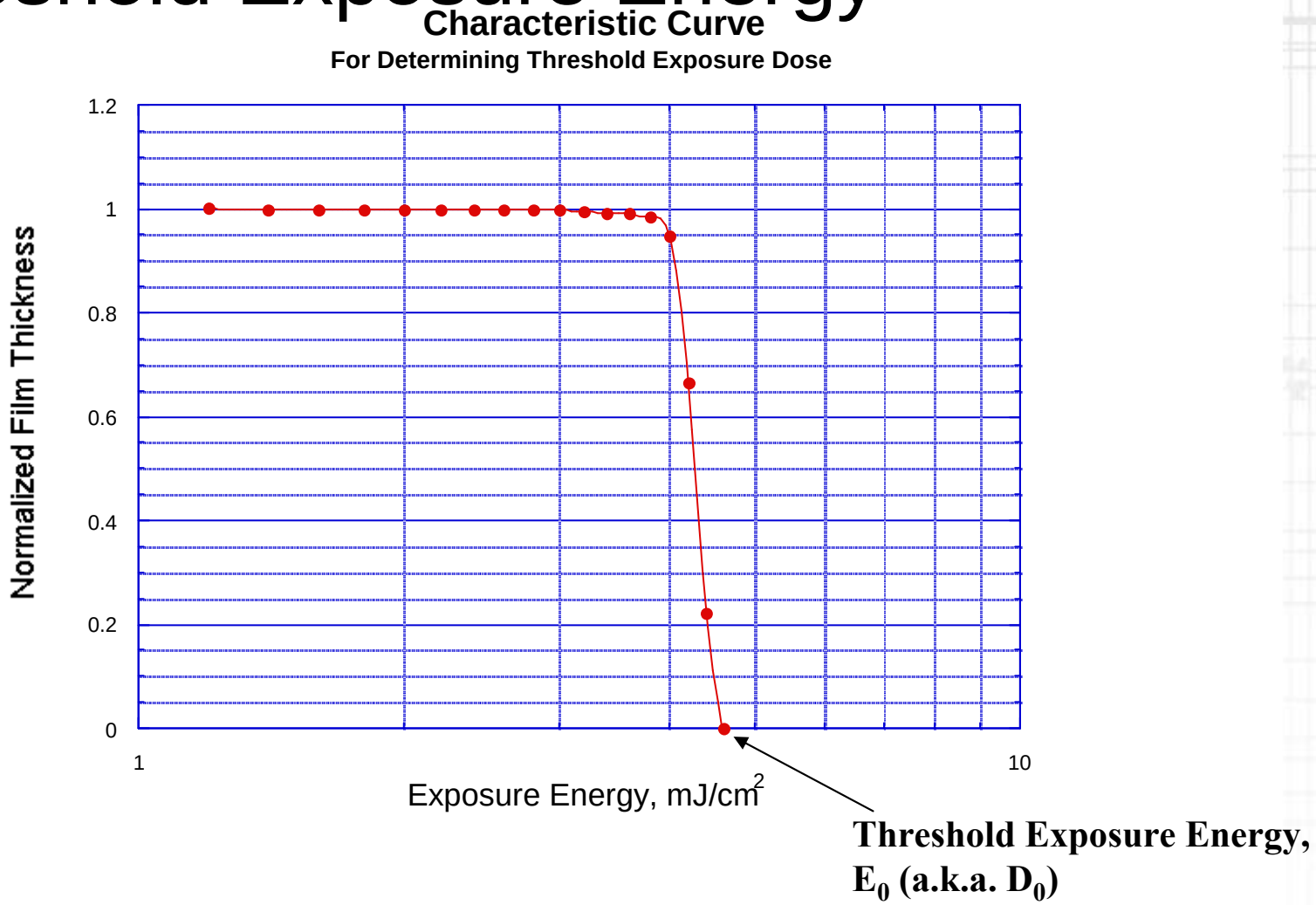
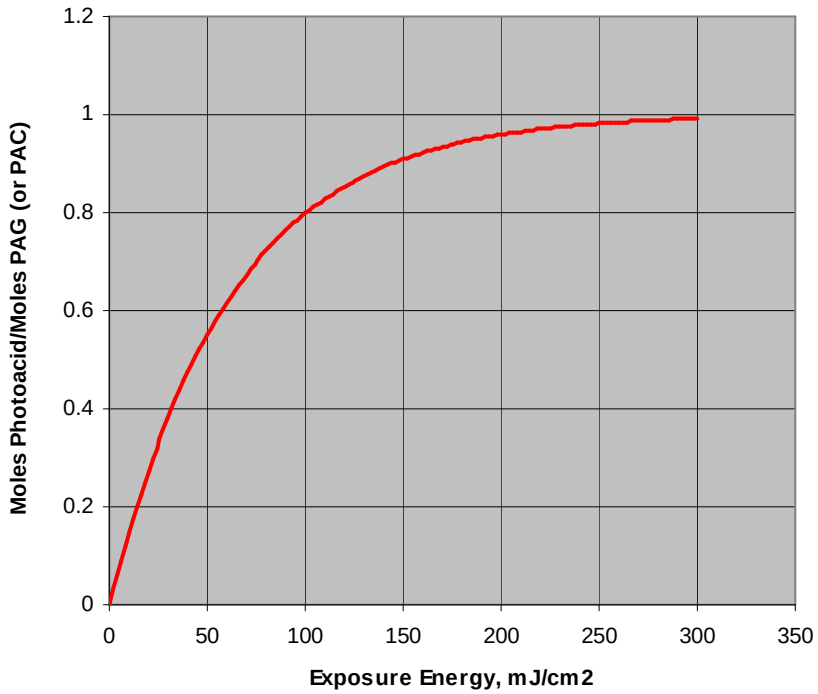
What Happens When Base Is Added to the Resist?

- Adding base (say, 1% mol/mol based on PAG) will increase the threshold exposure dose by Δ.
- Adding 2% mol/mol will increase the threshold exposure dose by $2*\Delta$.
- Etc. up to about 10%
- Two assumptions were made:
  - First order kinetics
  - $e^{-x} \sim 1-x$ for small x. So we must make it so.
- This is just like the tried and true “standard addition method” from analytical chemistry – but run in reverse.

Threshold Exposure Energy



What is The C Parameter?



$$\frac{d[PAG]}{dt} = -I \times C \times [PAG]$$

$$\frac{d[PAG]}{dE} = -C \times [PAG]$$

$$[PAG] = [PAG]_0 \times e^{-C \times E}$$

$$[Photoacid] = [PAG]_0 \times (1 - e^{-C \times E})$$

- One follows diazonaphthoquinone photolysis by monitoring absorption.
- PAGs usually do not bleach or darken upon exposure in a manner characteristic of acid production.
- It is necessary to measure actual acid output with PAGs by another method.

C Parameters are First Order Rate Constants… … and Cross Sections

- cm^2/mJ
- $nm^2/photon$
- $cm^2/\mu C$
- $nm^2/electron$
- nm^2/ion

Determining C

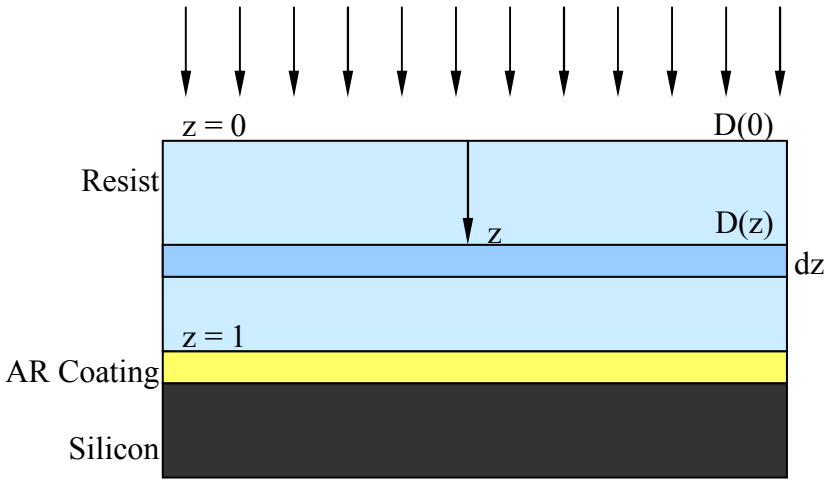
When There is Attenuation by the Film Stack

• Resist on AR coating (if necessary). Reflection from the resist-AR coating interface should be < 0.5 %.

• Radiation makes essentially one pass through the film.

• Variables:
  • z = normalized resist thickness.
  • E(0) = exposure energy at the top of the resist.
  • E(z) = exposure energy at z.

• Goal: compute total acid by integrating through the film



Theory of the Method

- PAG photolysis is first order.

$$\frac{dP}{dE} = -C \cdot P \quad \Rightarrow \quad P = P_0 \cdot e^{-C \cdot E} \quad \Rightarrow \quad A = P_0 \cdot (1 - e^{-C \cdot E})$$

Initial PAG concentration

- Integrate through the film to obtain the total acid. Include attenuation due to absorption.

$$A_t = P_0 \int_0^1 (1 - e^{-C \cdot E(z)}) dz = P_0 \int_0^1 (1 - e^{-C \cdot E(0) \cdot e^{-a \cdot z}}) dz$$

- Simplify: $e^{-x} \sim 1 - x$. True for $x \leq 0.1$.

$$A_t = P_0 \int_0^1 (1 - e^{-C \cdot E(0) \cdot e^{-a \cdot z}}) dz \approx P_0 \int_0^1 (C \cdot E(0) \cdot e^{-a \cdot z}) dz$$

- The acid concentration is linear in E(0).

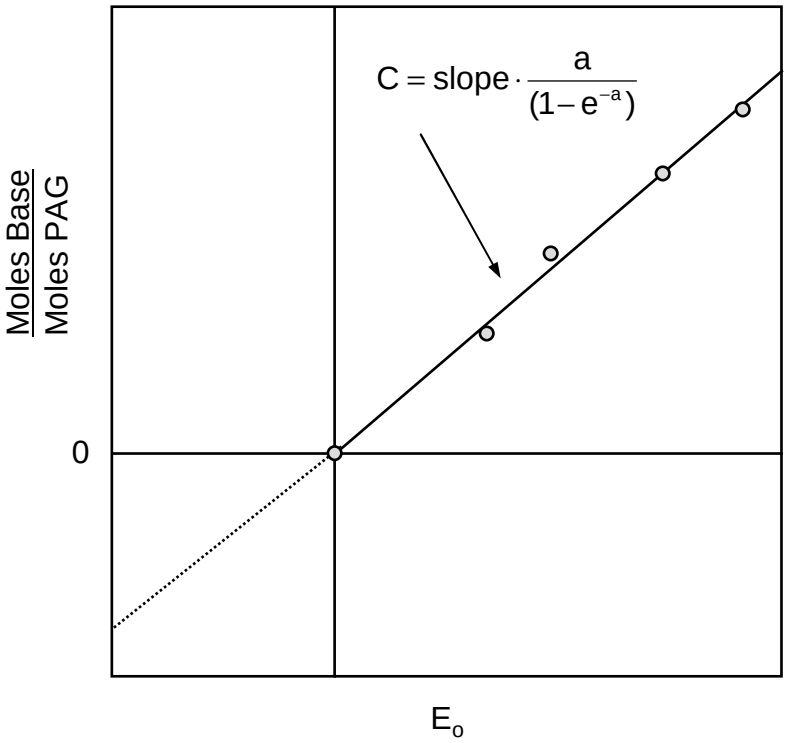
$$A_t = P_0 \cdot E(0) \cdot C \cdot \frac{(1 - e^{-a})}{a} \qquad A_n = E(0) \cdot C \cdot \frac{(1 - e^{-a})}{a}$$

Normalized acid concentration

- To determine C, find the slope and correct for absorption.

$$C = \text{slope} \cdot \frac{a}{(1 - e^{-a})}$$

Method of Determining the First Order Rate Constant



- Measure E_o for various Base Loadings
- Keep the mole ratio < 10%
- Plot the data as shown.
- The slope is the uncorrected C Parameter.
- Our technique is very much like the "standard addition method."
- The negative of the intercept is the threshold acid concentration.

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What is the Average Distance Between Acid Molecules?

- [A] = P0*(1-exp(-C*E))
- Exposure = 30 mJ/cm^2 we have an exposure of about 10 mJ/cm^2 at the mask edge. For TPS-OTf, C = 0.055 cm^2/mJ. P_0 = 50 μmol/cm^3.
- [A] = 21.2 μmol/cm^3 = 0.013 acid molecules nm^3.
- So, the average distance between acid molecules is about 4.3 nm.

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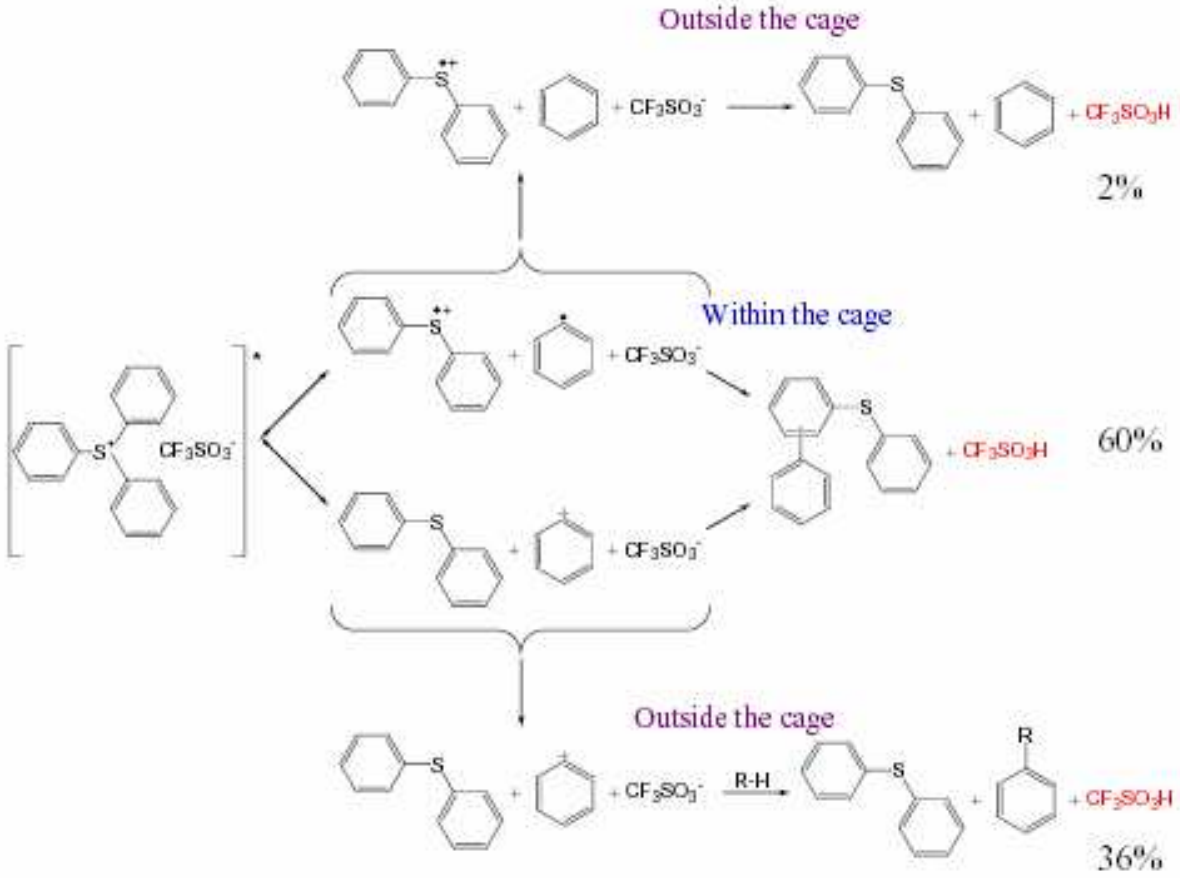
Onium PAG Function

Heterolysis and Homolysis of PAGs at 248 nm*



- Most of the reactions occur within the cage.
- Recombination plays a significant role in limiting acid generation.
- Heterolysis and homolysis lead to similar products within the cage, but different products outside the cage.
- Iodonium PAGs should give similar - but not identical results.

*See J. L. Dektar and N. P. Hacker, J. Am. Chem. Soc., **112,** (1990), 6004. For numerical data on heterolysis vs. homolysis see S. Tagawa, S. Nagahara, T. Iwamoto, M. Wakita, T. Kozawa, Y. Yamamoto, D. Werst and A. Trifunac, Proc. SPIE Adv. Resist Technol. and Processing, **3999,** (2000), 204.

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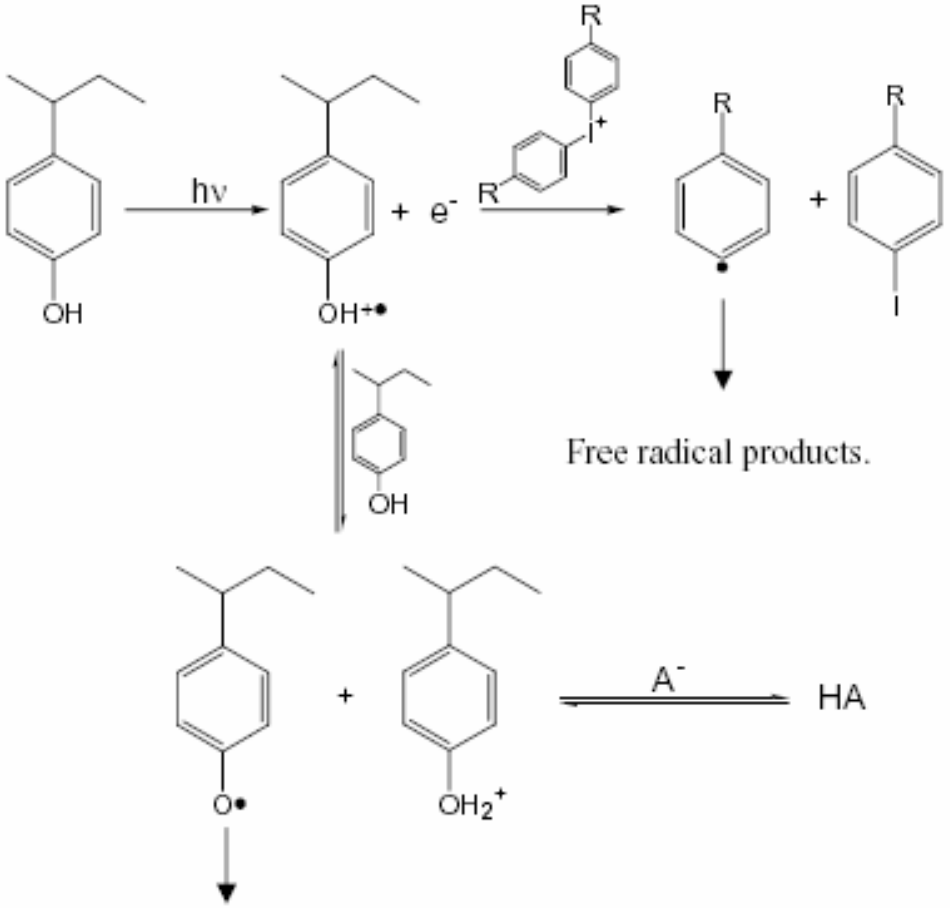
Onium PAG Function

Mechanism based on radiation chemistry* in the phenolic matrix.



- At 157.6 nm, hν = 7.88 eV.
- The ionization energy of phenol (gas phase) is 8.38 eV.
- Condensed phase ionization energies are usually reduced.
- Onium decomposition may result from electron capture (from actual ionization) or simple electron transfer from the excited phenol.
- In any case, the electron is energetically available to the PAG cation acceptor.
- Recombination is not available as a mechanism for quenching acid generation.

*S. Tagawa, S. Nagahara, T. Iwamoto, M. Wakita, T. Kozawa, Y. Yamamoto, D. Werst and A. Trifunac, Proc. SPIE Adv. Resist Technol. and Processing, **3999,** (2000), 204.

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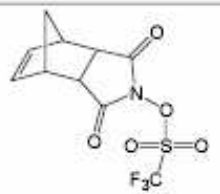
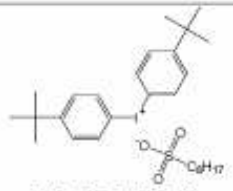
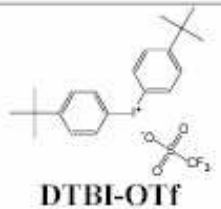
C Parameters

(Ionizing Radiation)

	Units	 ND-OTf	 TPS-OTf	 DTBI-PFOS	 DTBI-OTf
248 nm DUV Phenolic Matrix	C, cm^2/mJ	0.018	0.037	0.053	0.062
	σ, $nm^2/photon$	0.0014	0.0029	0.0043	0.0050
	$[A_t]$, $\mu mol/cm^3$	7.8	6.5	23.8	12.3
30 keV e-beam Phenolic Matrix	C, $cm^2/\mu C$	0.0167	0.033	0.011	0.11
	σ, $nm^2/electron$	0.27	0.54	0.18	1.70
	$[A_t]$, $\mu mol/cm^3$	7.1	14.6	15.0	58.3
50 keV e-beam Phenolic Matrix	C, $cm^2/\mu C$	-	0.034	0.015	-
	σ, $nm^2/electron$	-	0.55	0.24	-
	$[A_t]$, $\mu mol/cm^3$	-	33.8	67.5	-
13.4 nm EUV Phenolic Matrix	C, cm^2/mJ	0.024	0.043	0.021	0.074
	σ, $nm^2/photon$	0.036	0.064	0.031	0.11
	$[A_t]$, $\mu mol/cm^3$	5.0	13.2	10.4	21.5
1 nm X-Ray Phenolic Matrix	C, cm^2/mJ	0.00054	0.0013	0.00046	0.0016
	σ, $nm^2/photon$	0.011	0.026	0.0091	0.032
	$[A_t]$, $\mu mol/cm^3$	7.0	22.3	16.0	26.3
75 keV He^+ Phenolic Matrix	C, $cm^2/\mu C$	0.96	0.91	2.78	1.62
	σ, nm^2/ion	15.3	14.6	44.5	26.0
	$[A_t]$, $\mu mol/cm^3$	15.4	7.6	25.5	20.5

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Relative Cross Sections
Based on nm^2/particle (Terpolymer Matrix)

	MDT		TPS-OTf		DTBI-PFOS		DTBI-OTf	
	nm2/particle	Rel Cross Section	nm2/particle	Rel Cross Section	nm2/particle	Rel Cross Section	nm2/particle	Rel Cross Section
248 nm	0.0014	**1**	0.0029	**1**	0.0043	**1**	0.005	**1**
30 keV electrons	0.27	193	0.54	186	0.18	42	1.7	340
50 keV electrons			0.55	190	0.24	56		
13.4 nm	0.036	**26**	0.064	**22**	0.031	**7**	0.11	**22**
X-ray	0.011	8	0.026	9	0.0091	2	0.032	6
He+ Ion Beam	15.3	10929	14.6	5034	44.5	10349	26	5200

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Mask Edge Acid Concentrations and Average Intermolecular Distances (Acid Molecules)

Mask Edge Photoacid Concentrations

	C, cm2/mJ	C, nm2/photon	PAG Loading, umol/cm3	Mask Edge Energy, mJ/cm2 1	Mask Edge Energy, mJ/cm2 3	Mask Edge Energy, mJ/cm2 5	Mask Edge Energy, mJ/cm2 10
Phenolic Matrix	0.075	0.111	100	7.2	20.1	31.3	52.8
Acrylic Matrix	0.17	0.252	100	15.6	40.0	57.3	81.7
Phenolic Matrix	0.075	0.111	150	10.8	30.2	46.9	79.1
Acrylic Matrix	0.17	0.252	150	23.5	59.9	85.9	122.6

Mask Edge Intermolecular Photoacid Distances

	C, cm2/mJ	C, nm2/photon	PAG Loading, umol/cm3	Mask Edge Energy, mJ/cm2 1	Mask Edge Energy, mJ/cm2 3	Mask Edge Energy, mJ/cm2 5	Mask Edge Energy, mJ/cm2 10
Phenolic Matrix	0.075	0.111	100	6.1	4.4	3.8	3.2
Acrylic Matrix	0.17	0.252	100	4.7	3.5	3.1	2.7
Phenolic Matrix	0.075	0.111	150	5.4	3.8	3.3	2.8
Acrylic Matrix	0.17	0.252	150	4.1	3.0	2.7	2.4

C parameter data courtesy of Ted Fedynyshyn.

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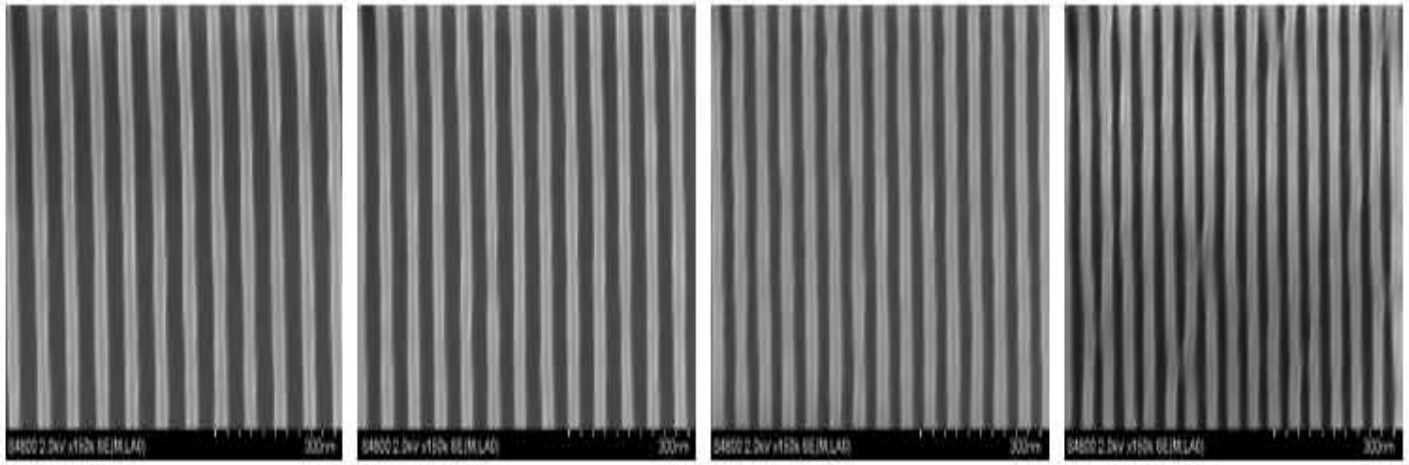
XP-6627Q @ Berkeley– 27mJ- LER 3.2nm for 32nm half pitch



40nm 36nm 32nm 28nm

Observations and Urgings

- We are not yet at the point where “shot noise” dominates resist performance.
  - Photons are doing much more work. The first ionization event probably gives rise to lower energy secondary electrons.
  - Chemistry clouds the even more.
  - The “blur” may mitigate the discrete stochastic events.
- The acid distance at the feature edge correlates well with the LER.
- Diffusion – if it plays any role at all – does little to change that.
  - If diffusion is not a part of the rate limiting step, it will not even be observed.
- Please reconsider and test whether diffusion is significant. The answer may be much simpler.