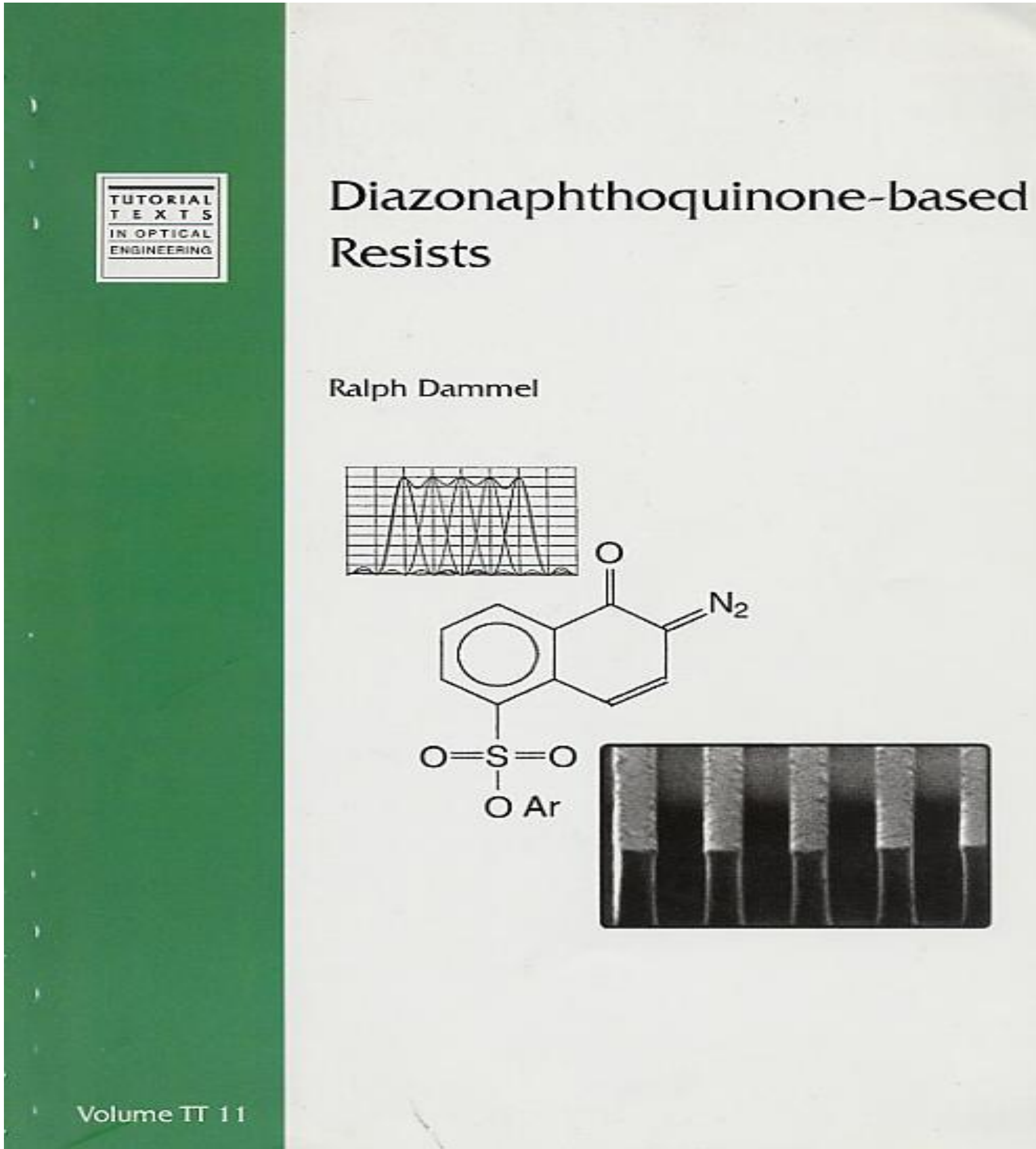
Lecture 13

Chemical Engineering for Micro/Nano Fabrication


TUTORIAL TEXTS IN OPTICAL ENGINEERING
Diazonaphthoquinone-based Resists
Ralph Dammel
O
N2
O=S=O
O Ar
Volume TT 11

F

Intrinsic Reactivity — Quantum Yield

$$A \xrightarrow{h\nu} B$$

$$\Phi_A = \frac{\text{Molecules of "A" Consumed}}{\text{Photons of Light Absorbed}} = \frac{\text{Molecules}}{\text{Photon}}$$

$$\Phi_B = \frac{\text{Molecules of "B" Produced}}{\text{Photons of Light Absorbed}}$$

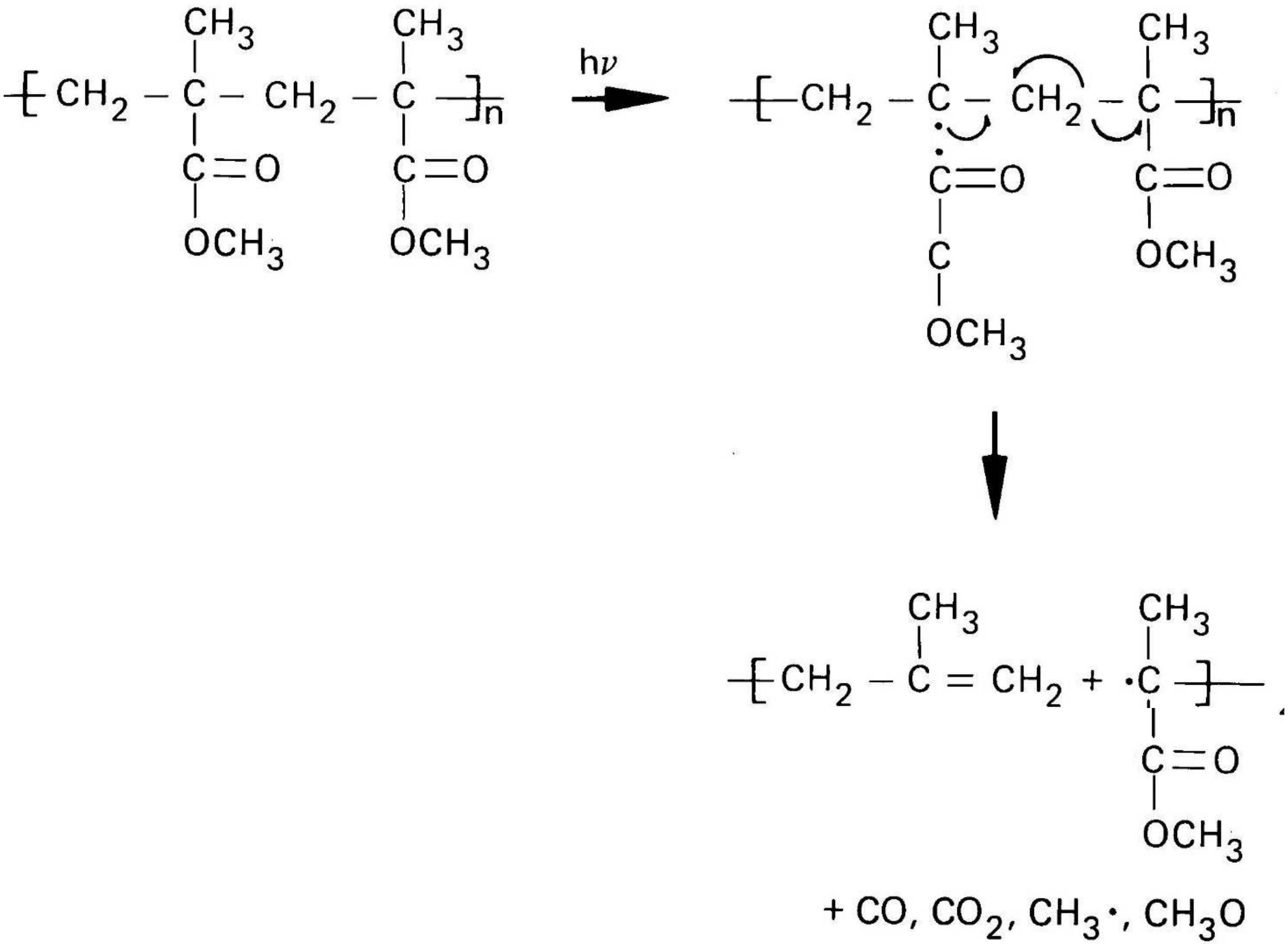
Measurement of Φ Simplified in Solution

1. Solution optically dense so that all incident photons absorbed.
2. Reactions run to low conversion so that rate of light absorption ~ constant
3. Diffusion is rapid in dilute solutions

Measurement More Difficult in Solid State

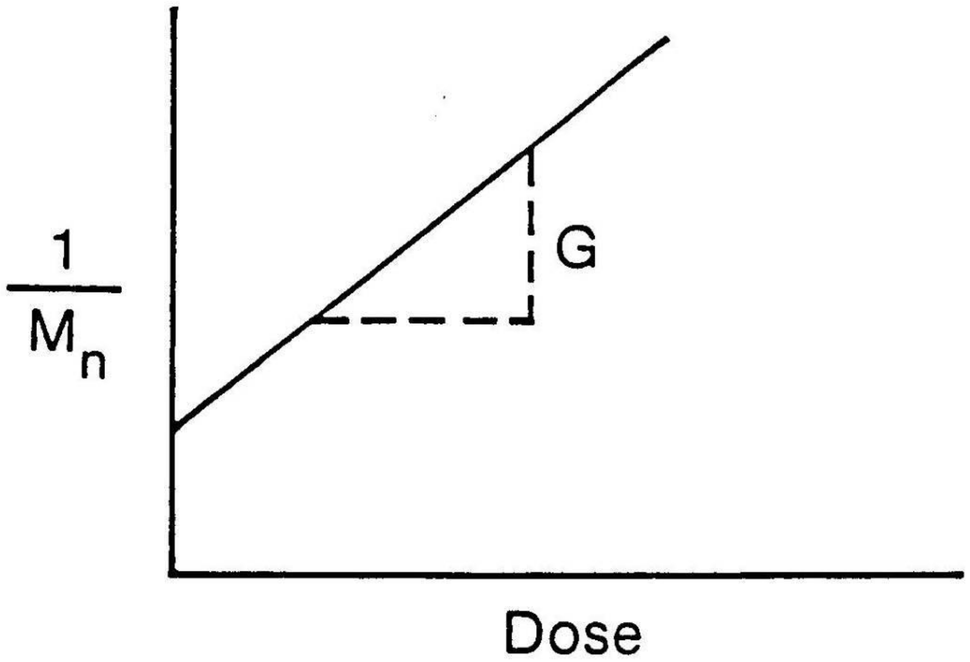
Diazoquinones	$\Phi \sim 0.2 — 0.3$
Bis Azides	$\Phi \sim 0.5 — 1.0$

Radiation Induced Decomposition of Poly(methyl methacrylate), PMMA

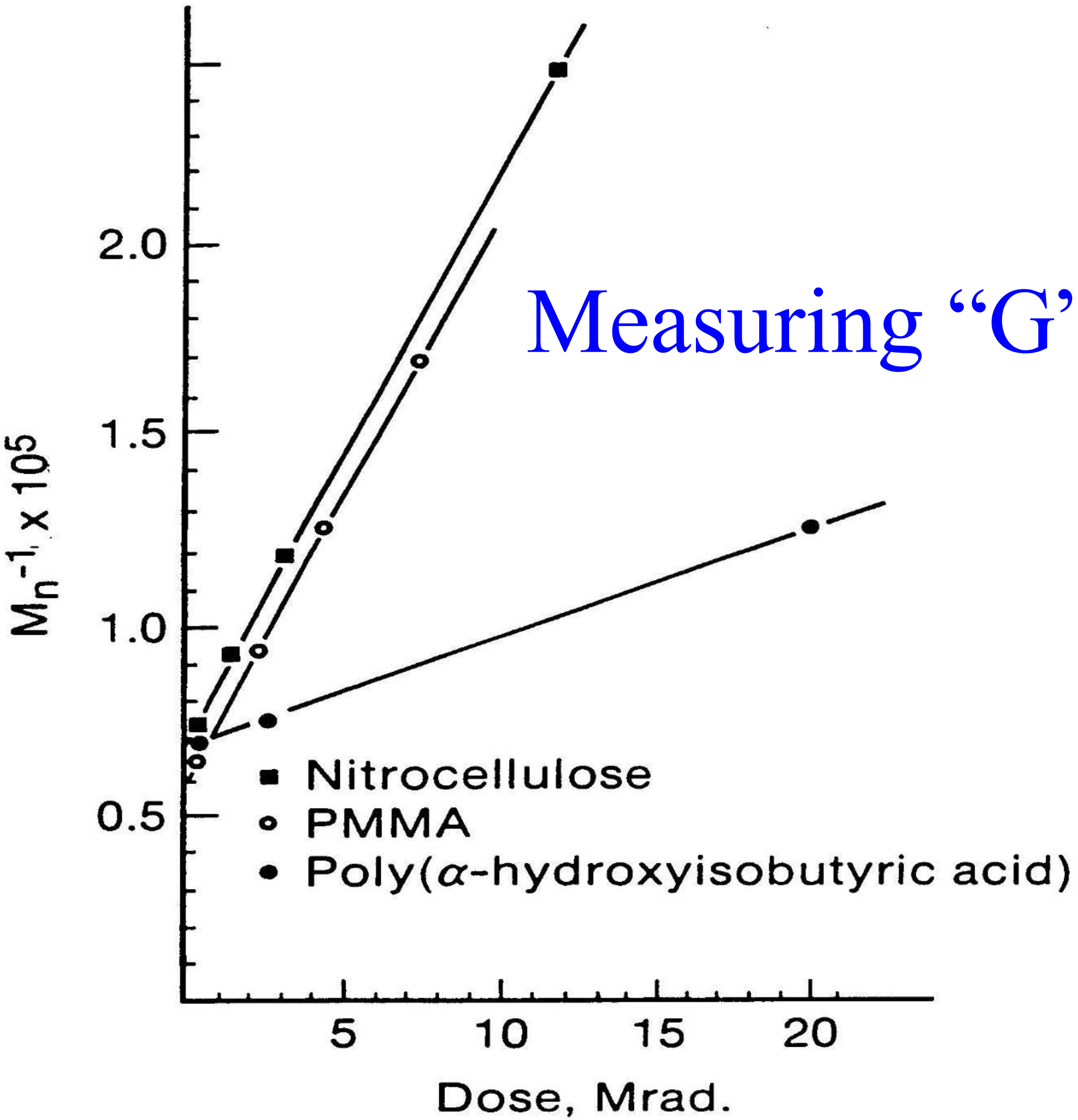


Dependence of Molecular Weight on Dose for Polymers that Scission

$$\frac{1}{M_n^*} = \frac{1}{M_n^0} + \left(\frac{G}{100N}\right) D$$

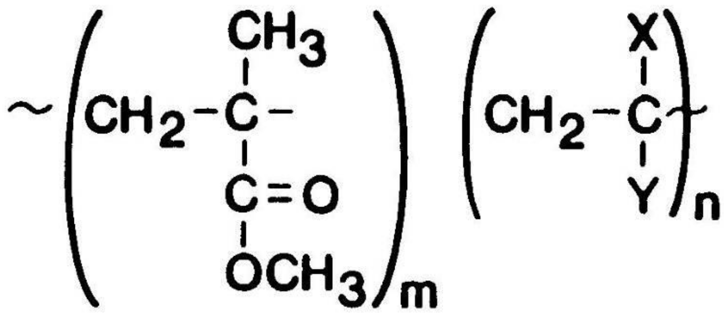


Measuring "G" Values



"G" Values

Copolymers

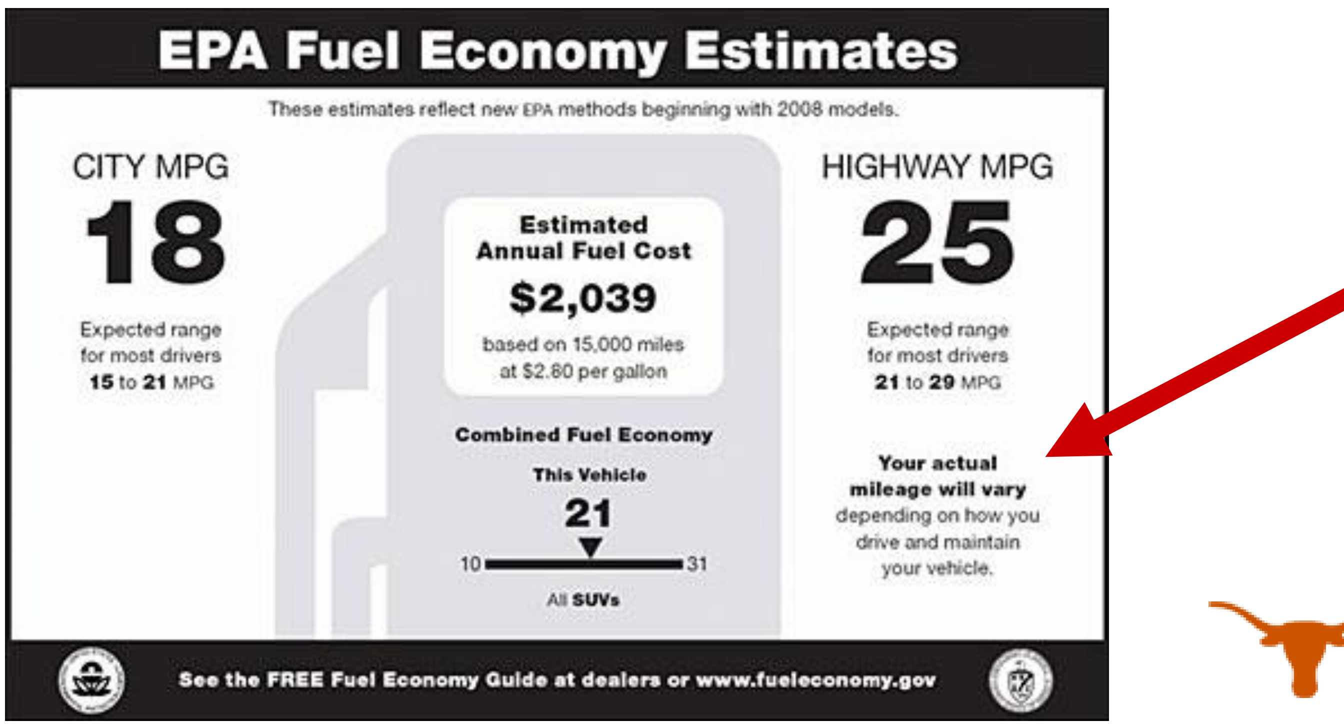


Copolymer	(15 Kv) Sensitivity, $\mu coul/cm^2$	G_s
PMMA	40	1.5
PMMA-MA ($X=CH_3$, $Y=COOH$)	35	2.0
PMMA-MAN ($X=CH_3$, $Y=CN$)	12	3.1
PMMA-IB ($X=CH_3$, $Y=CH_3$)	14	3.5
PMMA-α CL-Acrylate (X=CL)	14	3.3
PMMA-α CR-Acrylate (X=CN)	12	3.5
PMMA-MA-MANH	7	4.5

Lithographic Sensitivity

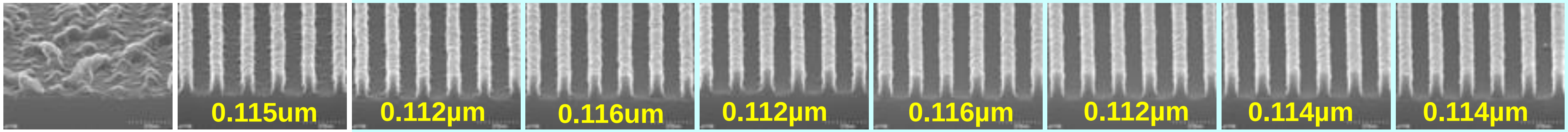
CAUTION…

RESIST SENSITIVITY EXPRESSED IN TERMS OF DOSE/UNIT AREA IS LIKE AN EPA MILEAGE RATING… USE IT FOR COMPARISON ONLY. YOUR OWN MILEAGE WILL VARY DEPENDING ON…

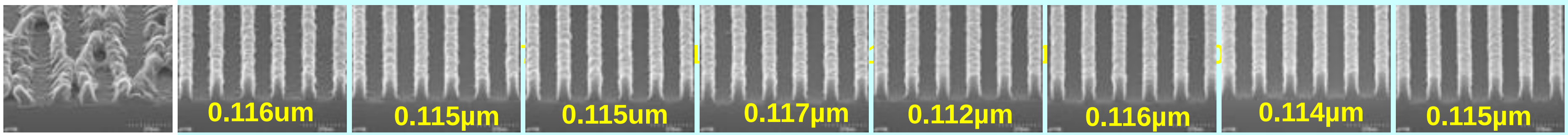


Defocus Behavior: a 193 nm Resist

100nm (1:1.1) Trench DOF @ 38.0 mJ/cm^2

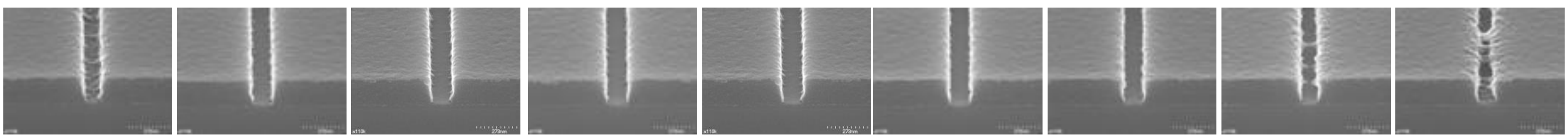


-0.40µm -0.35µm -0.30µm -0.25µm -0.2µm -0.15µm -0.10µm -0.05µm 0.0µm



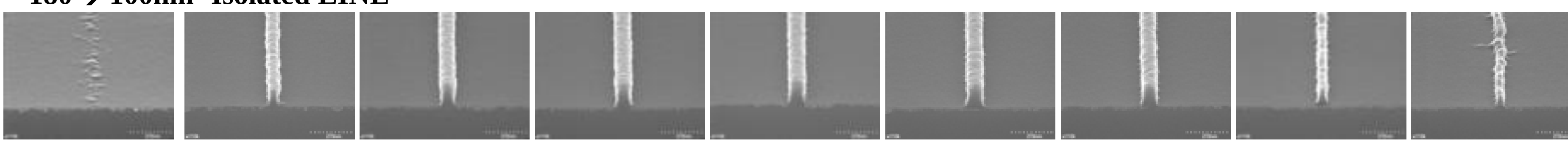
+0.45µm +0.4µm +0.35µm +0.30µm +0.25µm +0.2µm +0.15µm +0.10µm +0.05µm

120→100 nm Isolated Trench



-0.15µm -0.10µm -0.05µm 0.00µm + 0.05µm +0.10µm +0.20µm +0.30µm +0.35µm

180→100nm Isolated LINE



-0. 15µm -0.10µm -0.05µm 0.0µm +0.05µm +0.10µm +0.20µm +0.35µm +0.40µm

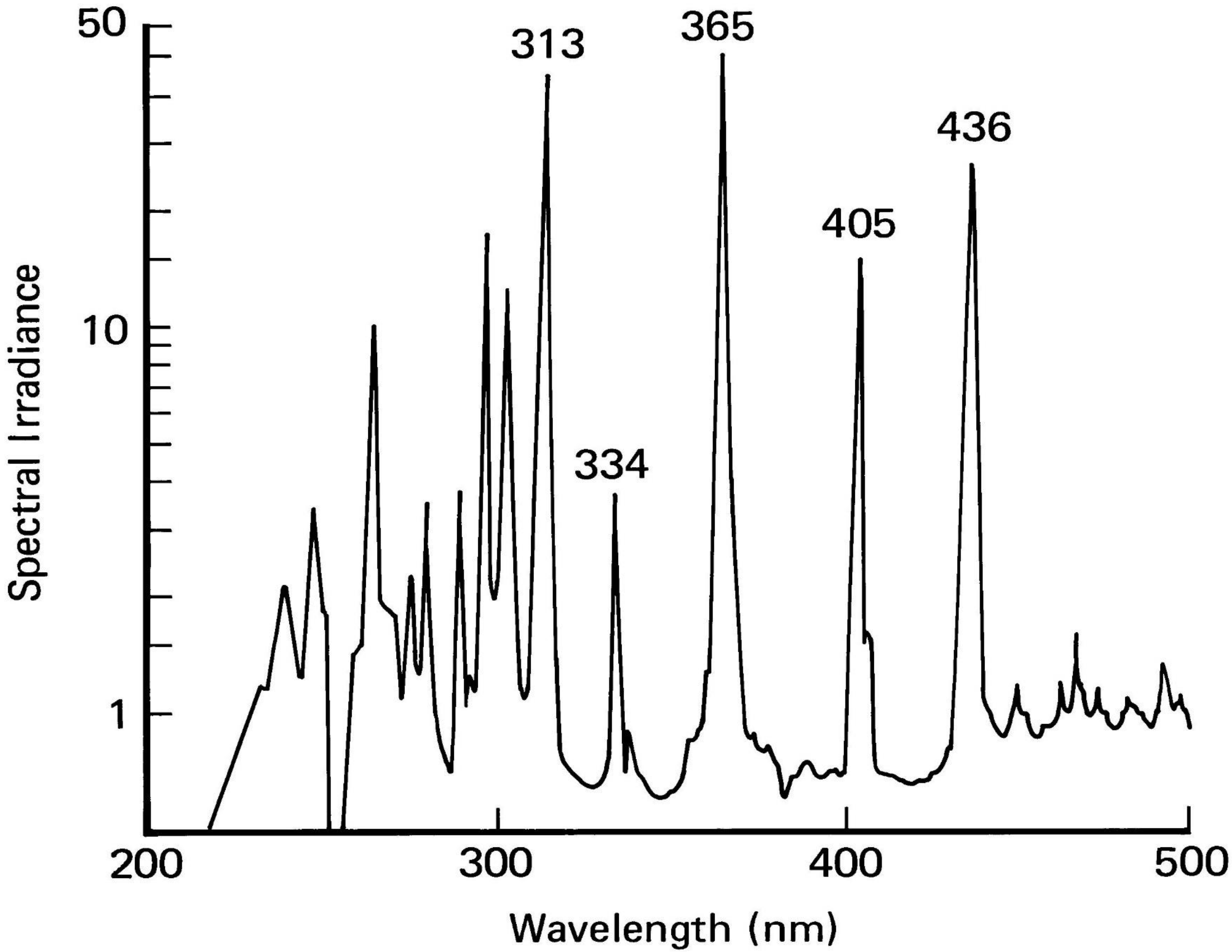
Exactly what does this measure???

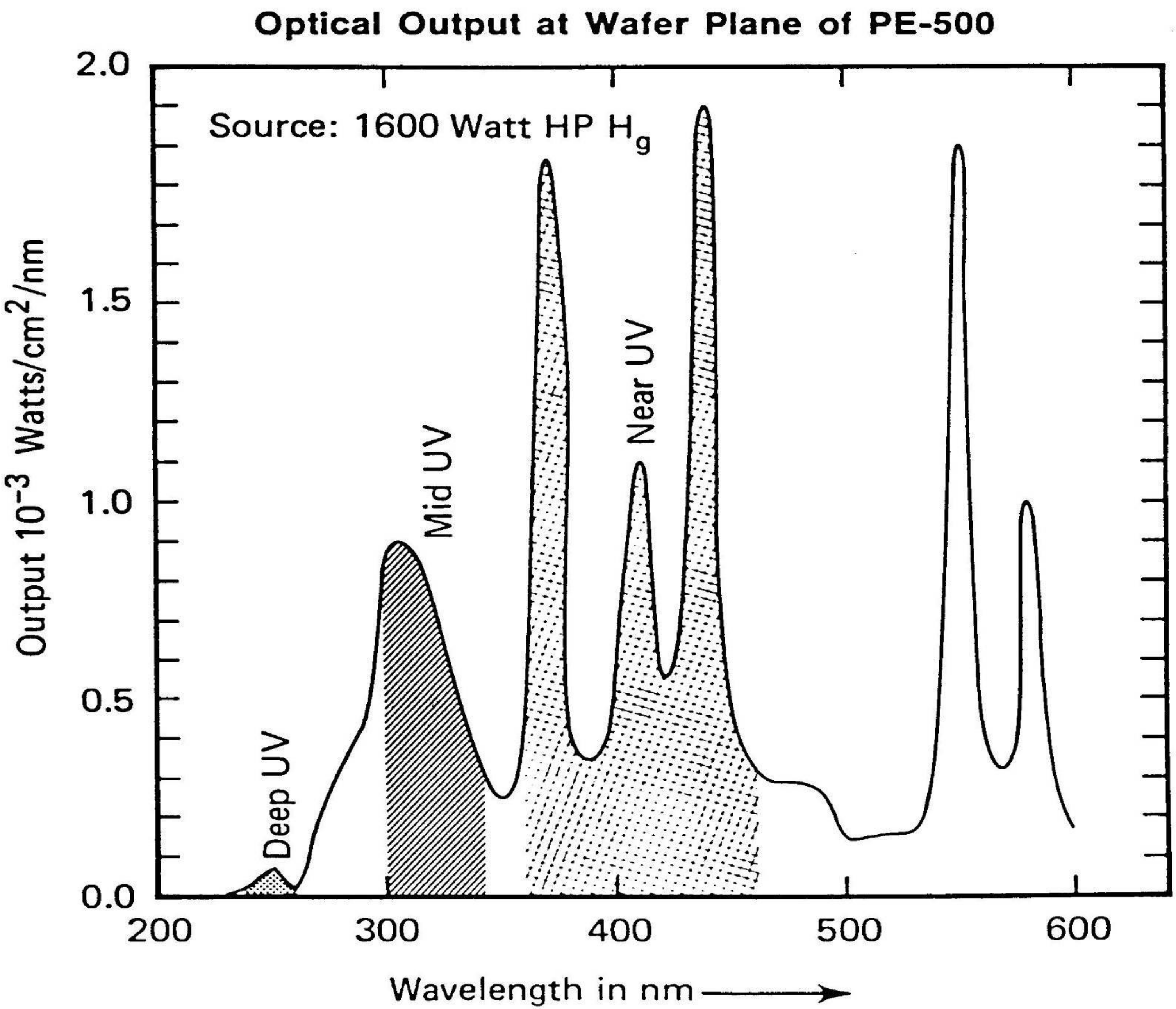
Chemical Amplification

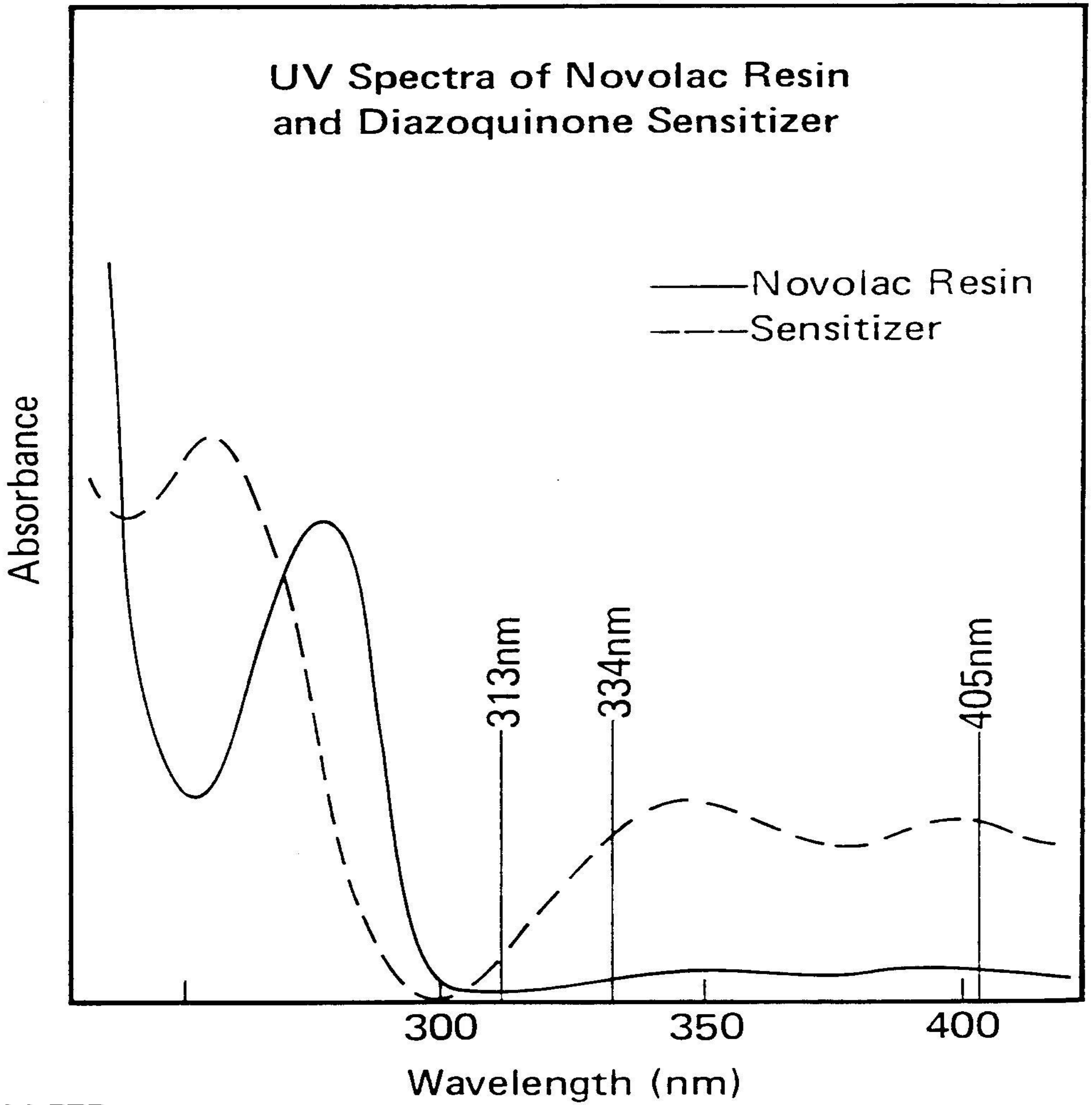
Hiroshi Ito

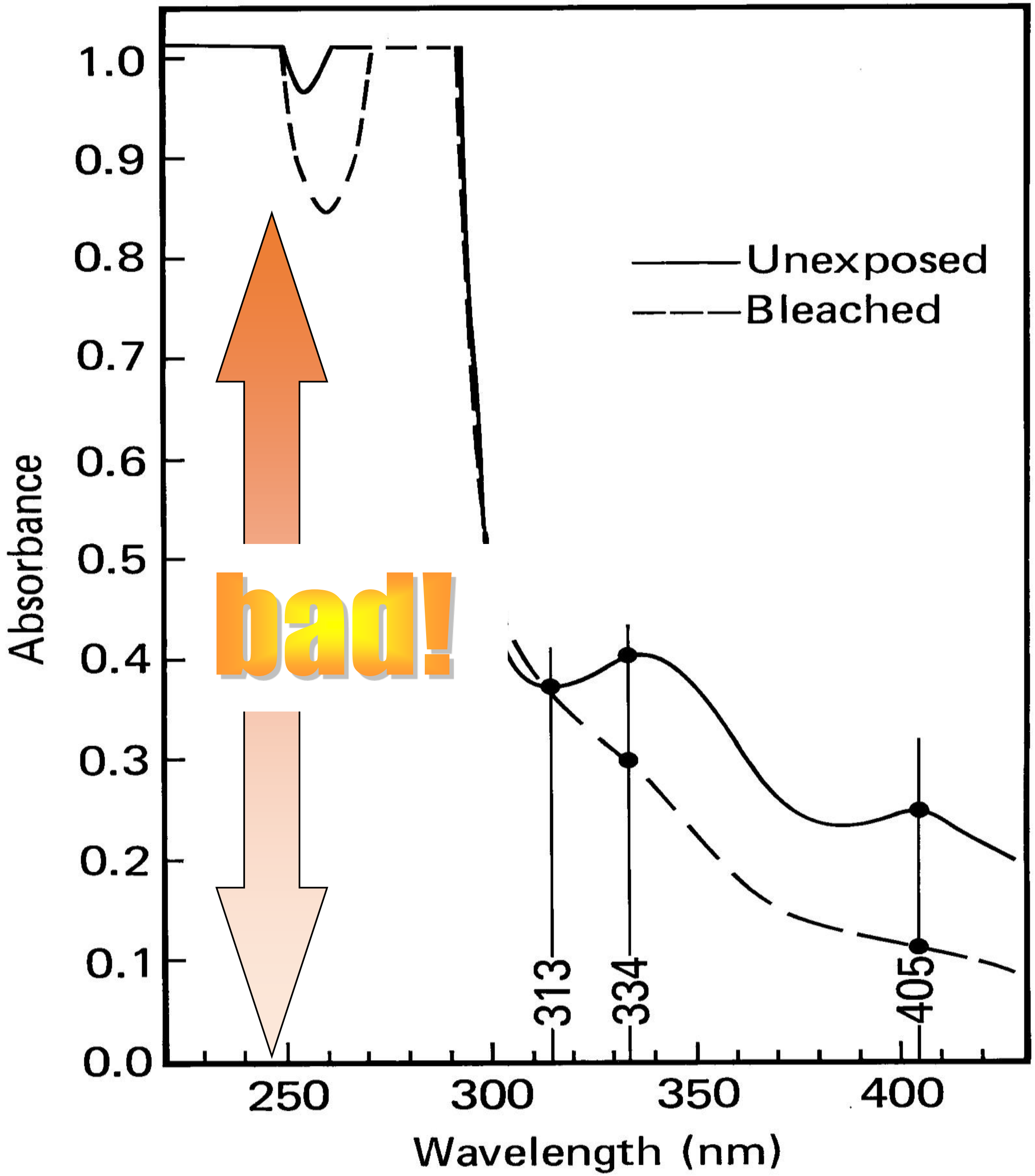
Jean Fréchet

Mercury Xenon Lamp Output

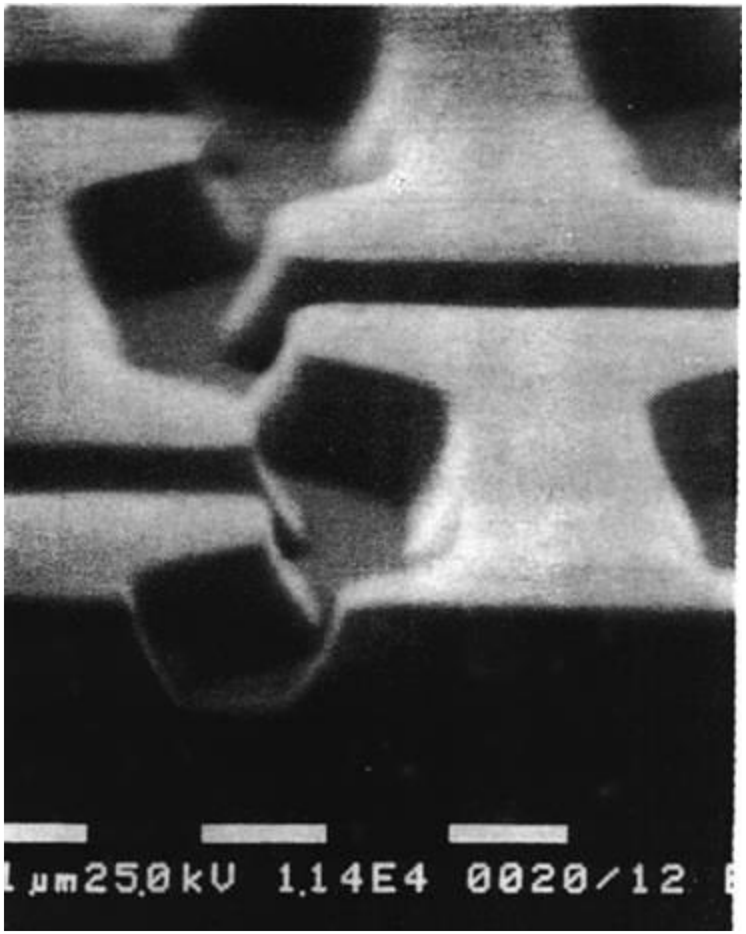



Optical Output at Wafer Plane of PE-500
Source: 1600 Watt HP Hg
Output 10⁻³ Watts/cm²/nm
Wavelength in nm
Deep UV
Mid UV
Near UV
0.0
0.5
1.0
1.5
2.0
200
300
400
500
600

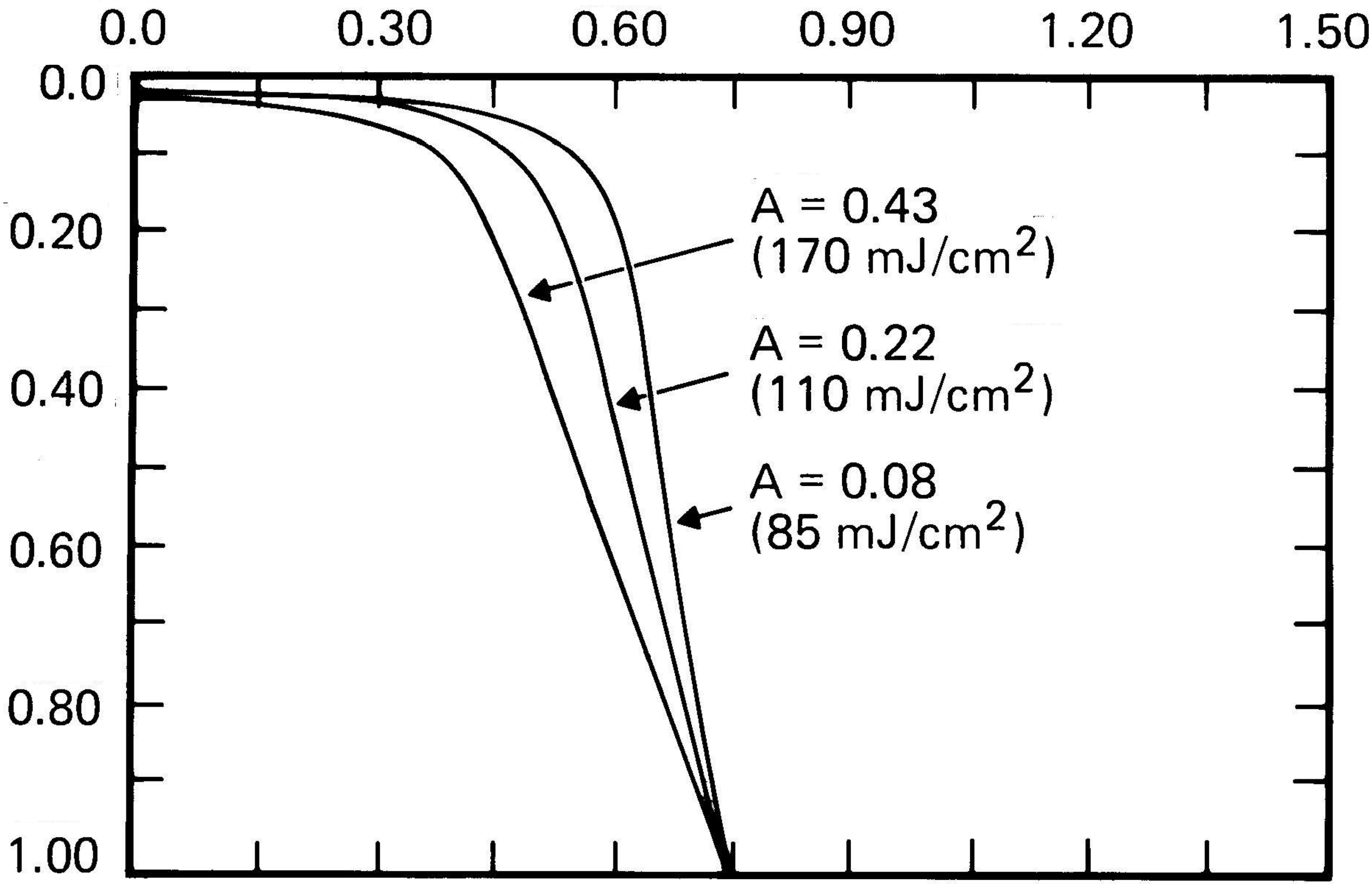

UV Spectra of Novolac Resin
and Diazoquinone Sensitizer
Novolac Resin
Sensitizer
Absorbance
313nm
334nm
405nm
300
350
400
Wavelength (nm)


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Absorbance
Unexposed
Bleached
bad!
313
334
405
250
300
350
400
Wavelength (nm)

Sloped Sidewalls In Novolac-Based DUV Resists



High unbleachable absorption leads to heavily sloped sidewalls in novolac-based resists imaged at 248 nm.


0.0
0.30
0.60
0.90
1.20
1.50
0.0
0.20
0.40
0.60
0.80
1.00
A = 0.43
(170 mJ/cm2)
A = 0.22
(110 mJ/cm2)
A = 0.08
(85 mJ/cm2)

Photochemistry Counts Photons

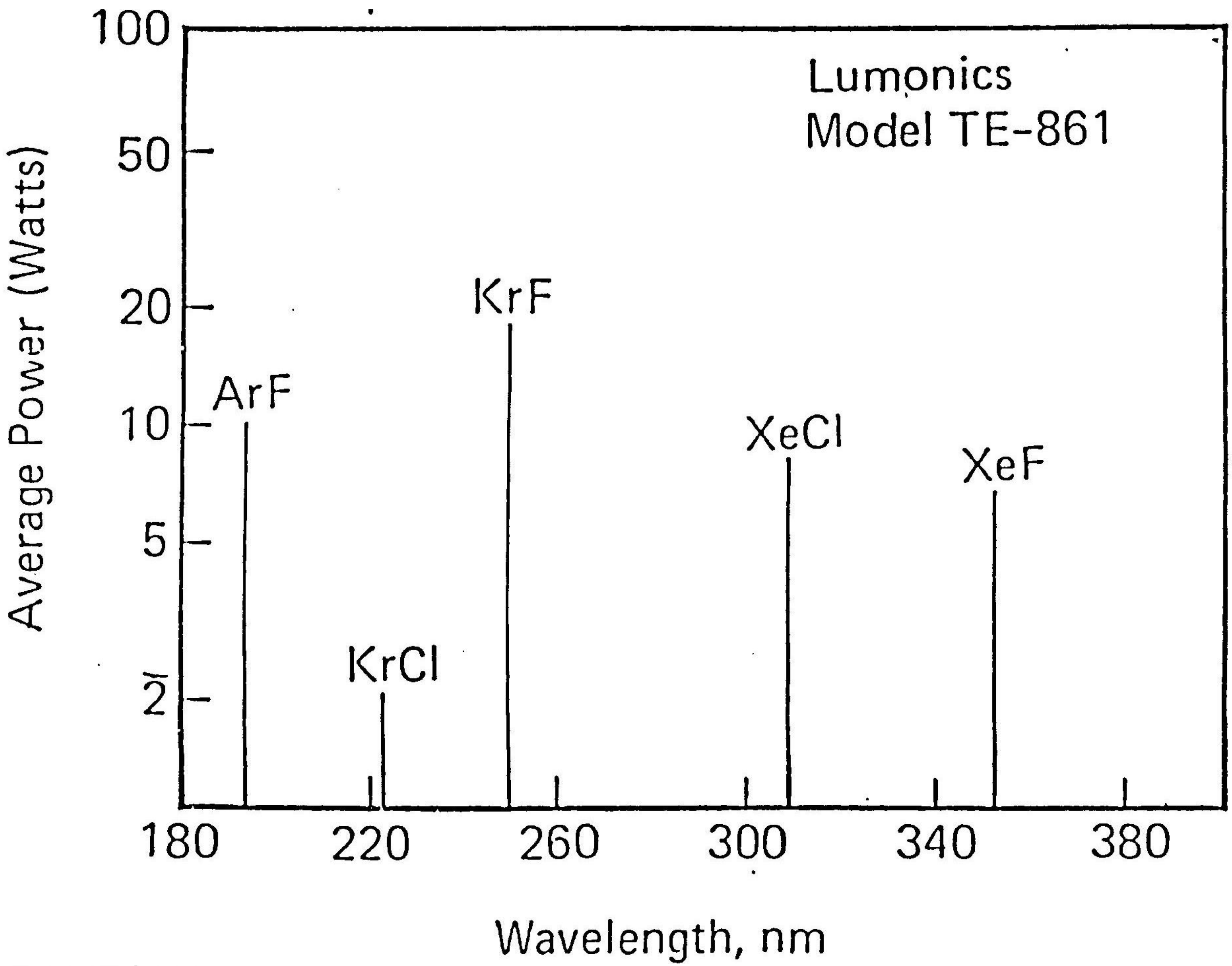
Starting Material + Photon ⟶ Product

Energy/Photon, $E = h\nu = hc/\lambda$

As Wavelength Decreases, Energy/Photon Increases

- Fewer Photons are Available for a Given Exposure Measured in millijoules/area
- Mercury Lamp Produces far less Energy in the Deep UV
- Throughput Therefore Requires
  - -- Brighter Light Bulbs
  - -- More Sensitive Resists

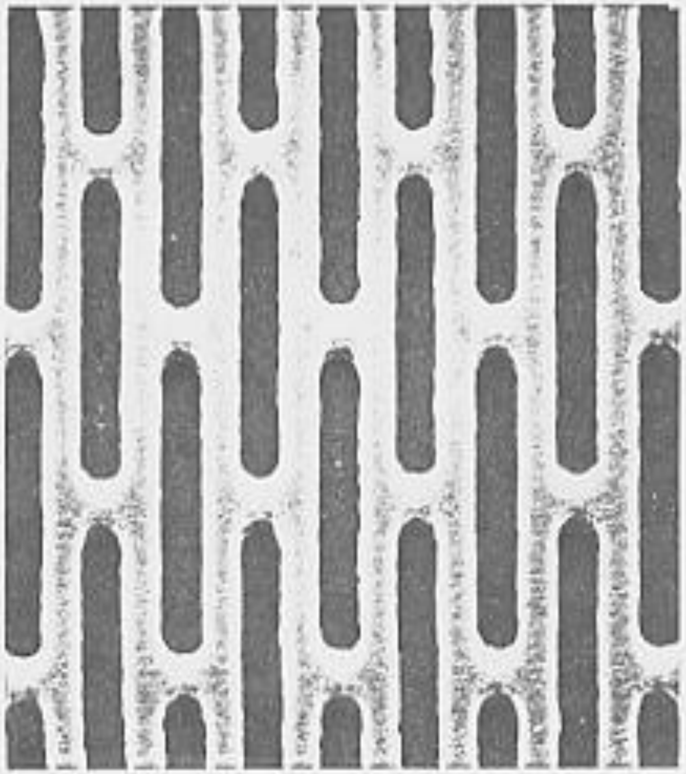
Excimer Lasers are very bright "lights"



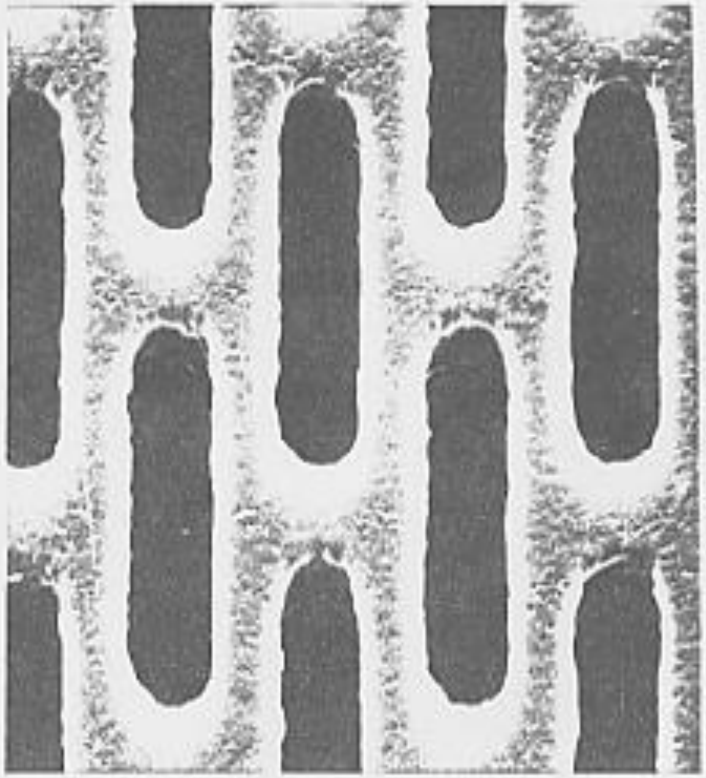
Excimer Lasers

Pulsed or CW?	:	Pulsed
Pulsewidth	:	~ ns to 1 μs
Repetition Rate	:	$<$ 1 Hz to $>$ 1 kHz
Pulse Energy	:	μJ to J
Peak Power	:	$<$ 1 KW to $>$ 100 MW
Average Power	:	μ W to $>$ 10 W

First Excimer Laser Lithography Experiment



1µm lines and spaces



0.5µm lines and spaces

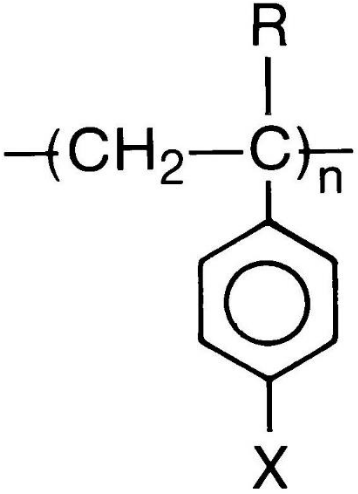
XeCl Laser, λ = 308 nm
AZ 2400 Resist

Reciprocity proof!!

JAIN et. al. IBM J.
Res. & Develop. 26 (2) 15/ (82)

Single Component Negative Tone

Polystyrenes

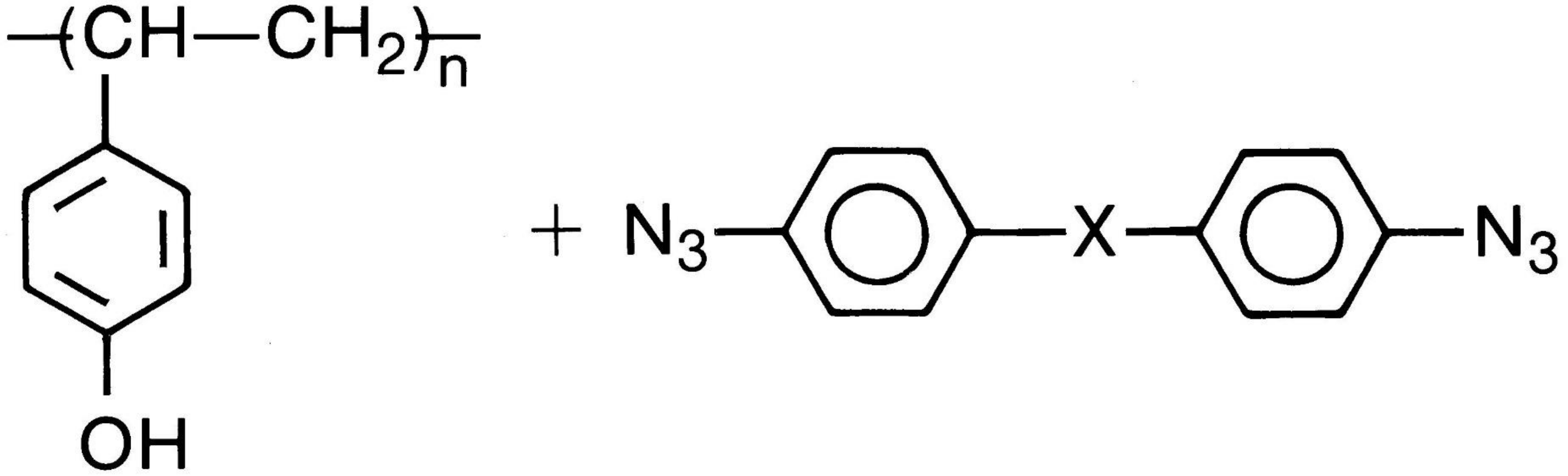


- Limited Resolution

R = H, CH_3, Cl

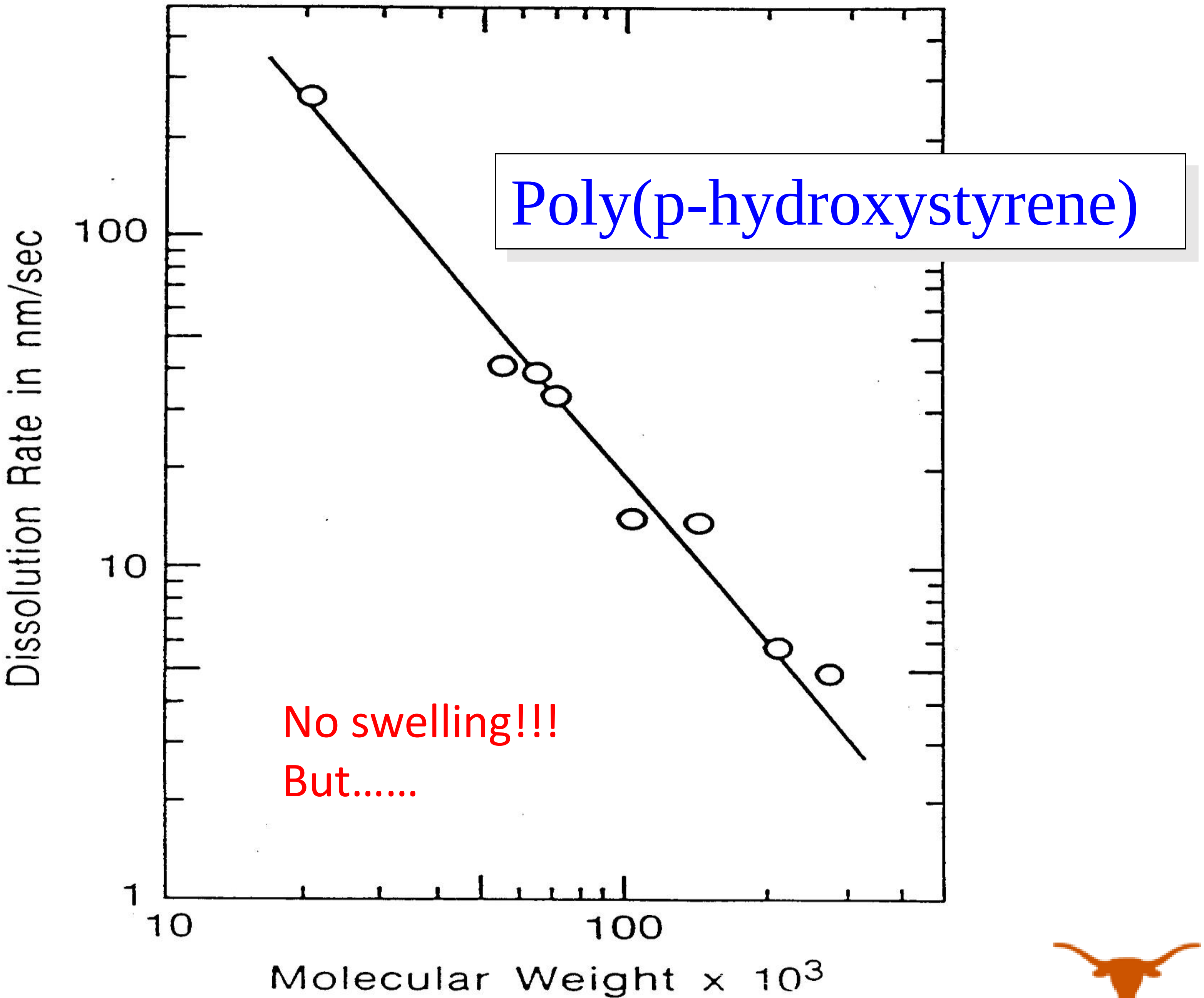
X = Cl, $-CH_2Cl$

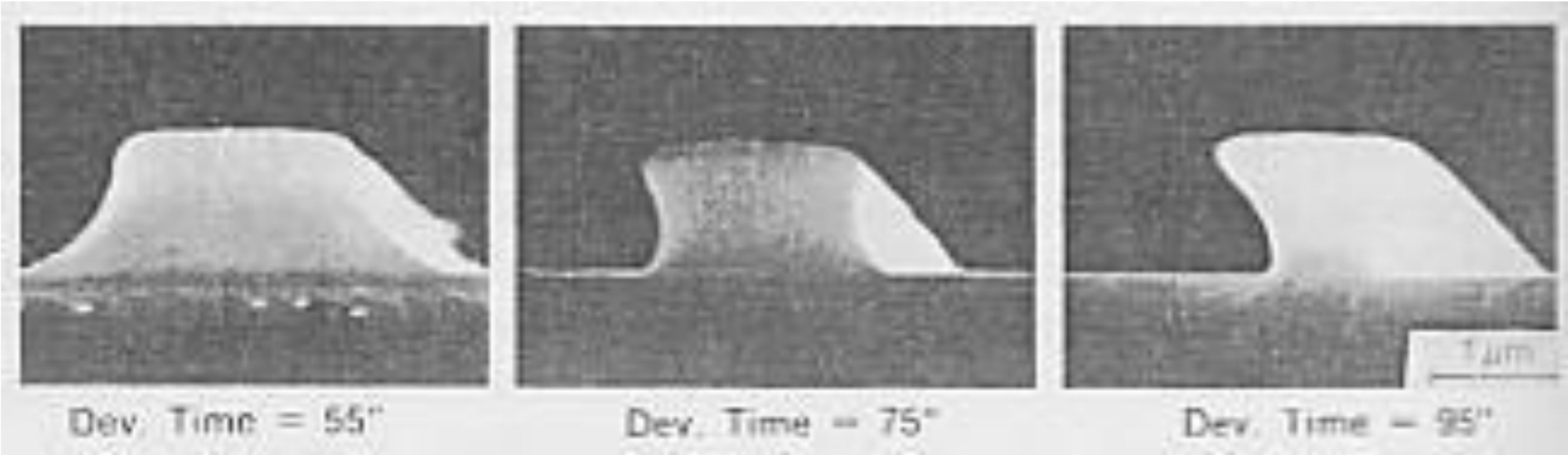
Two Component Systems - Negative tone



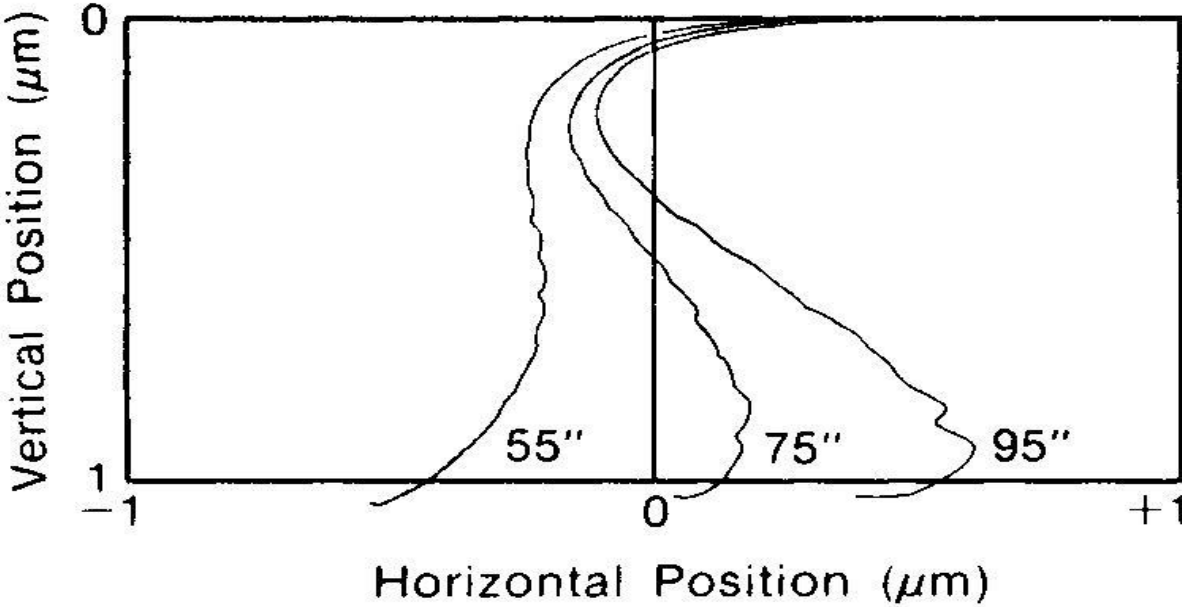
- Non-Swelling
- ~20 mJ/cm^2 sensitivity

Hitachi


Dissolution Rate in nm/sec
100
10
1
10
100
Molecular Weight x 10^3
Poly(p-hydroxystyrene)
No swelling!!!
But……

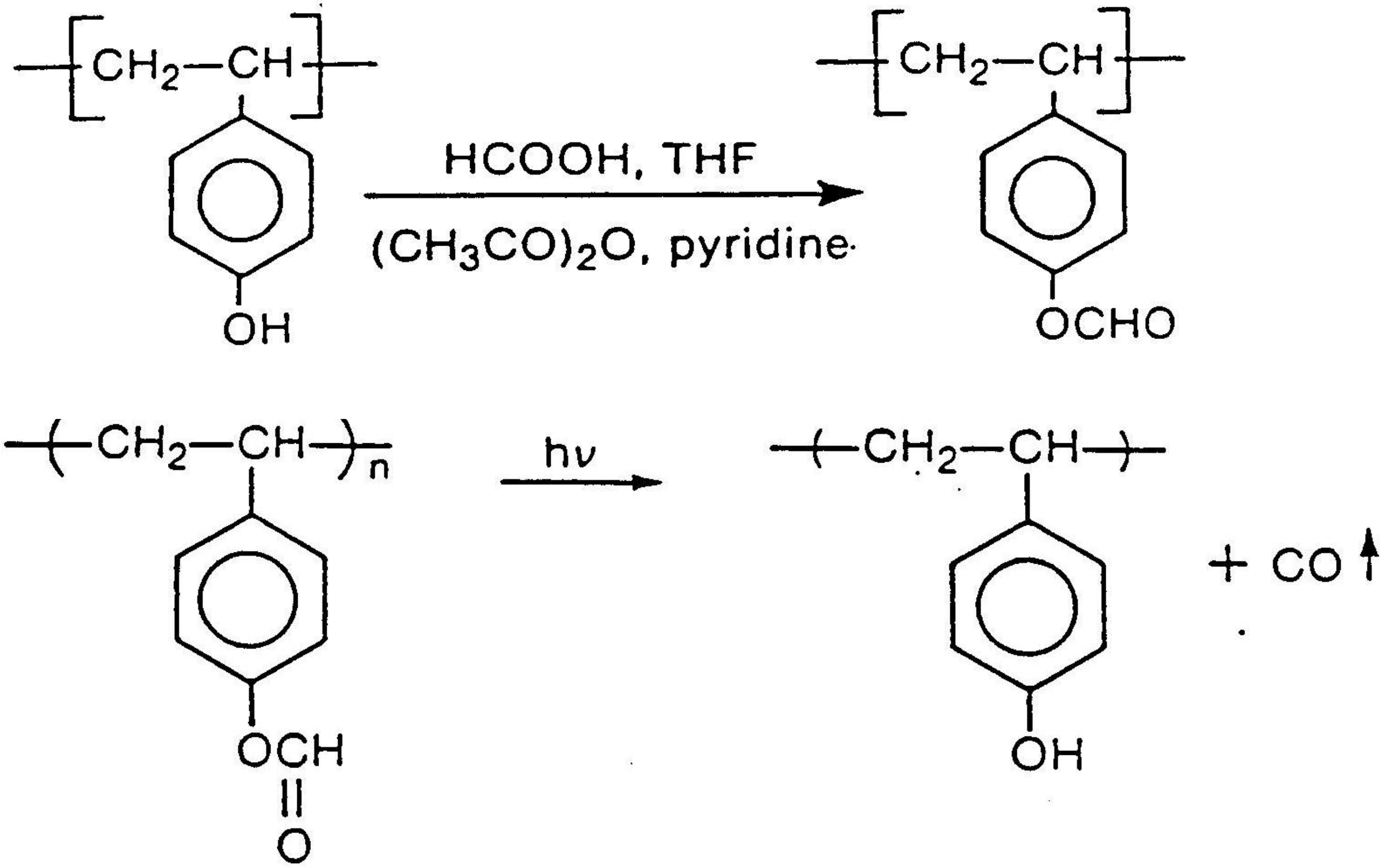


(**a**) Experiment

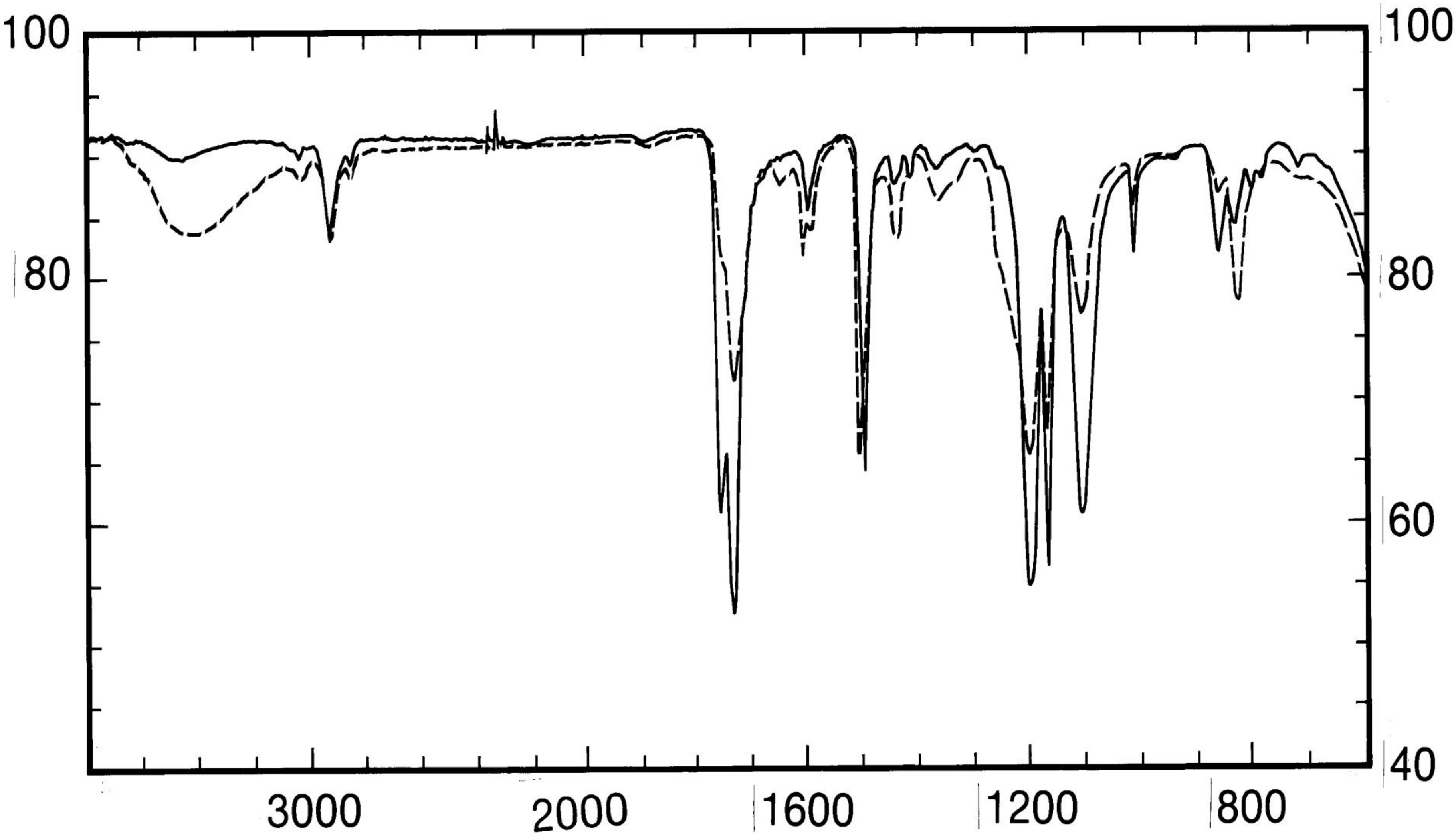


(**b**) Simulation

Side Chain Deprotection Design



Infrared Spectrum before and after Exposure



Is there an I-line like positive resist for DUV???

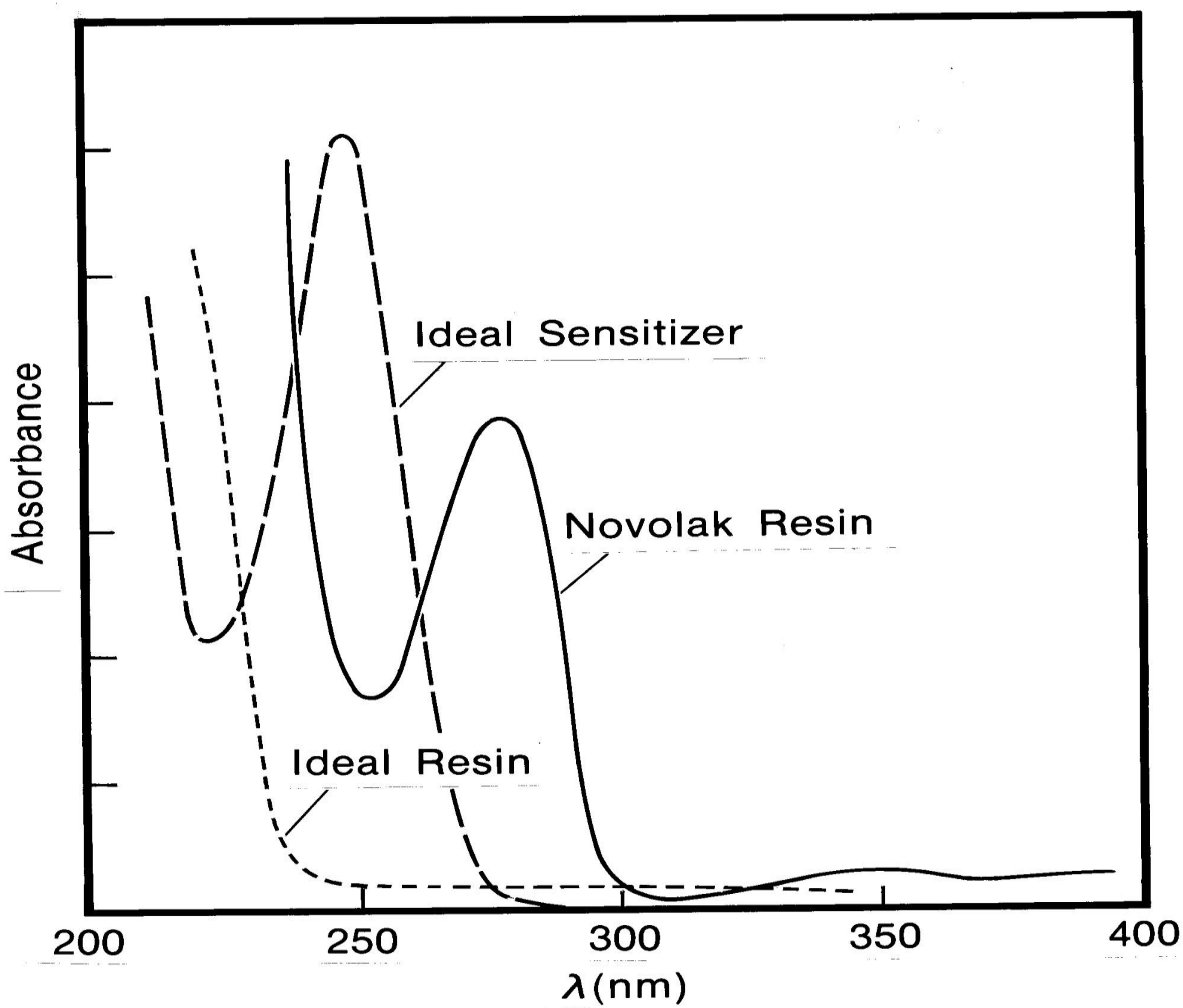
If this can be done in the DUV… it will require:

- New Photoactive Compound ..not DNQ
- New Resin…not Novolac
- More light than an Hg lamp can provide

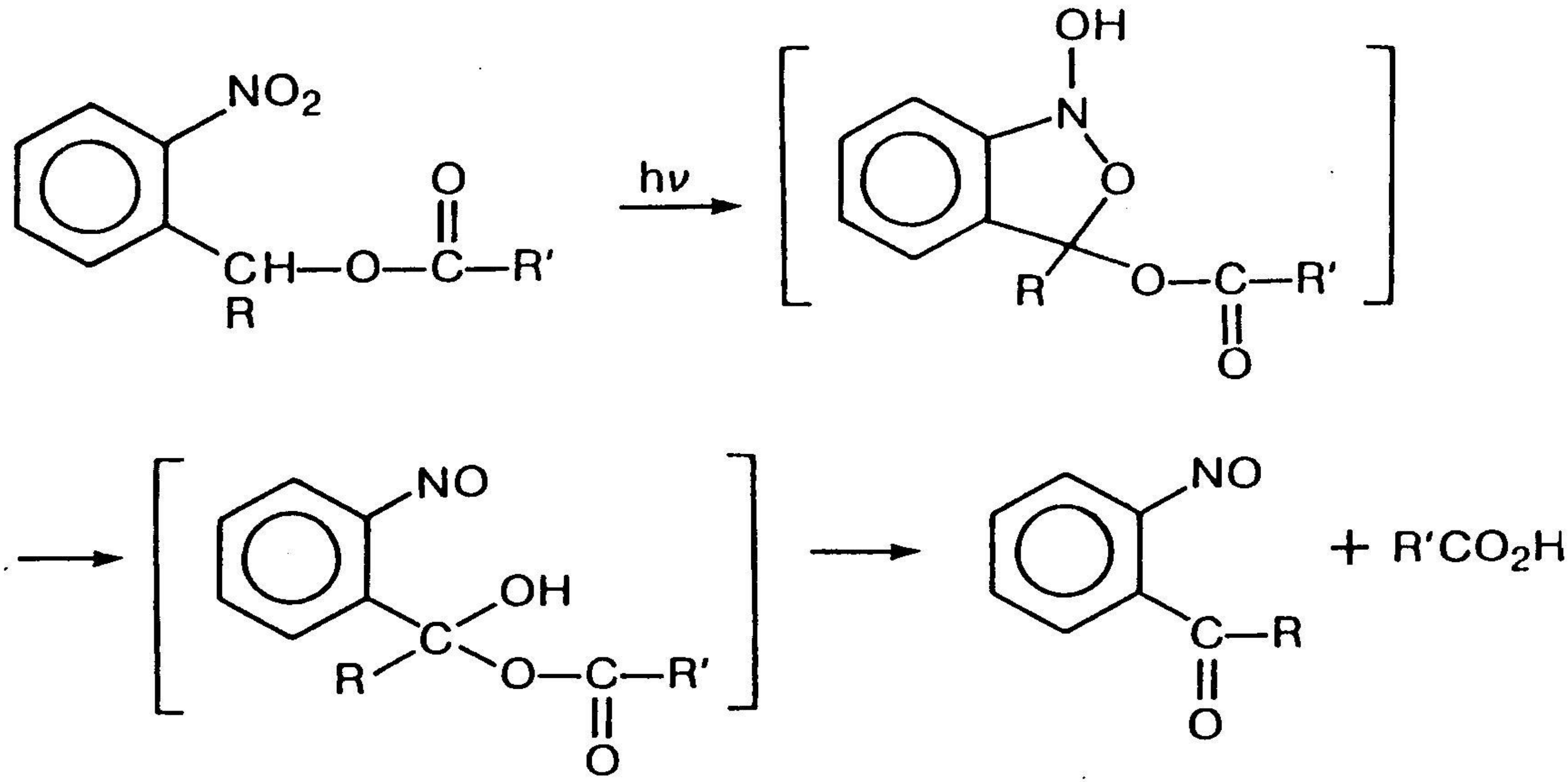
Ideal Sensitizer Characteristics

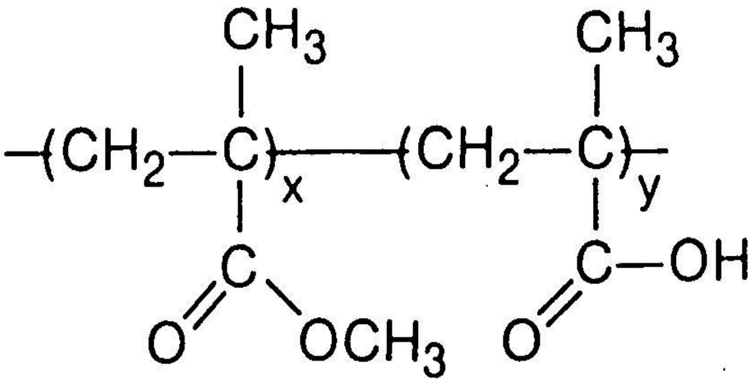
- High Extinction at 254nm
- High Quantum Efficiency
- Photoproducts Transparent at 254nm
- No Absorbance Above 300nm
- Useful Change in Polarity
- Thermal Stability
- Solubility
- Synthetic Access

Spectral Properties

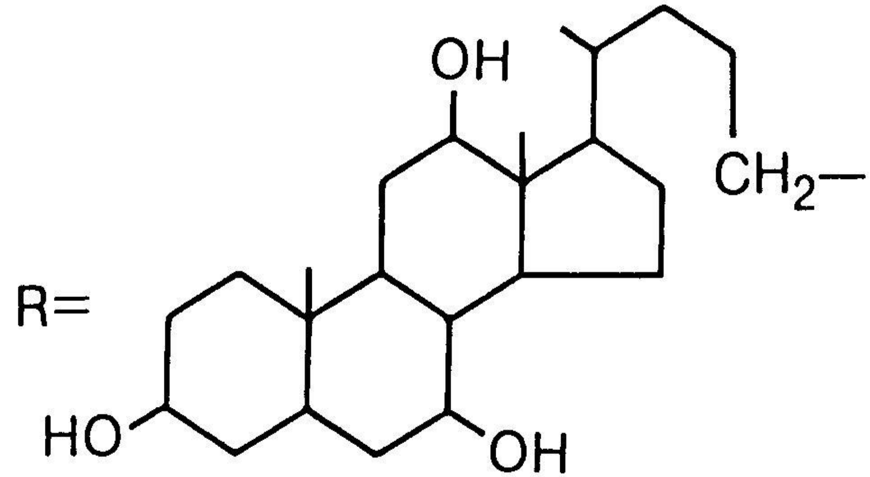


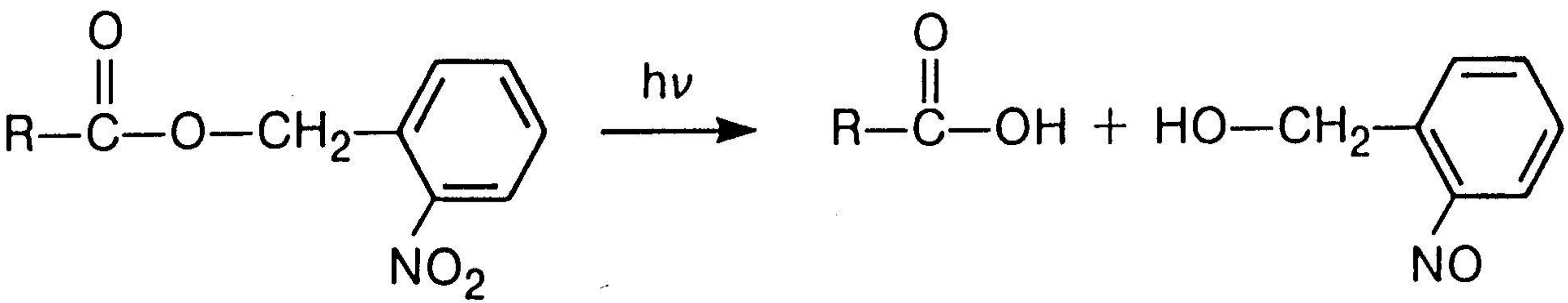
Photolysis of o-Nitrobenzyl esters





Methacrylate resin

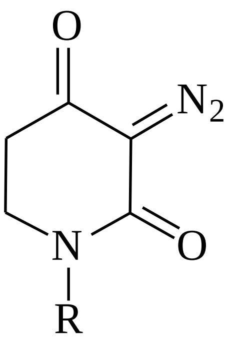


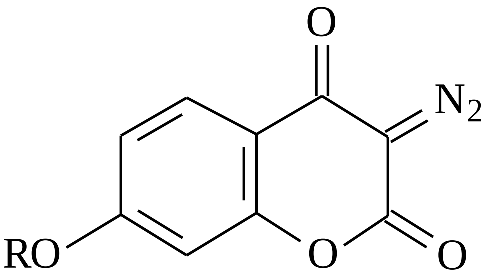


O-Nitrobenzylcholate

Candidate 1,3-Diacyl-2-diazo chromophores

- Bleach in the DUV.
- Good film forming properties.
- Quantum efficiency of ~ 0.3
- Carboxylic acid photoproducts
- *N*-substituted 3-diazopiperidine-2,4-diones
- *O*-substituted 3-diazo-7-hydroxy-4-oxocoumarin





Willson C. G., Miller R. D., McKean D. R., Pederson L. A., Regitz M.; *SPIE* Vol. 771 Advances in Resist Technology and Processing IV **1987**, 2.

Willson, C. G.; Leeson, M. J.; Yeuh, W.; Steinhausler, T.; McAdams, C. L.; Levering, V.; Pawolski, A.; Aslam, M.; Vicari, R.; Sheehan, M. T.; Sounik, J. R.; Dammel, R.R.; *Proc. SPIE*, **1997**, *22*, 226

Nishimura, et. al 6923-50 SPIE 2008

These systems are ALL FAR TOO SLOW!!

Control of Resist Sensitivity

$$A + XPhotons \longrightarrow B$$

$$\Phi = B / X$$

$$B = [\Phi][X]$$

- Increased Conversion ot Product at Constant Dose Rate Demands:

  – Increased absorption > X or

  – Higher Quantum Efficiency > Φ

Chemical Amplification