Nanometer Scale Patterning and Processing

Spring 2016

Lecture 5

Resist Technology

Resist Technology

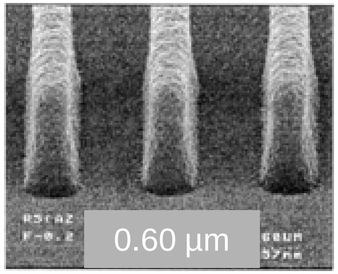
- Photoresist components
  - A resin or base material
  - A photoactive compound (PAC)
    - Dissolution inhibitor and sensitizer
  - A solvent
    - Controls viscosity
- Resolution and sensitivity
  - Resolution: based on both resist and lithography tool
  - Sensitivity: trade off with resolution

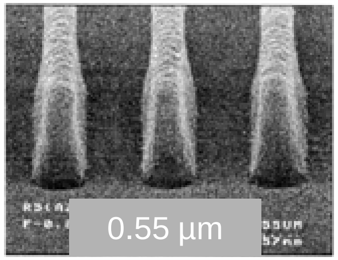
Resist: the Unsung Hero

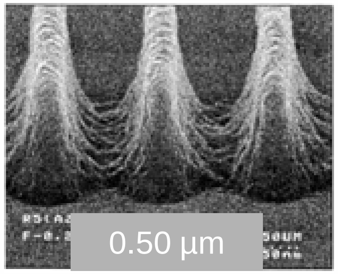
introduced in:	**1984**	**1990**	**1996**
resist name:	AZ$^{®}$1500	AZ$^{®}$6200	AZ$^{®}$7900

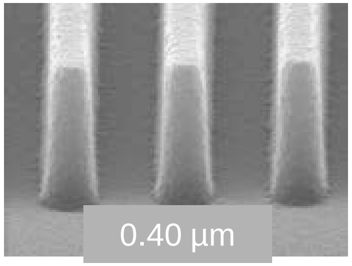
all resists on Nikon$^{®}$ NA=0.54 i-line stepper

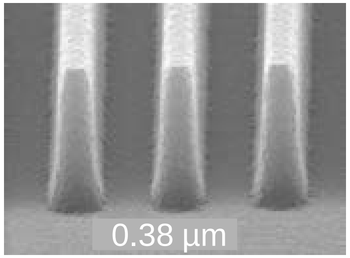
AZ1500: no Post Exposure Bake

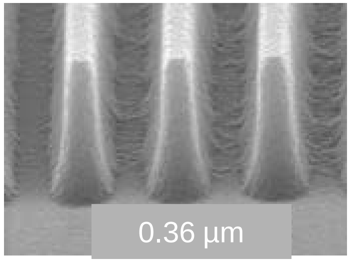


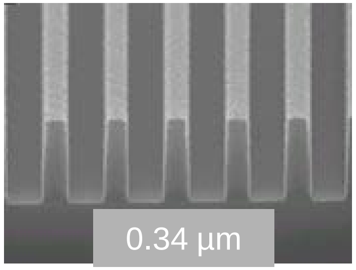


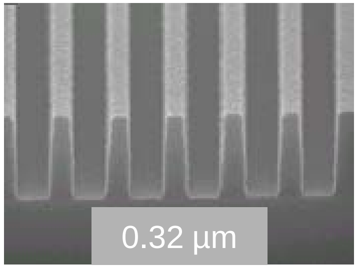


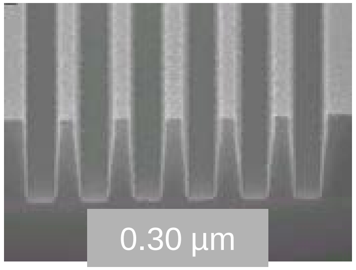




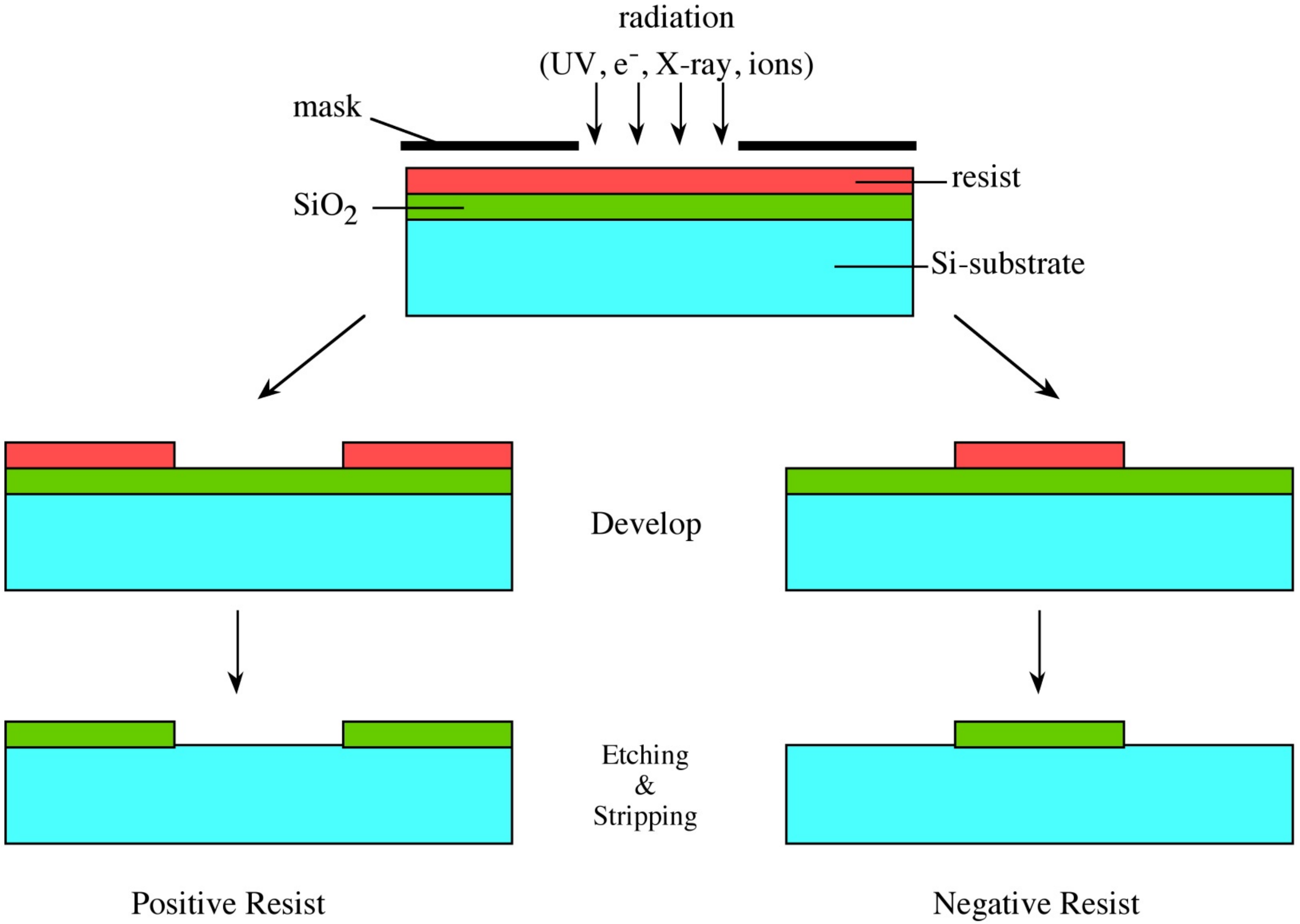






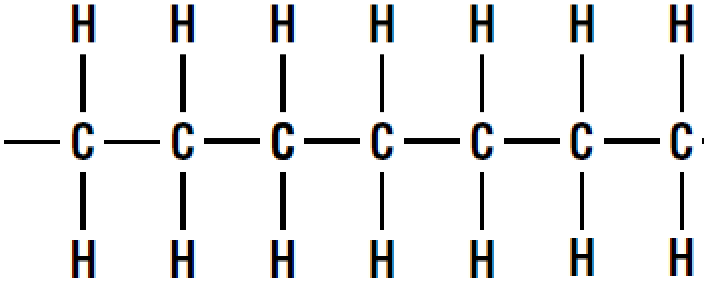


Polarity of (Photo)resists

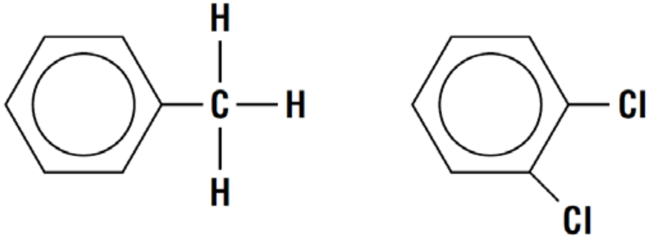


http://cnx.org/content/m25525/latest/

Organic Materials and Polymers



Polyethylene

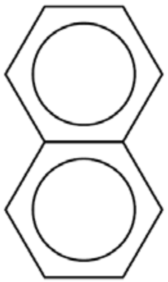


Toluene

(A)

Ortho-Dichlorobenzene

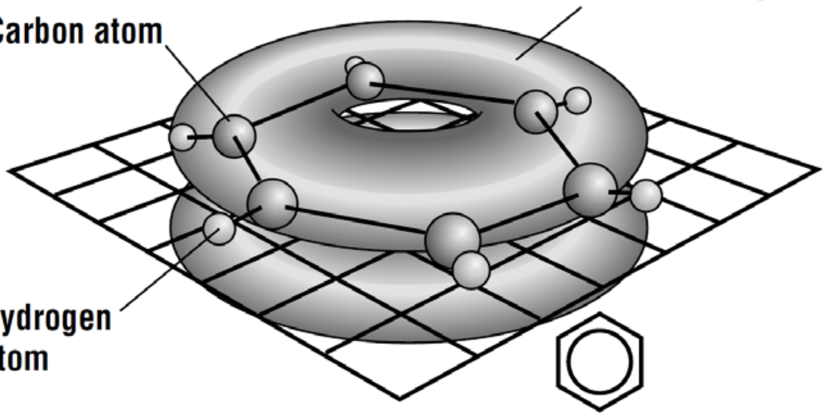
(B)



Naphthalene

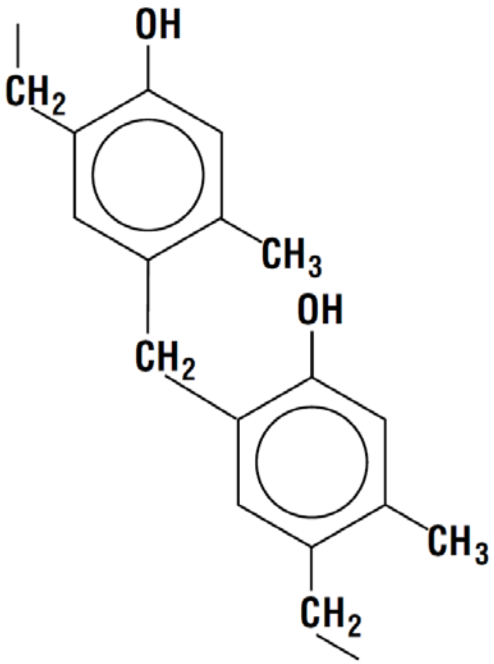
(C)

Benzene (C_6H_6) molecular model

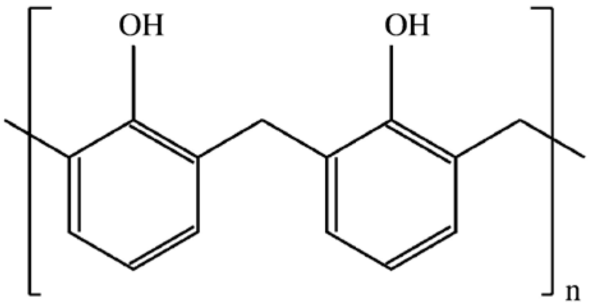


- Aromatic rings: six-carbon rings
- Graphene: 2D array of benzene

Novolac Resins



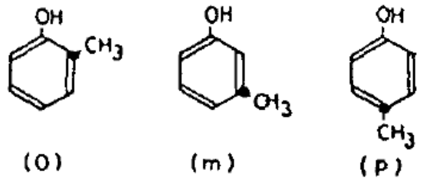
Meta-Cresol Novolac



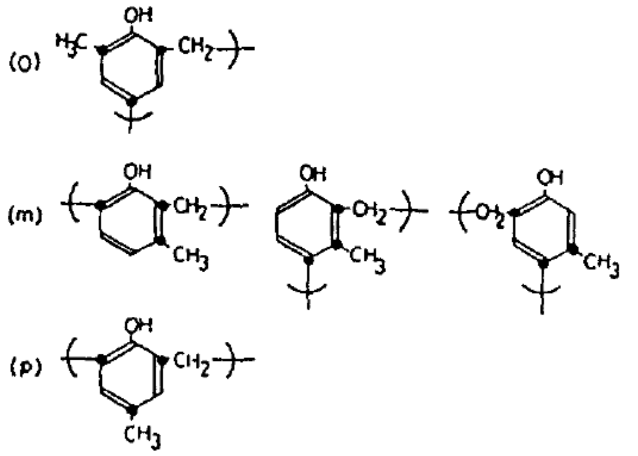
General Novolac resins

(1) Molecular Weight

(2) Isomeric Structure of Cresol



(3) Methylene Bond Position

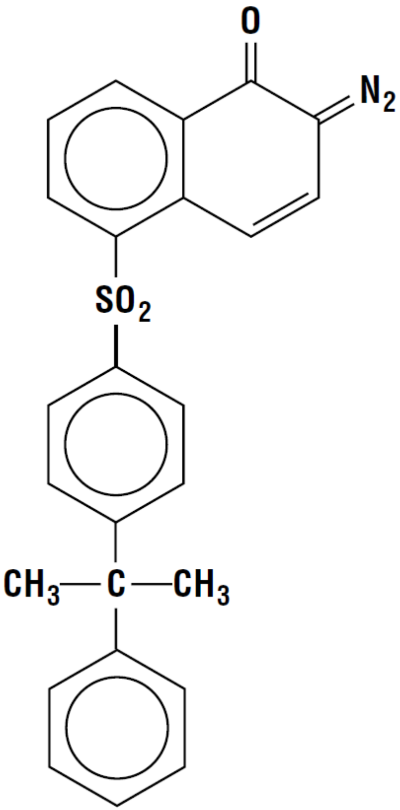


(4) Molecular Weight Distribution

(5) Content of Quinonediazides

(6) Kinds of Phenolic Compounds

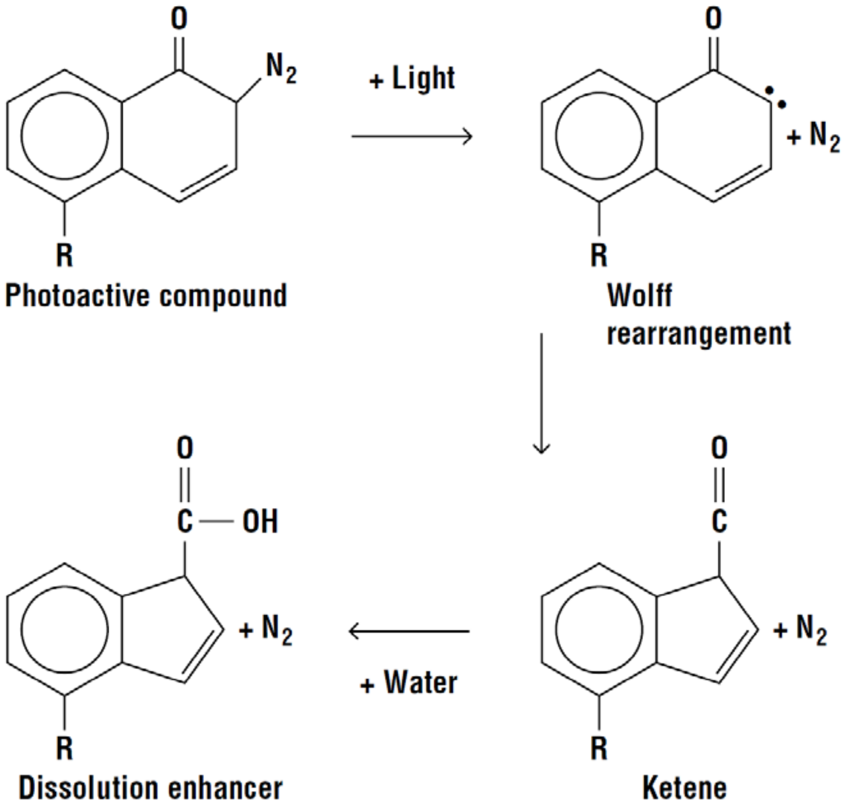
Diazo Quinone (DQ)



- Most common PhotoActive Compound (PAC) for g and i-lines
- Structures below SO_2 not critical

Novolak/Diazide positive resist

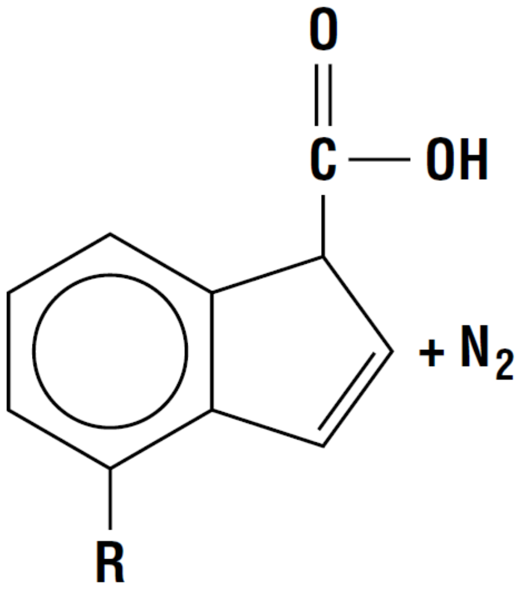
- Novolac: resin, non-photosensitive, transparent
- DNQ: photosensitive and dissolution inhibitor.
- DNQ: Bleachable absorber, ensures uniform exposure through the entire resist thickness



Typical dissolution rates of novolac/ DNQ type photoresist in developer	
•pure novolac resin	~5 nm /sec
•unexposed photoresist (i.e., resin plus inhibitor)	~0.5 nm/sec
•fully exposed photoresist	~500 nm/sec

- Generation of N_2 aids development
- Sensitive to i-line (365 nm)
- Previously dominant resist

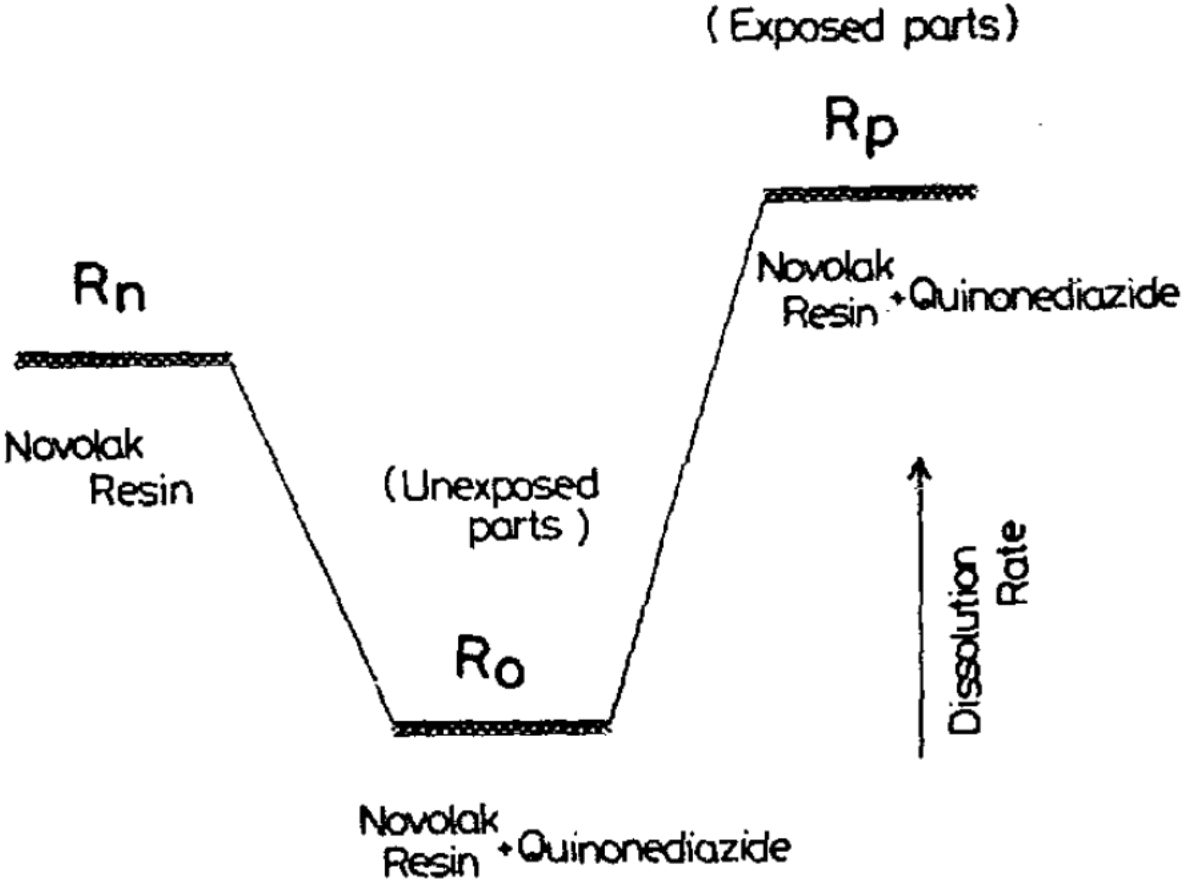
Enhancing the Resin Solubility



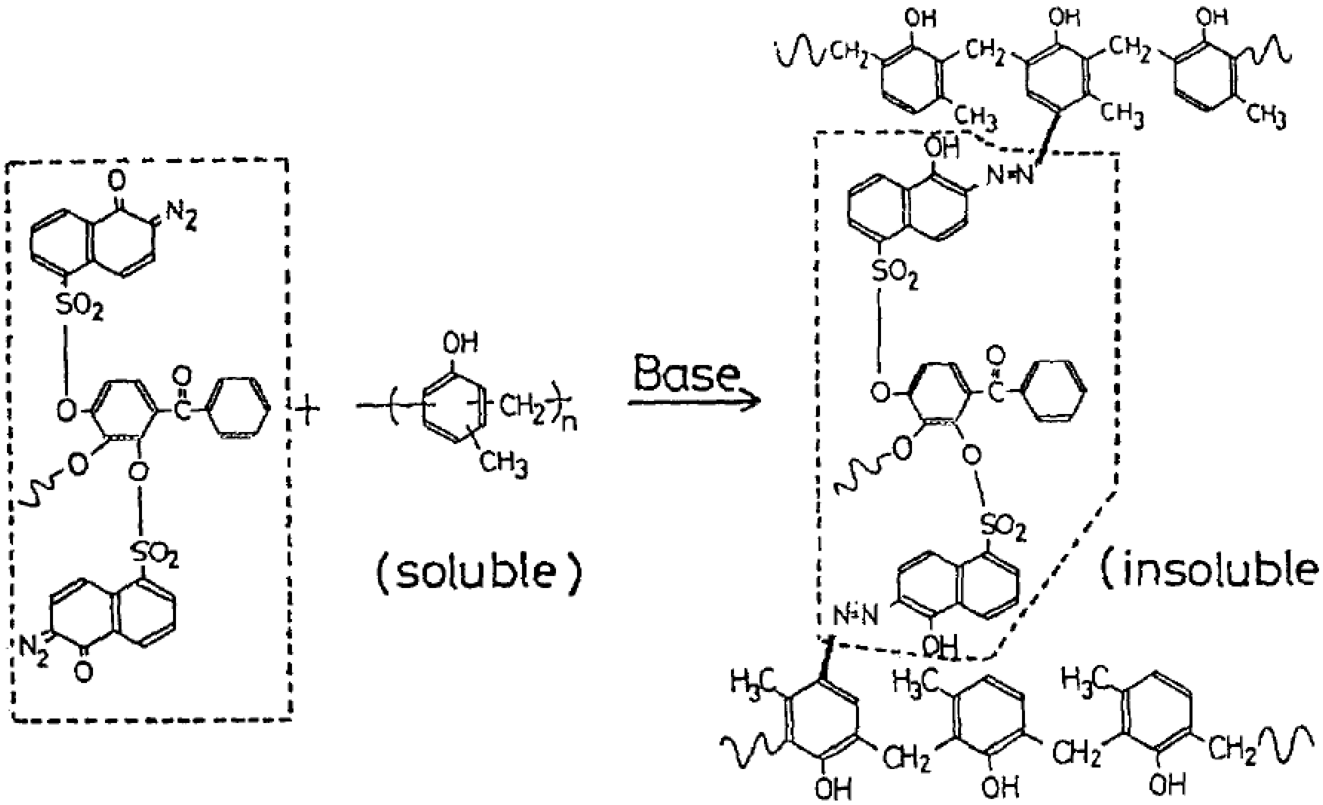
- Carboxylic acid reacts and dissolves in basic solutions
- Resin/carboxylic acid mixture will rapidly take up water
- The Nitrogen released foams the resist

Polymer (Resin) solubility

- Dissolution rate proportional to MW^{-2}.



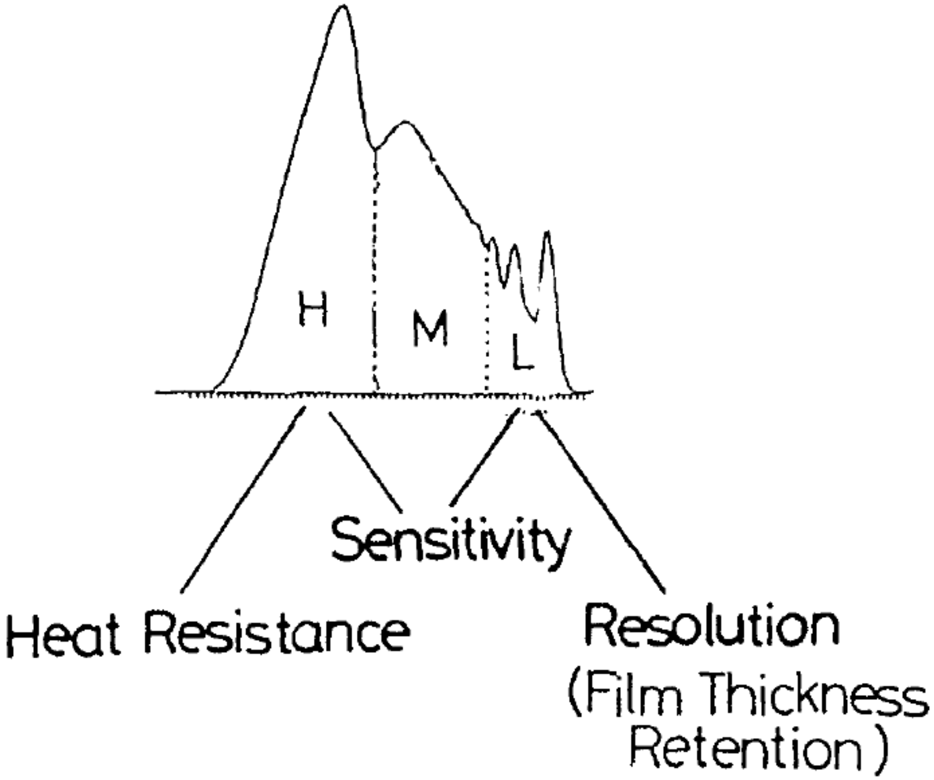
Inhibition of the Resin Dissolution

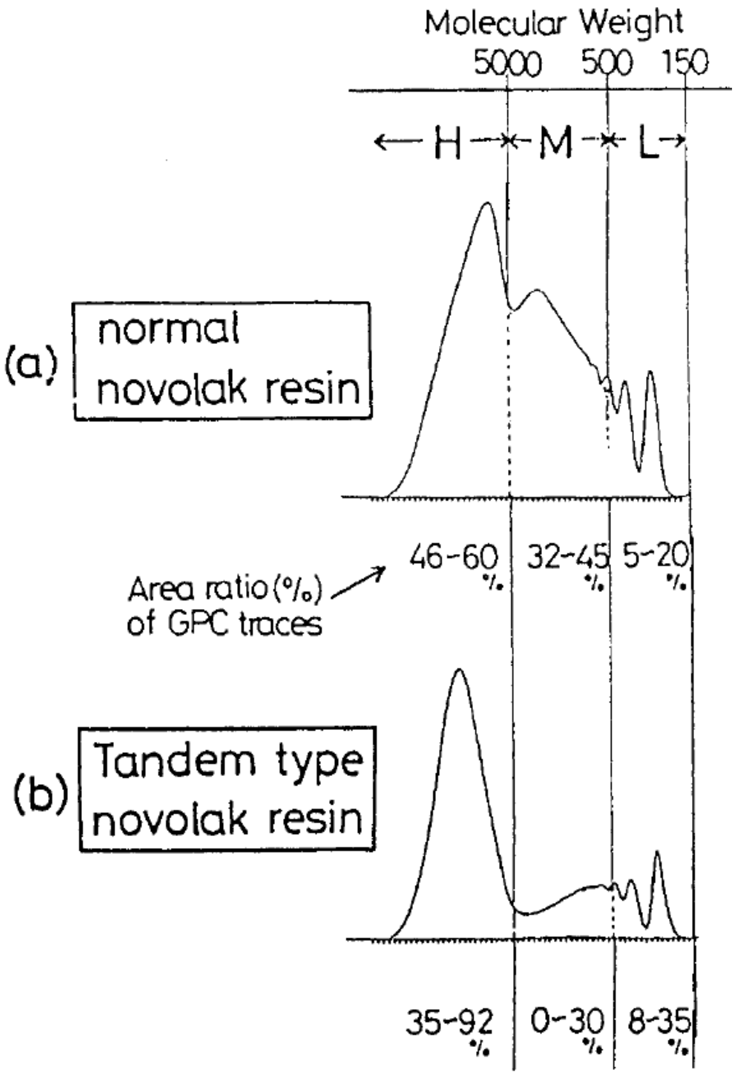


- Reaction occurs at interface of resin and developer
- Increases the Molecular weight
- pH ~ 12.5 for developer solution

http://scitation.aip.org/content/avs/journal/jvstb/7/4/10.1116/1.584621

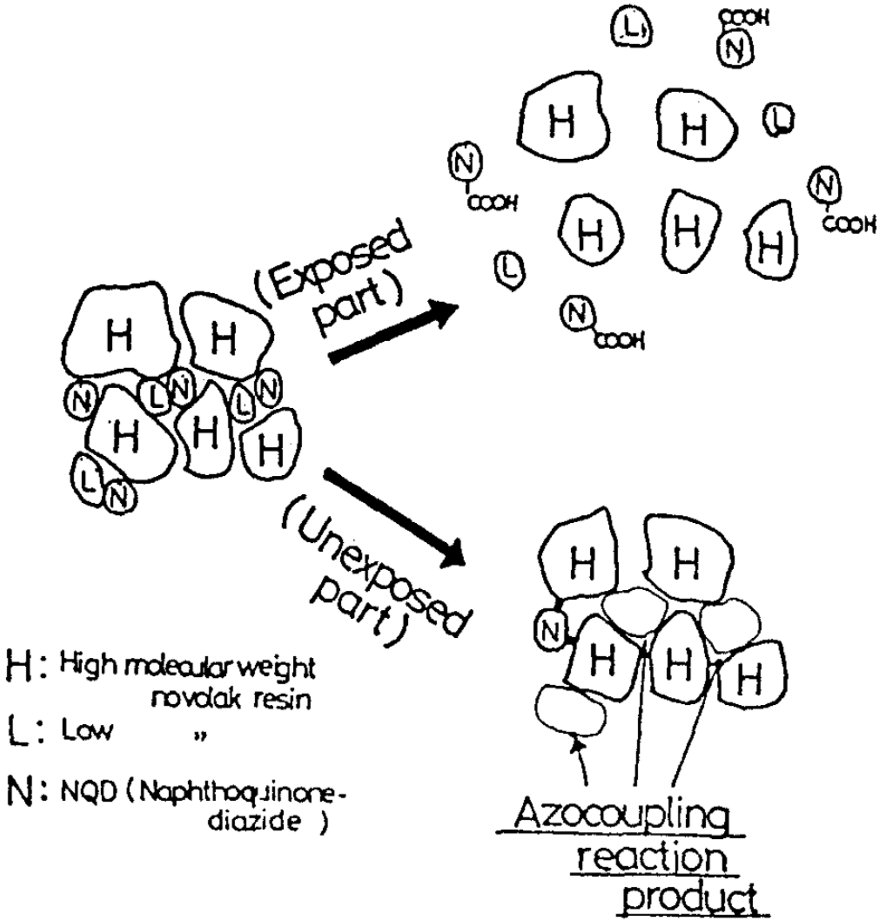
Heat Resistance





- Molecular Weight distribution of Novolac

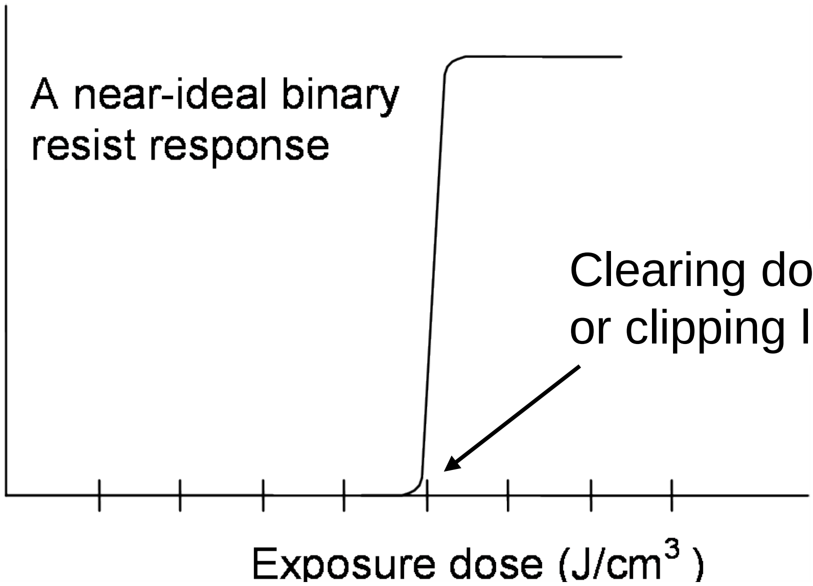
Stone Wall Model



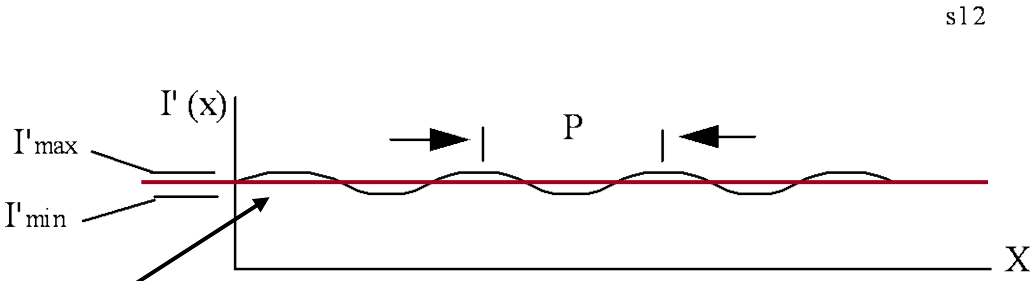
Sensitivity, resolution and heat resistance

http://dx.doi.org/10.1002/pen.760322009

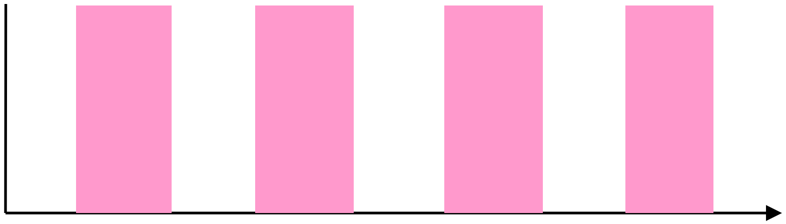
Contrast (or the magic) of resists



Clearing dose
or clipping level

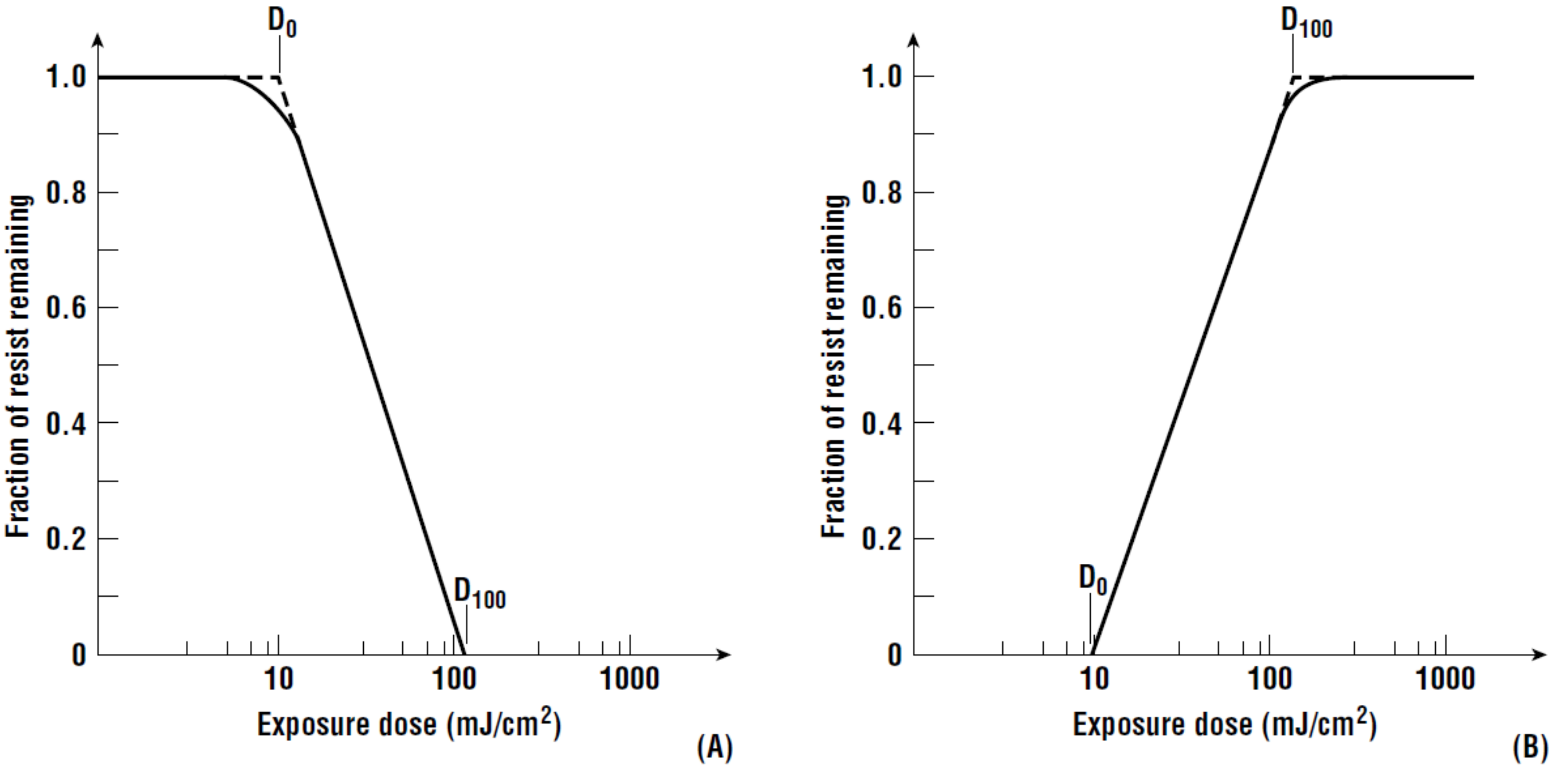


Latent image in resist



Developed resist profile

Contrast of Practical Resists



Typical values: 2-5

$$\gamma = \frac{1}{\log_{10}(D_{100}/D_0)}$$

Area dose: J/cm² for UV and x-ray lithography

C/cm² for e-beam exposure

Fundamental quantity: Energy or number of particles absorbed/unit volume

Complete resist processing

1. Dehydration bake (150 – 200 C, vacuum or N_2)
2. Adhesion promoter application (HMDS)
3. Resist application (spin coat or dip, spray, or laminate)
4. Softbake (SB)
5. Exposure
6. Post-Exposure bake (PEB)
7. Develop (immersion or spray)
8. Hardbake
9. Resist stabilization

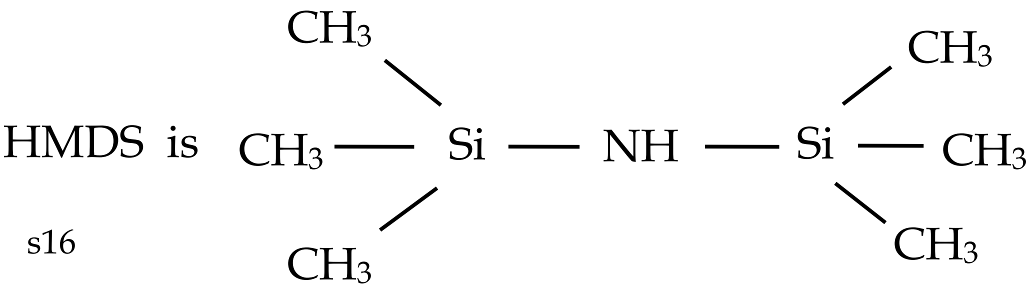
Adhesion of Novolac resists to SiO_2

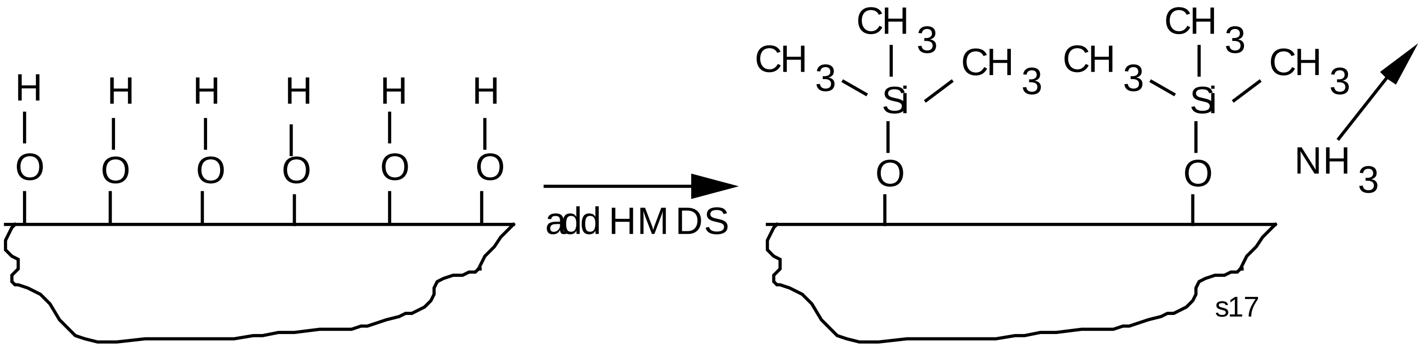
Novolac resists: hydrophobic

SiO_2: hydrophilic

Adhesion promoter: HMDS

(Hexamethyldisilizane)





Vapor priming in an oven

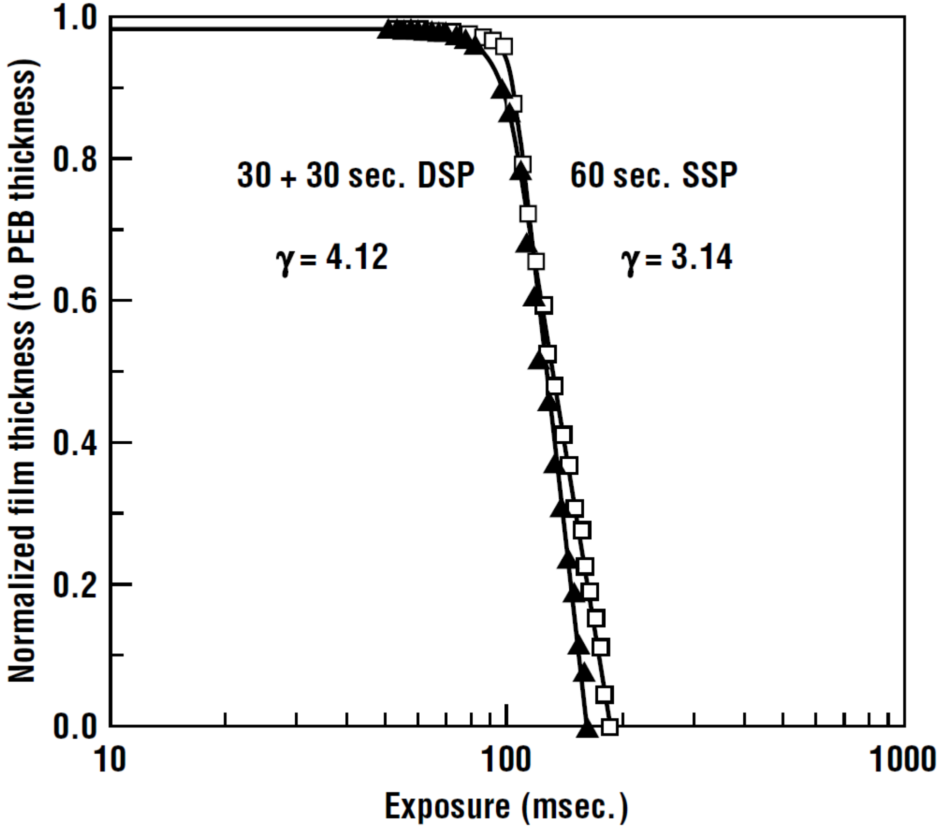
Or spin coating HMDS on the wafer (wasting a lot of materials, but avoids oven)

Softbake

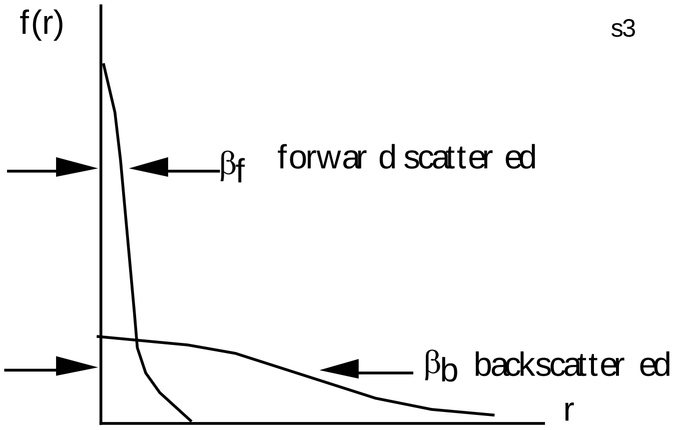
- Shorter time or lower temp
  - Increased dissolution rate → higher sensitivity
  - Lower contrast
- Higher temp
  - Start to drive the photochemistry of PAC
  - Resist dissolution of unexposed areas
- 90 – 100 C , 30 sec – 90 sec hot plate
  - Remaining solvent less than 5%

Developers

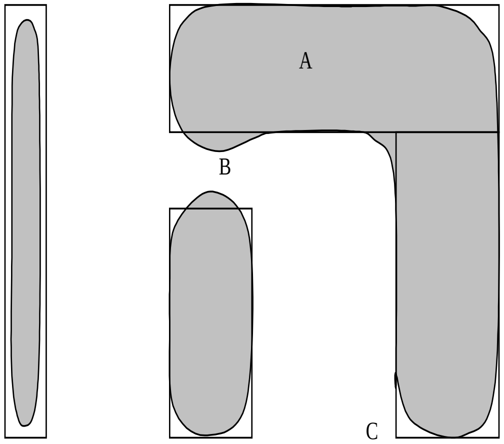
- Basic solutions: pH ~ 12.5
  - Alkaline: such as KOH
  - Tetramethyl ammonium hydroxide (TMAH)
    - Eliminates Na^+ or K^+ that could reduce transistor reliability
  - Temperature needs to be controlled to within 1 C
  - Optimizing development can increase contrast



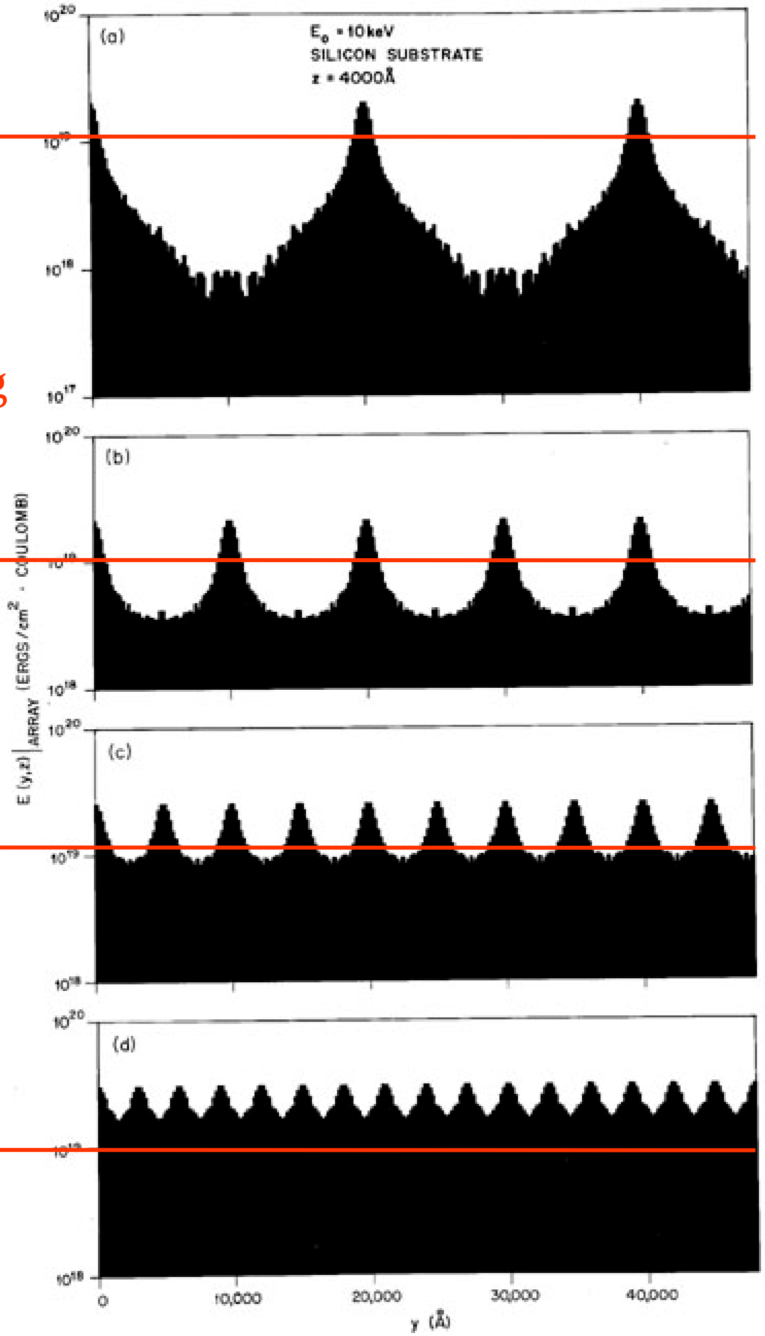
Proximity effect distorts the resist patterns



Lateral density distribution of an incident e-beam



Exposed pattern as a result of proximity effects

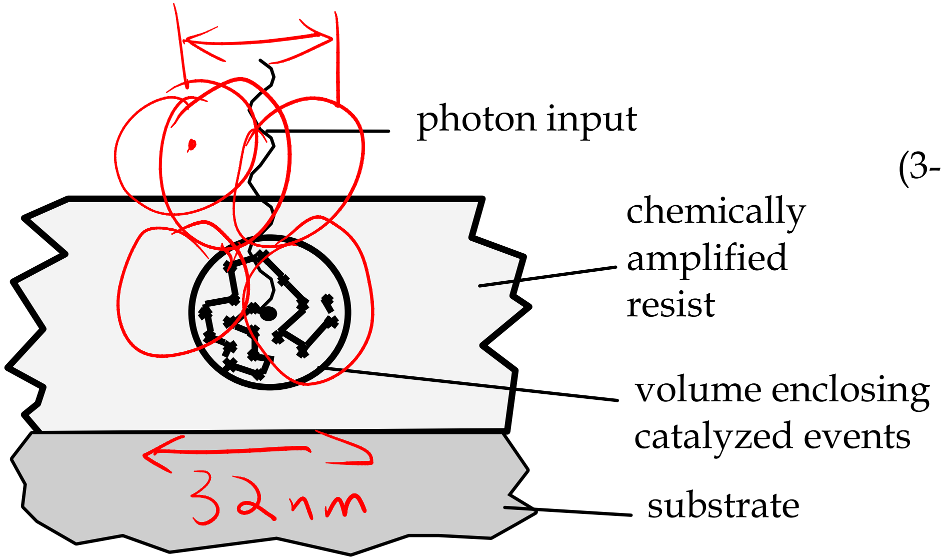


Resist

Clipping

line

Chemically Amplified Resist (CAR)



Acid Catalysis
(3-D random walk of acid)

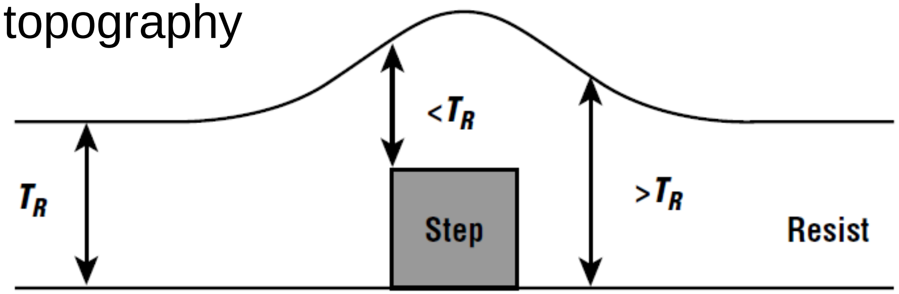
s15

- All resist for radiation wavelengths ≤ 248 nm are CARs
- Provides much higher sensitivity
- Post-exposure bake is necessary
- The diffusion length of the photo-generated acid limits the resolution
- Vulnerable to airborne basic contaminants such as NH_3, short shelf life
- Developer track needs to be enclosed. Expensive!

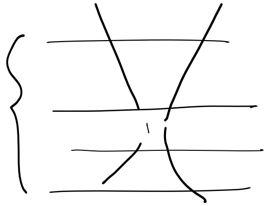
32nm

Separate the functions of Image Recording and "Resistance"

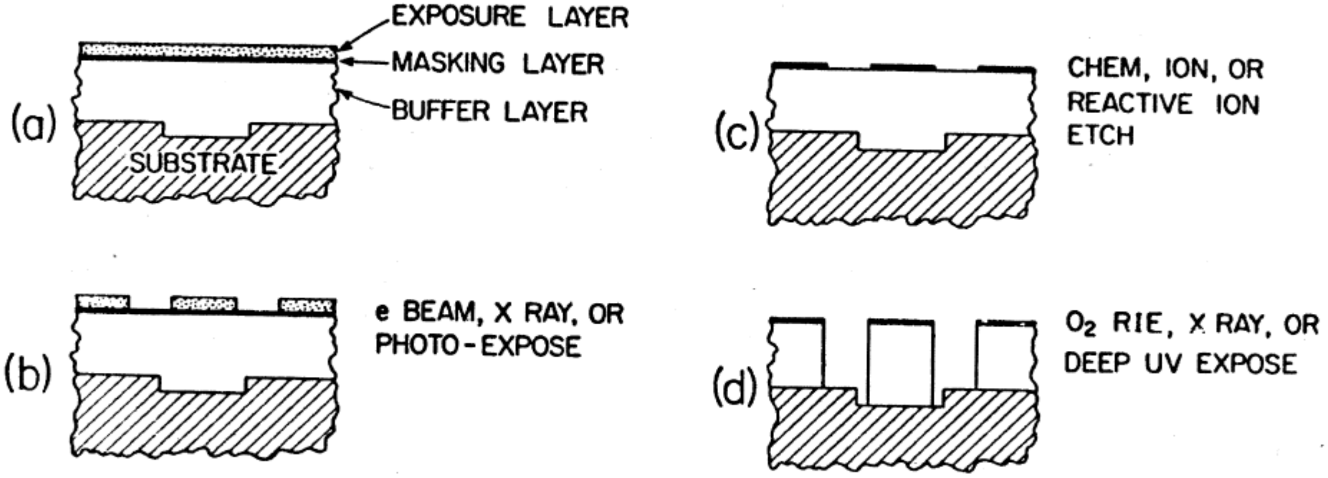
Substrate topography



Depth of focus



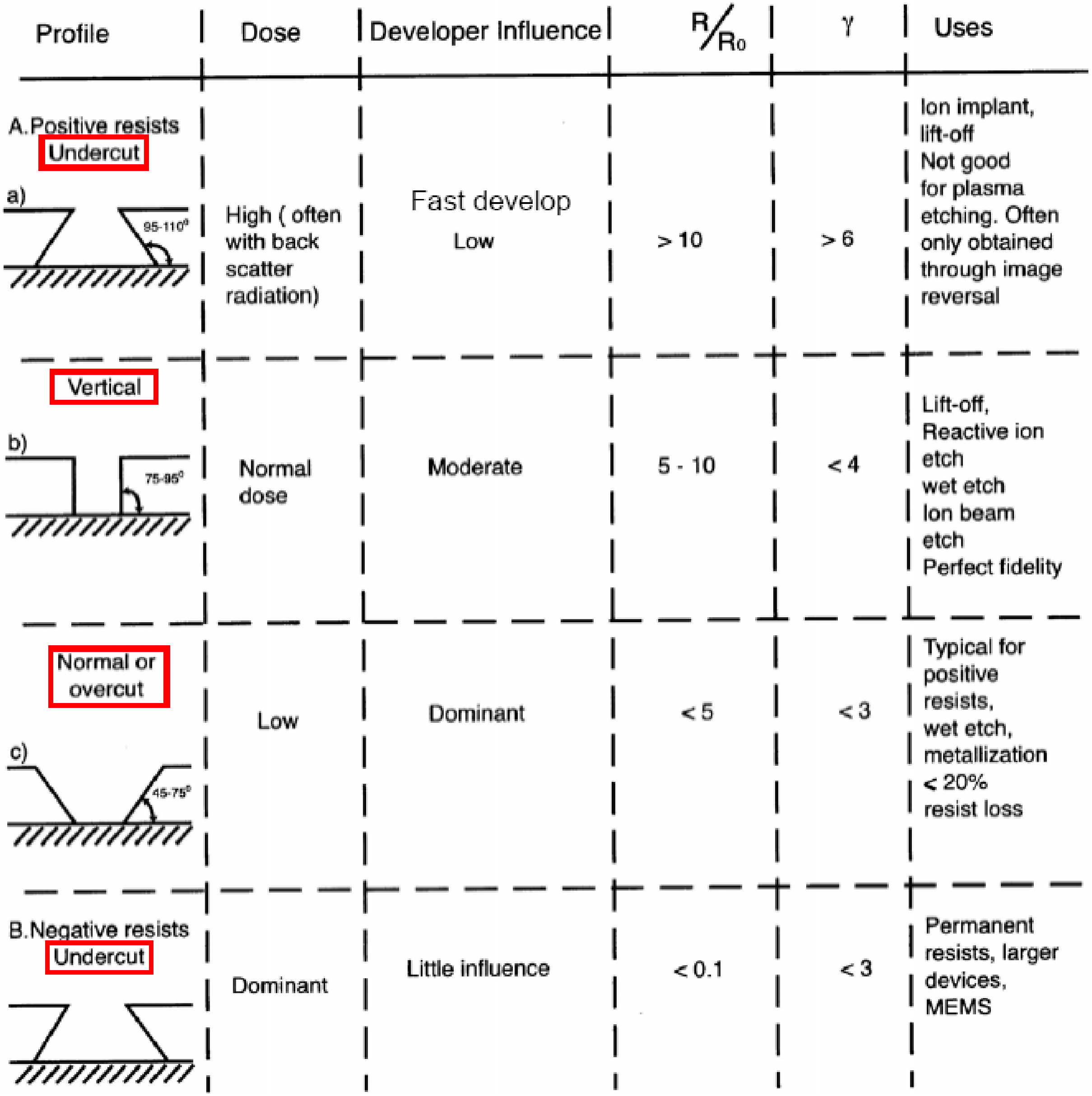
MULTILAYER RESIST TECHNIQUE



Can also perform the function of planarization, i.e. the substrate topology won't affect the linewidth

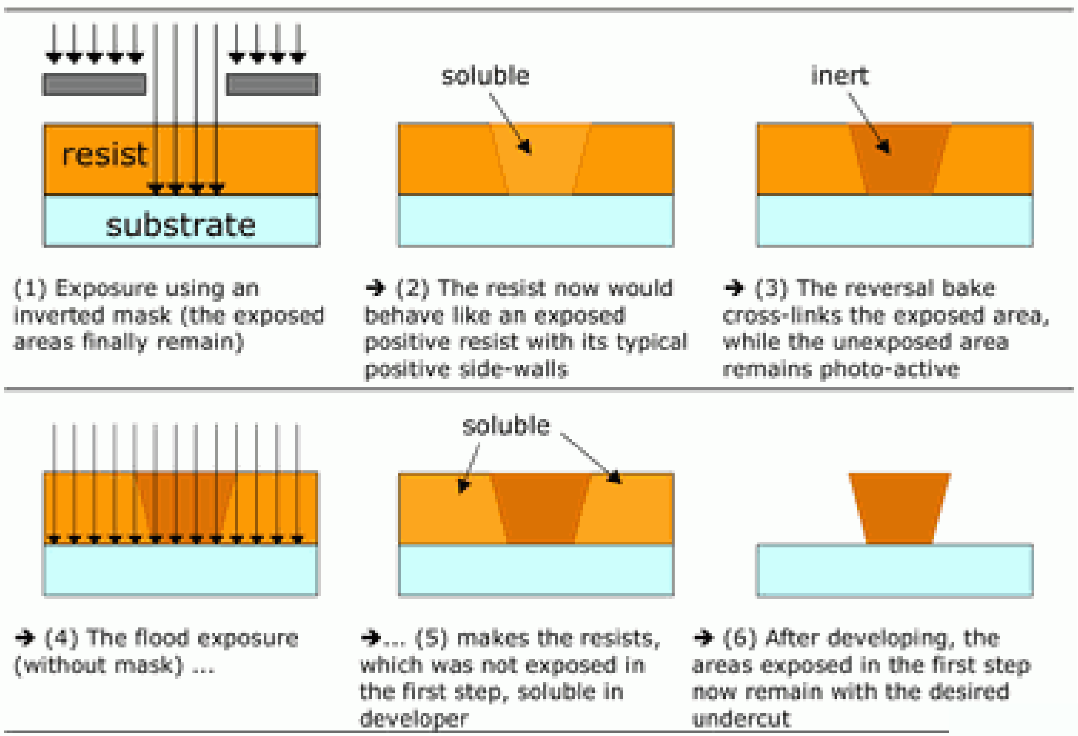
Photoresist Profiles

R: Development rate of the exposed region
R_o: Development rate of the exposed region
γ: Resist contrast



Profile	Dose	Developer Influence	R/R_0	γ	Uses
A. Positive resists Undercut a) 95-110°	High (often with back scatter radiation)	Fast develop Low	> 10	> 6	Ion implant, lift-off Not good for plasma etching. Often only obtained through image reversal
Vertical b) 75-95°	Normal dose	Moderate	5 - 10	< 4	Lift-off, Reactive ion etch wet etch Ion beam etch Perfect fidelity
Normal or overcut c) 45-75°	Low	Dominant	< 5	< 3	Typical for positive resists, wet etch, metallization < 20% resist loss
B. Negative resists Undercut	Dominant	Little influence	< 0.1	< 3	Permanent resists, larger devices, MEMS

Image Reversal



(1) Exposure using an inverted mask (the exposed areas finally remain)

➔ (2) The resist now would behave like an exposed positive resist with its typical positive side-walls

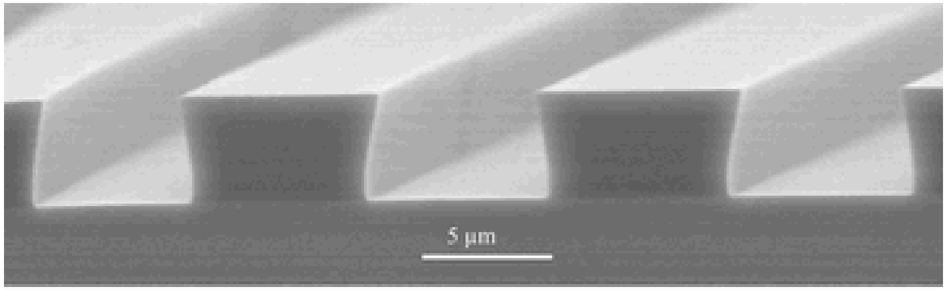
➔ (3) The reversal bake cross-links the exposed area, while the unexposed area remains photo-active

➔ (4) The flood exposure (without mask) ...

➔... (5) makes the resists, which was not exposed in the first step, soluble in developer

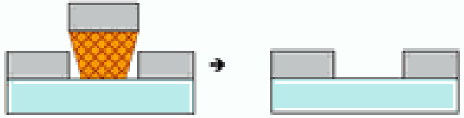
➔ (6) After developing, the areas exposed in the first step now remain with the desired undercut

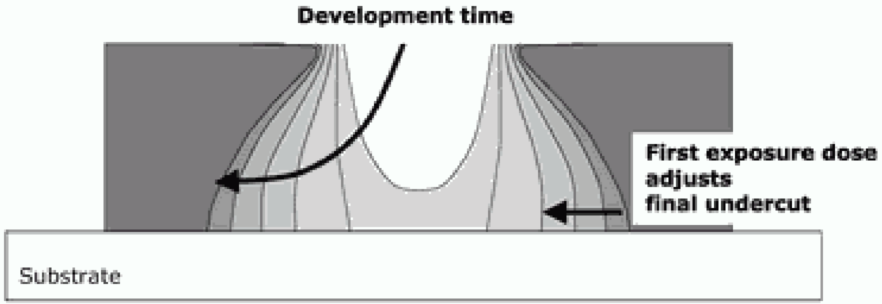
http://www.microchemicals.com/photoresist/photoresist_image_reversal_resists_eng.html



Resist with typical undercut on a Si substrate

Undercut allows Lift-off of evaporated or sputtered films:





Requirements for successful Resists

• contrast (i.e., “binary” response)	• transparency
• resolution	• process repeatability
• sensitivity	• safety
• resistance to acids, bases, plasmas, ion bombardment	• low defect density
• adhesion to a variety of substrates	• topographical coverage
• homogeneity	• high-temperature compatibility
• ease of removal after use	• shelf life
• chemical-compatibility	

Further Reading

- Annual proceedings of the SPIE conferences of *Microlithography* and *Advances in Resist Processing and Technology*
- Prof. Grant Willson at UT Austin
  - *http://willson.cm.utexas.edu/*
- Prof. Andrew Neureuther at UC Berkeley
  - http://www.eecs.berkeley.edu/~neureuth/