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Course: EE6601 / Advanced Wafer Processing

School: School of Electrical and Electronic Engineering

Lithography – Resist Technology

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Lithography Technology – Lesson Overview

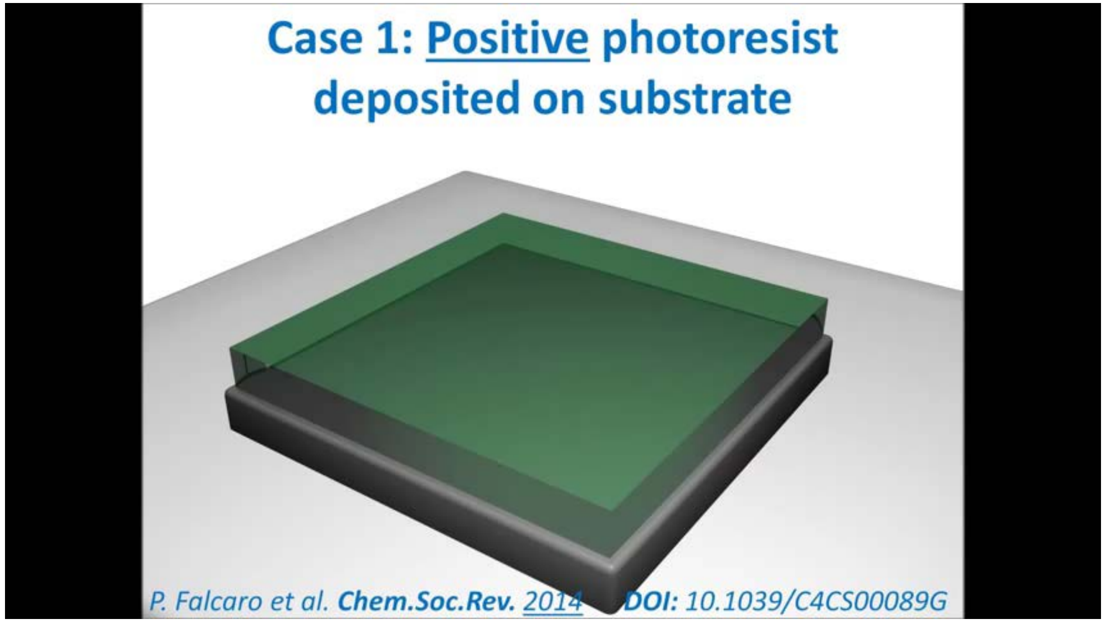
Resist technology:

- Chemistry of resist
- Metrics of resist
- Advantages and disadvantages of positive and negative resist

Chemistry of Resist

Positive and Negative Photoresist/ Resist

Positive Resist



Exposed region becomes **more soluble**

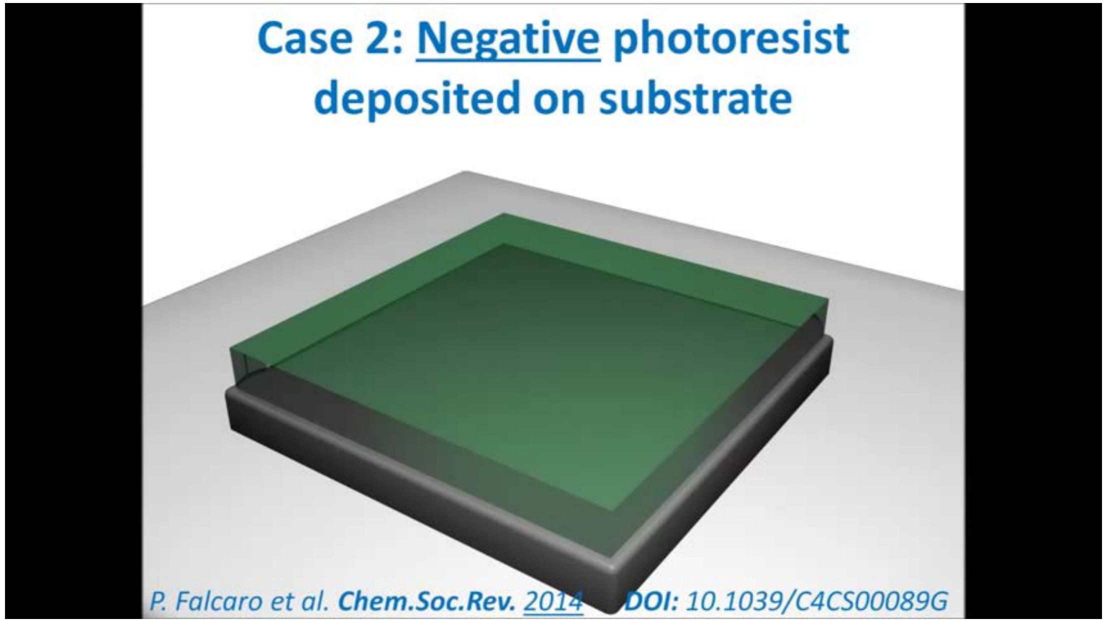
⬇

Wash away **exposed** region

⬇

Pattern formed on substrate is the **same as the mask**

Negative Resist



Exposed region becomes **less soluble**

⬇

Wash away **unexposed** region

⬇

Pattern formed on substrate is the **opposite from the mask**

Positive and Negative Photoresist/ Resist (Cont’d)

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Types of photoresist:

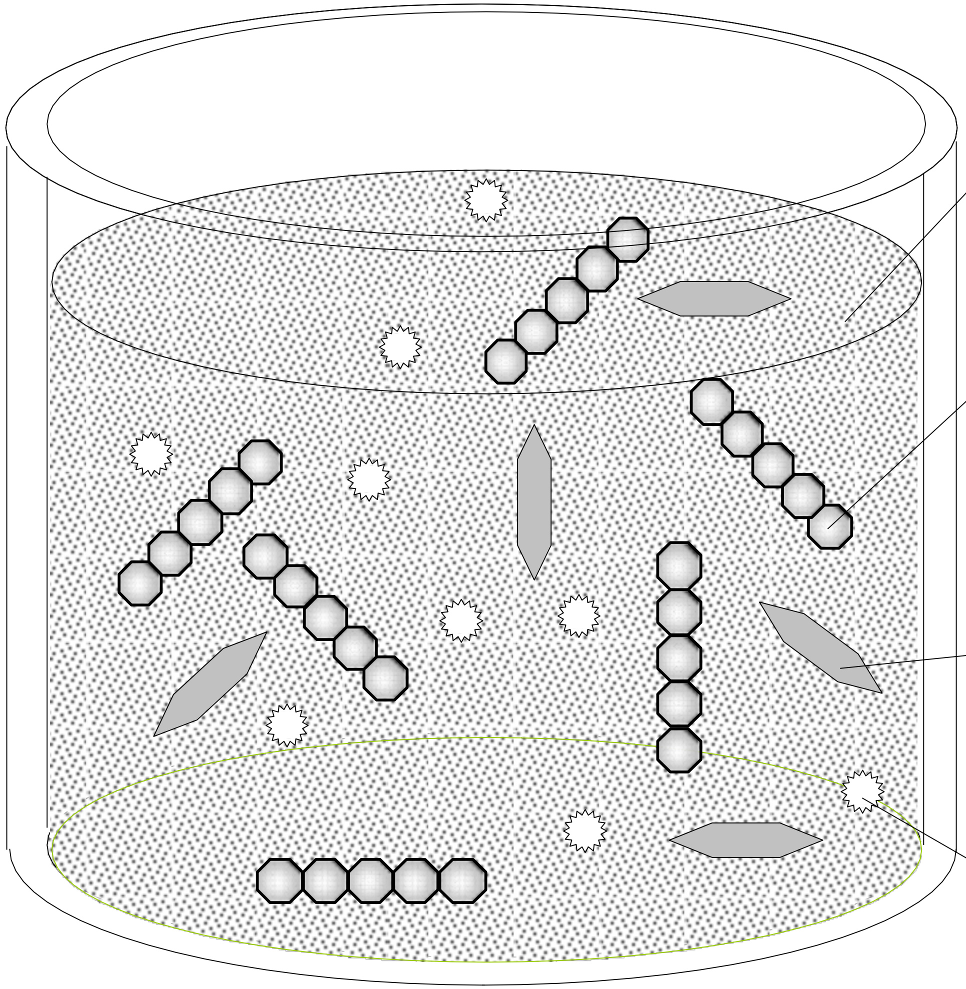
Positive Resist	**Negative Resist**
Exposed region becomes **more soluble**	Exposed region becomes **less soluble**
Exposed areas are removed and unexposed areas remain after *resist development	**Exposed areas remains** and unexposed areas are removed after *resist development
Patterns formed on the wafer are **the same as those of the mask**	**Patterns** formed on the wafer **are opposite as those of the mask**

Pause and read carefully

Pause and read carefully

**Resist development: A process to remove soluble region, will be discussed.*

Components of Resist



Solvent:
Gives resist its flow characteristics

Resin: 树脂
Mix of polymers used as binder; gives resist its mechanical and chemical properties

感光剂
Sensitisers:
Photosensitive component of the resist material

Additives: 添加剂
Chemicals that control specific aspects of resist material

Components of Resist (Cont'd)

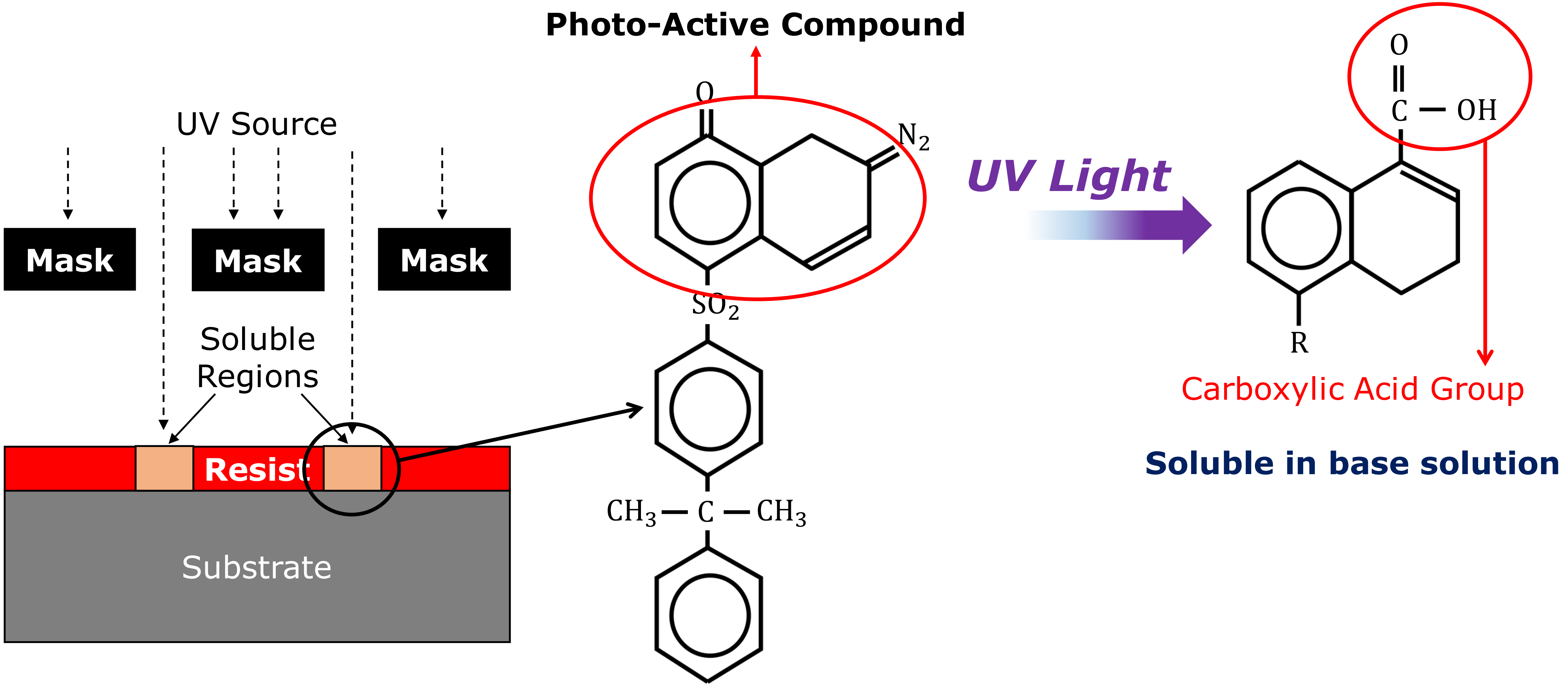
Main components for lithographic capability:

- Resin: Not opaque at λ
  - Give resist mechanical and chemical properties (reaction to developer, etc.)
- Sensitiser
  - Photo active compound/ group (PAC/ PAG) at λ
- Solvent
  - Keeps resist in liquid state
  - Allows spin coating of the resist
  - Solvent content determines viscosity and hence, the **thickness**
- Additives
  - Capability for further process: Etch resistivity/ implant blocking capability

Chemistry of Positive and Negative Resist

- Positive optical resist
  - **Resin** (Novolac resin)
  - **Sensitiser/ dissolution inhibitor** (PAC = Diazoquinones)
  - **Solvent** (Propylene Glycol Methyl Ether Acetate (PGMEA), N-Methyl Pyrrolidine (NMP), N-butyl acetate, xylene, etc.)
  - **Developer:** Hydroxides (TMAH, KOH, NaOH, etc.)
- Negative optical resist
  - **Resin** (Cyclised synthetic rubber resin)
  - **Sensitiser** (PAC = Bisarylzide)
  - **Solvent** (Aromatic solvent)
  - **Developer** (Organic solvents)

Positive and negative resist have different types of developer due to different photochemical reactions.


UV Source
Mask
Mask
Mask
Soluble Regions
Resist
Substrate
Photo-Active Compound
O
N2
SO2
CH3 — C — CH3
UV Light
O
C — OH
R
Carboxylic Acid Group
Soluble in base solution

Positive Resist

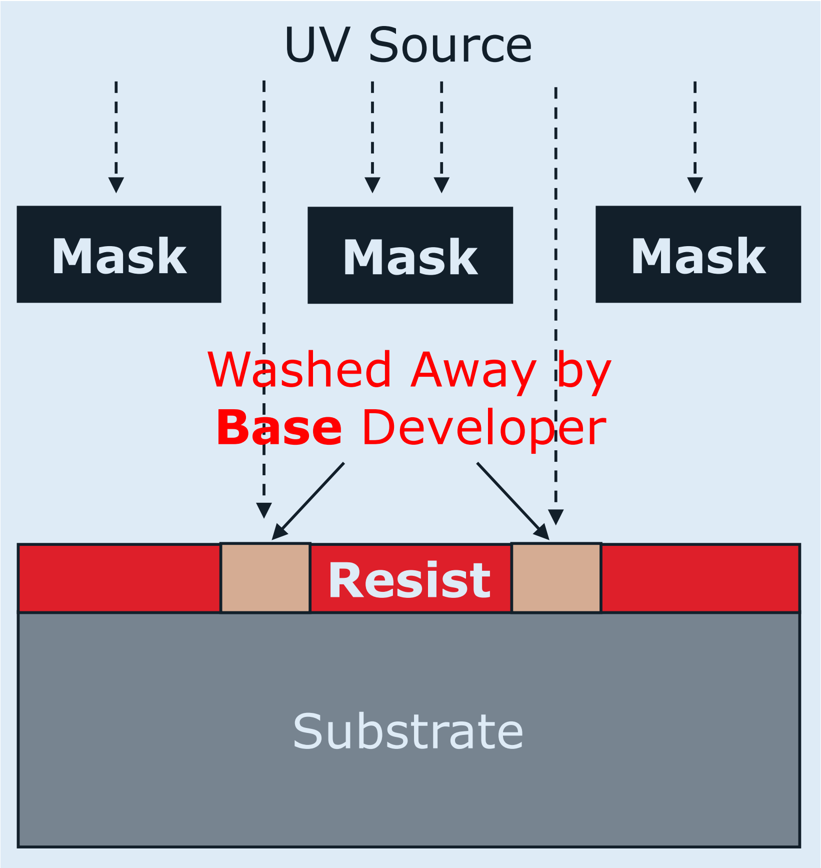
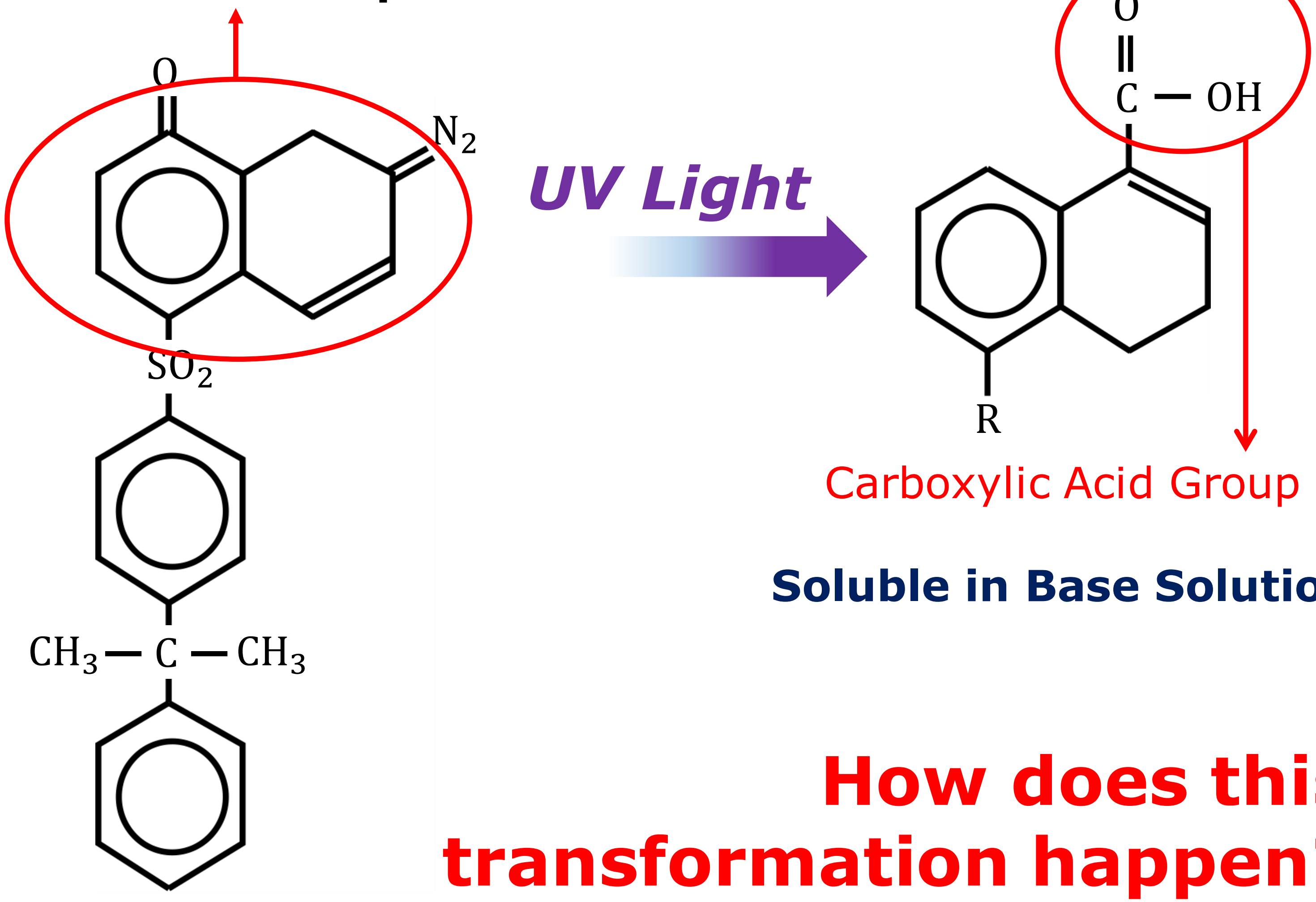


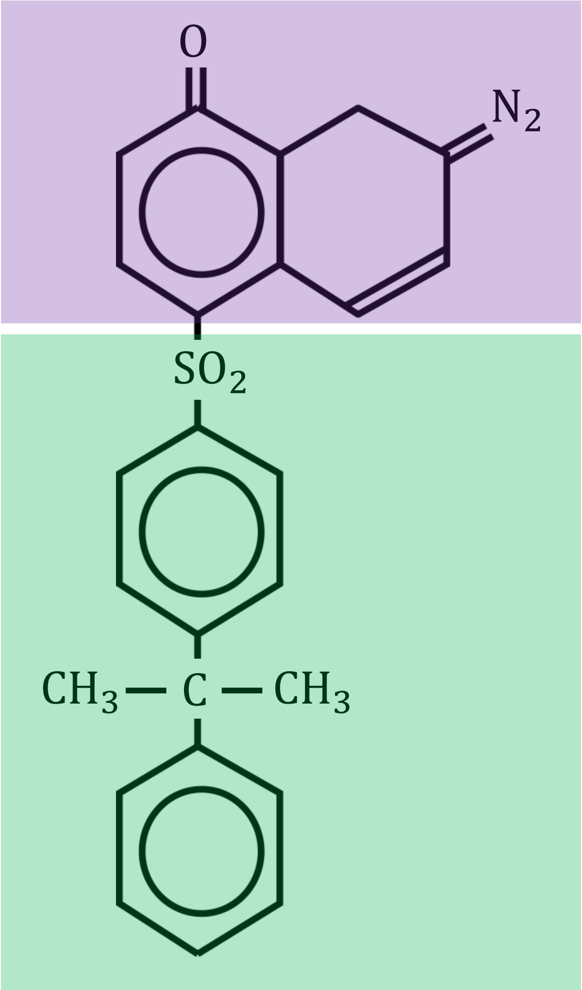
Photo-Active Compound



Soluble in Base Solution

How does this transformation happen?

Chemistry in Positive Resist - DQN

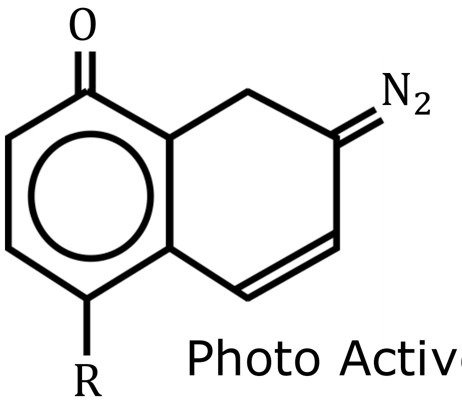


DQN

Diazoquinone (DQ) – Photoactive compound.

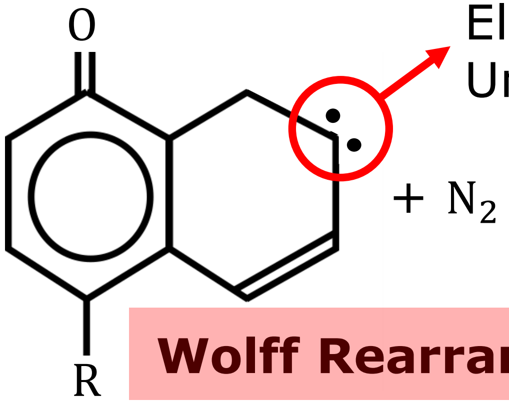
Novolac (N) – Two CH_3 and one OH groups, dissolves easily in aqueous solution.

Photochemical Reaction in Positive Resist



+ Light

Photo Active Compound

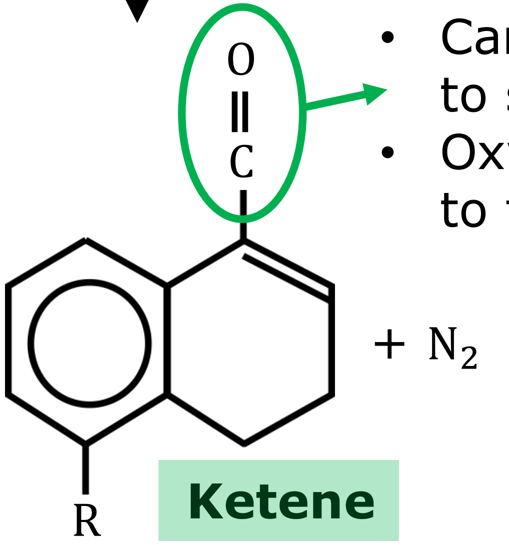


Electron pair – Unstable compound

Wolff Rearrangement

Unstable compound undergoes Wolff rearrangement to stabilise it.

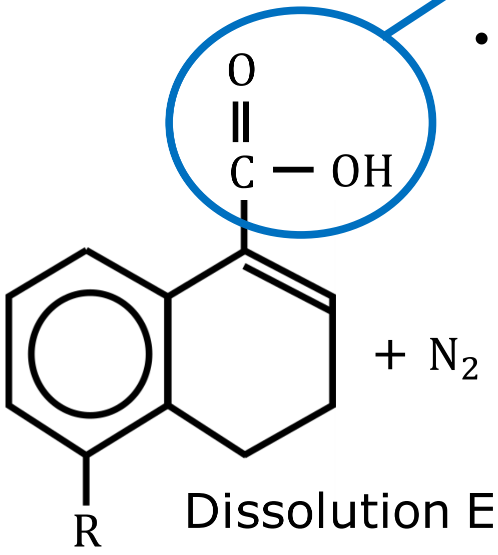
Pause and read carefully



- Carbon moved outside the ring to stabilise the compound.
- Oxygen atom covalently bonded to the carbon atom.

Ketene

+ Water

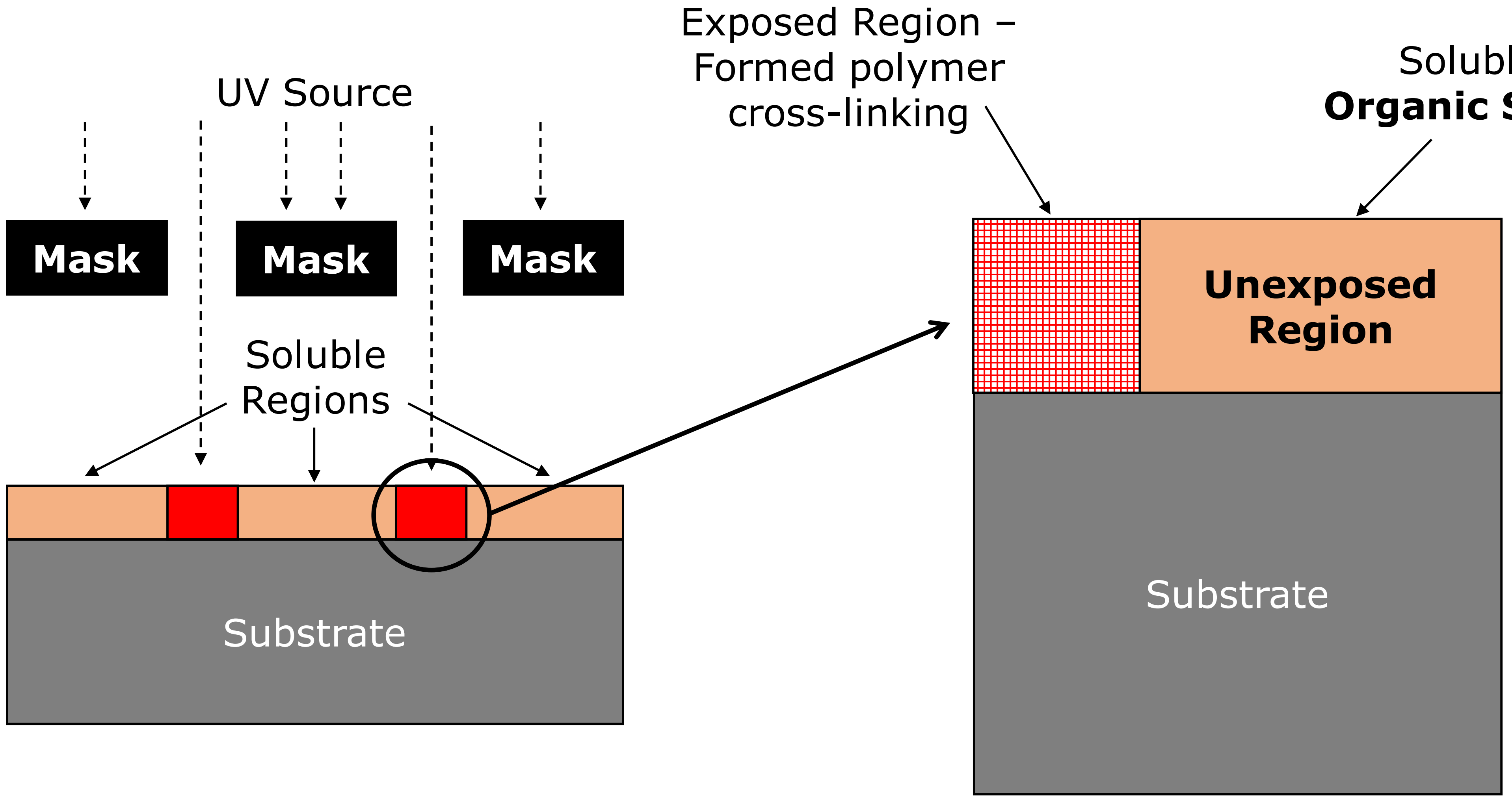


- OH group bonded to the compound.
- Forming carboxylic acid group - Soluble in base developer.

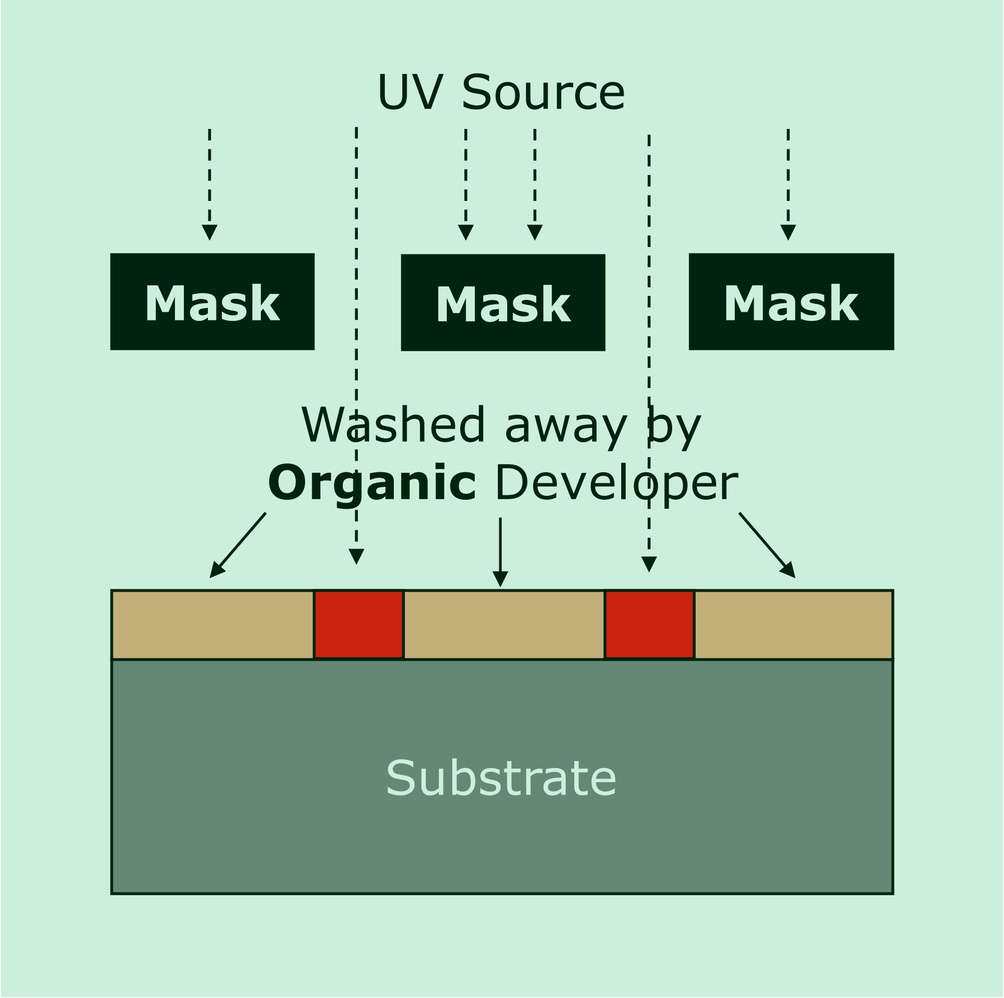
Dissolution Enhancer

Rapid Process

Negative Resist



Negative Resist



Reactions of Positive and Negative Resist

Pause and read carefully

Positive Resist	**Negative Resist**
Diazoquinones (DQ) **Insoluble in developer**	Natural Rubber-Based Polymer (Polyisoprene) **Soluble in Developer**
↓ UV Exposure	↓ UV Exposure
Carboxylic Acid **Soluble in Developer**	Cross-Linked Polymer **Insoluble in Developer**
Alkaline Developer (KOH)	***Organic Developer***

Practice Question

Fill in the blanks.

When **positive** resist is exposed to UV source, the light-sensitive chemical in the resist converted into **(carboxylic acid)** groups, which is soluble in **(base)** developer.

When **negative** resist is exposed to UV source, the light-sensitive chemical in the resist forms **(polymer cross-links)**, where the unexposed region can be washed away by **(organic)** developer.

Pause and try out this question

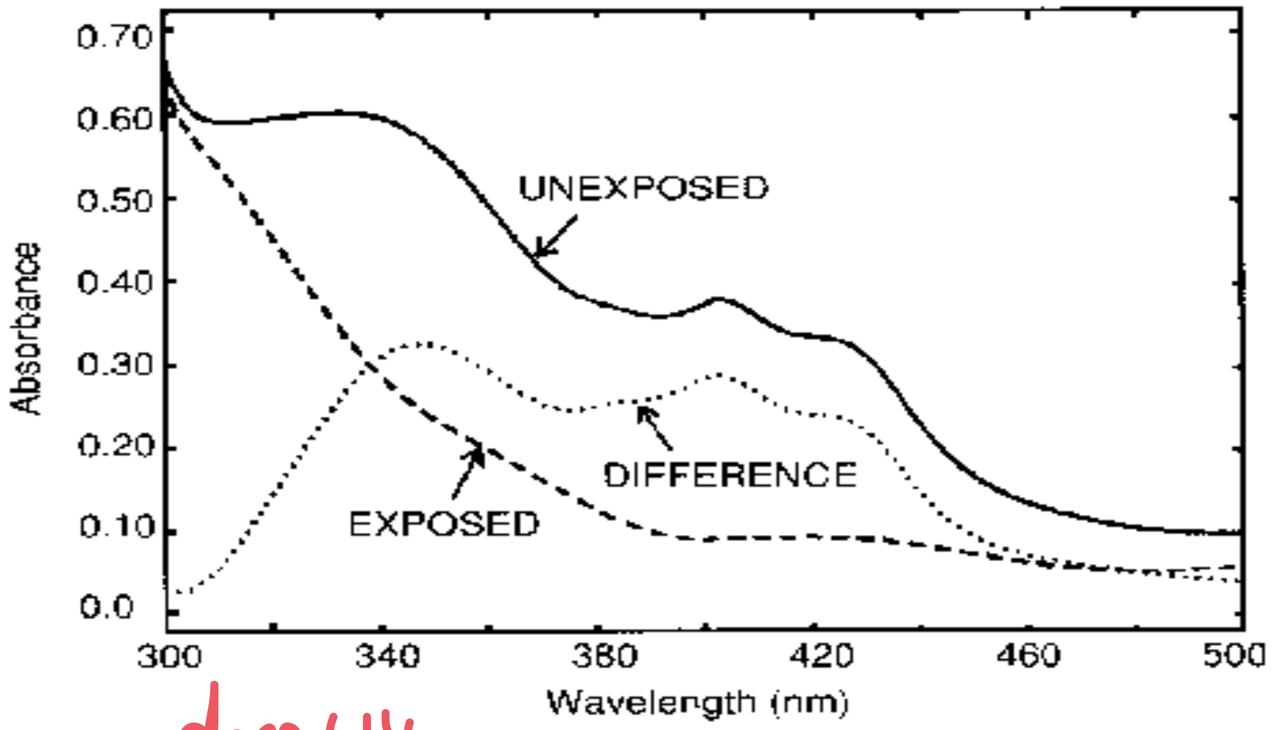
Chemically Amplified (CA) Resists 化学增强抗蚀剂

DNQ resist has large absorption problem below 365 nm wavelength and not suitable for DUV technology

DUV resists rely on a new principle, so-called chemically amplified (CA) resists.
A catalyst, the photo-acid generator (PAG), replaces the PAC.

Figure 2

ABSORBANCE VS. WAVELENGTH

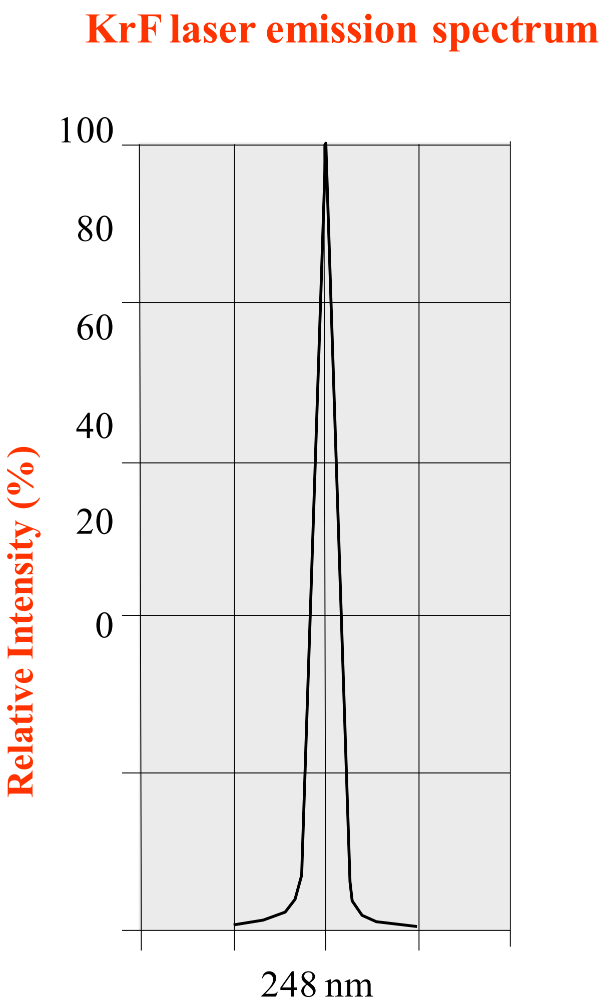


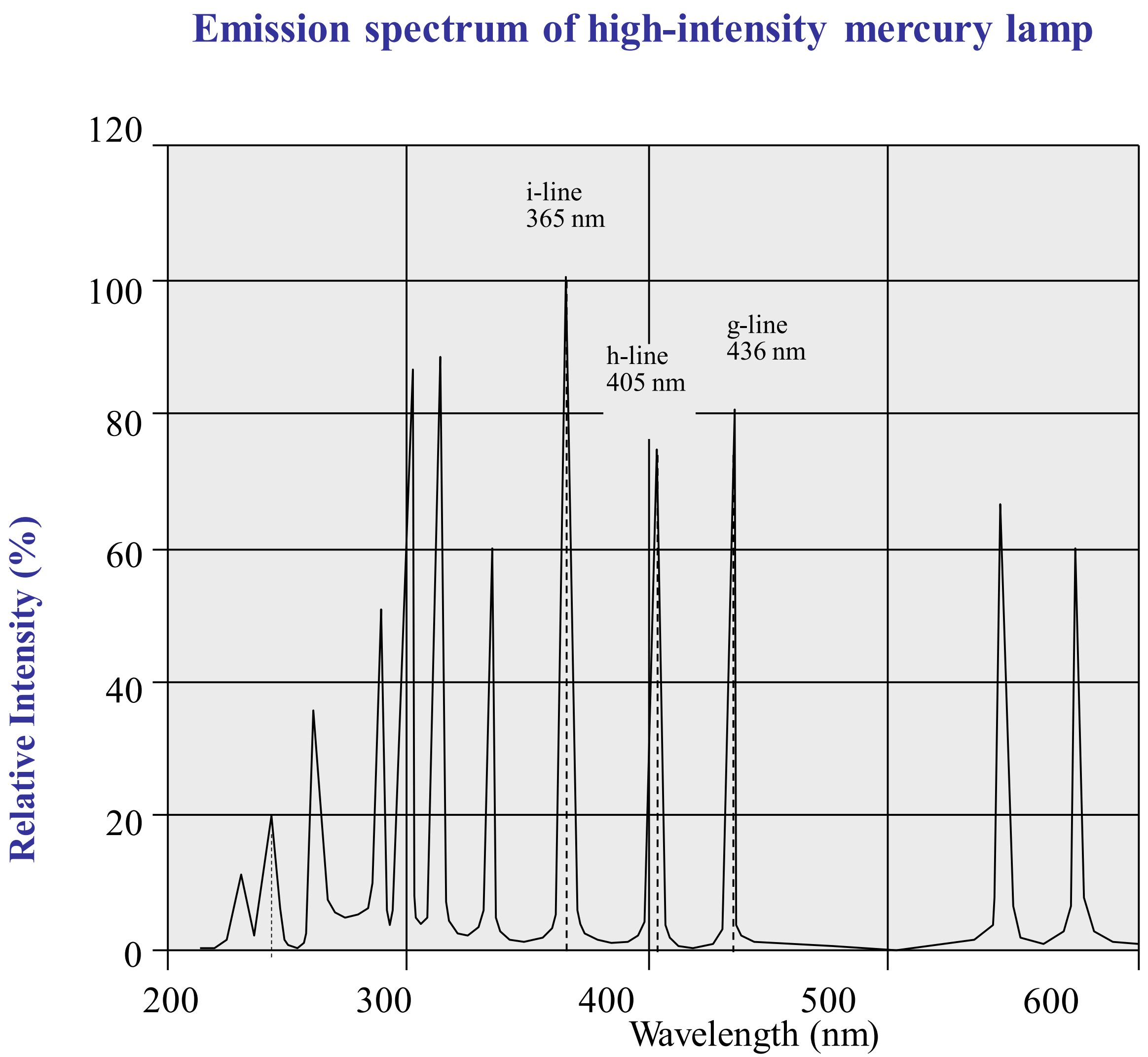
deep UV

Components of Chemically Amplified(CA) DUV Photoresists

Component	Typical Chemicals	Purpose	Remarks
Solvent	Propylene Glycol Methyl Ether Acetate (PGMEA)	**gives resist its flow characteristics**	Compatible to other components
Resin	- tertiary-butoxycarbonyl parahydroxystyrene (tBOC-PHS) (248nm) - phenolic copolymer - cyclic olefin / maleic anhydride (COMA) polymers (193nm)	tertiary-butoxycarbonyl (tBOC) dissolution inhibitor protection group for 248CA resist; gives resist mechanical and chemical properties	Protection group makes it insoluble in developer. Transparent to 193nm DUV Etch resistance to plasma
Sensitizers	triphenylsulfonium salt	Photo-Acid-Generator, PAG **photosensitive component of the resist material**	PAG acts as H+ catalyst for the de-protection of dissolution inhibitor of resin
Additives	Low MW additives to increase contrast, Surfactants, adhesion promoter, dyes	**chemicals that control specific aspects of resist material**	dyes can also be added into the photoresist composition to reduce scattered light from the reflection in the resist/substrate interface.

DUV Emission Spectrum





** Intensity of mercury lamp is too low at 248 nm to be usable in DUV photolithography applications. Excimer lasers, such as shown on the left provide more energy for a given DUV wavelength.*

Chemical reaction of DUV CA resists

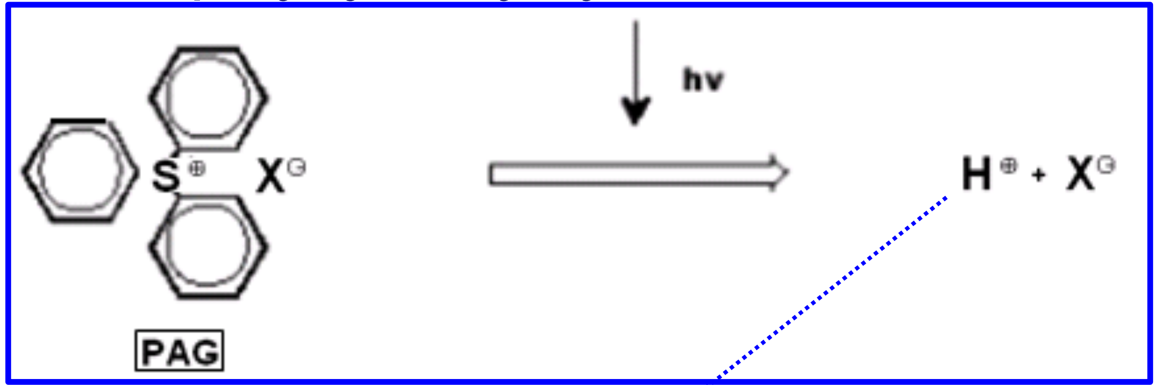
Chemically Amplified (CA) Resist for 248nm DUV

Two-steps chemistry; dissolution inhibition.

PAG – triphenylsulfonium salt

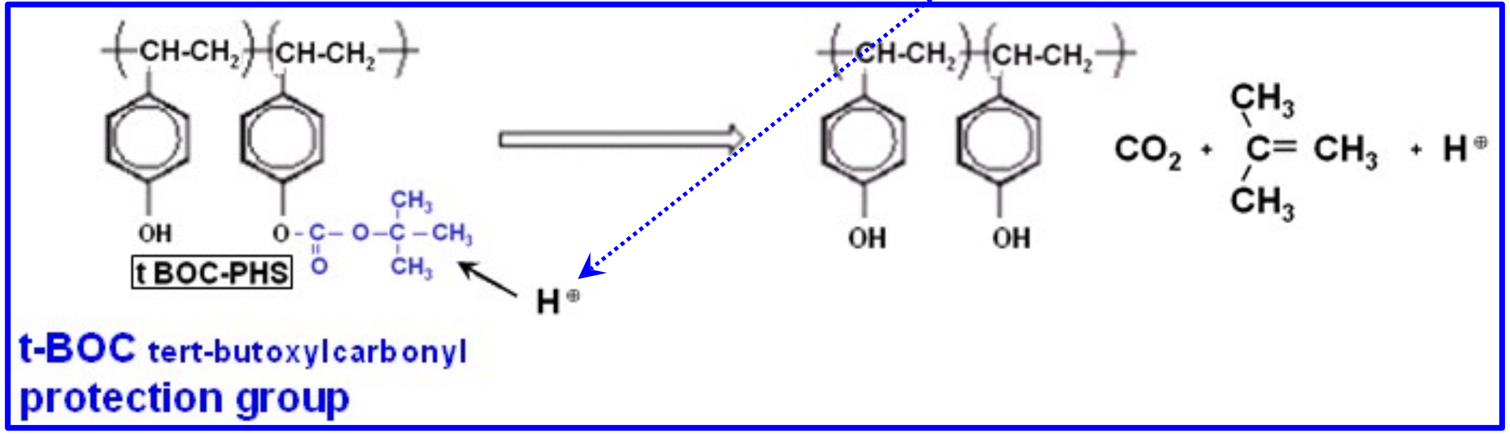
Polymer/Resin -- PHS - polyhydroxystyrene

Exposure



Pose Exposure Bake

PEB



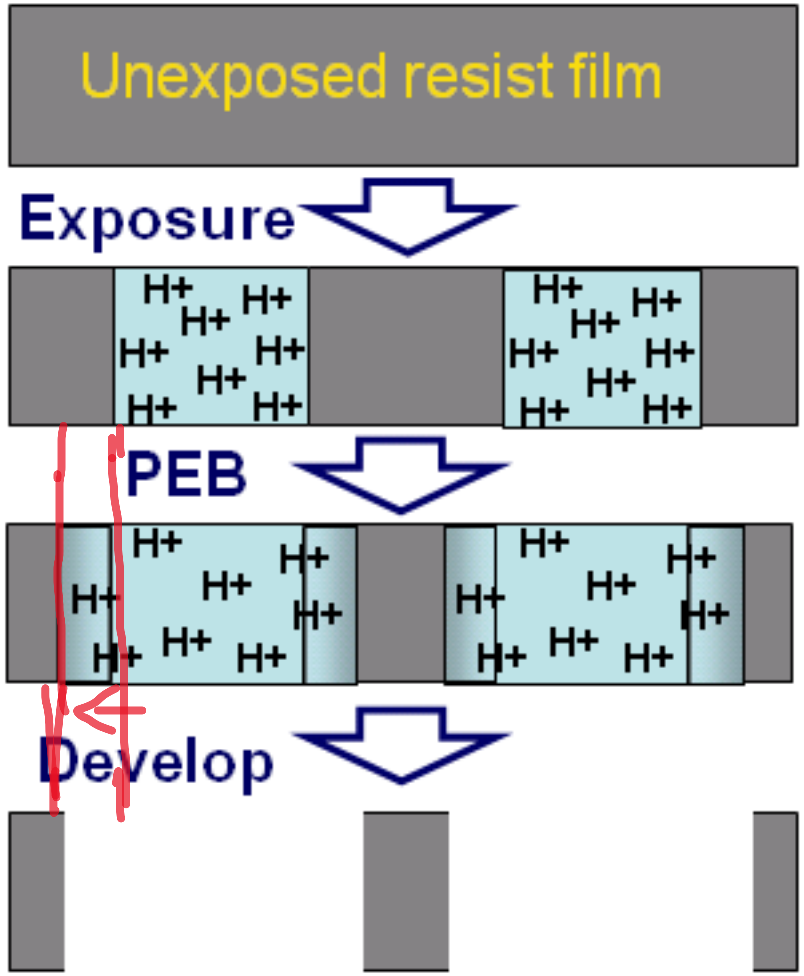
Chemically Amplified Resist

Exposure:
PAG irradiation forms acid at exposed areas.

PEB - Post Expose Bake:
Acid react with tBOC-PHS to form soluble PHS + acid; chain reaction and amplification.
Acid diffuses into the unexposed area.

Chain reaction stops at end of PEB process.

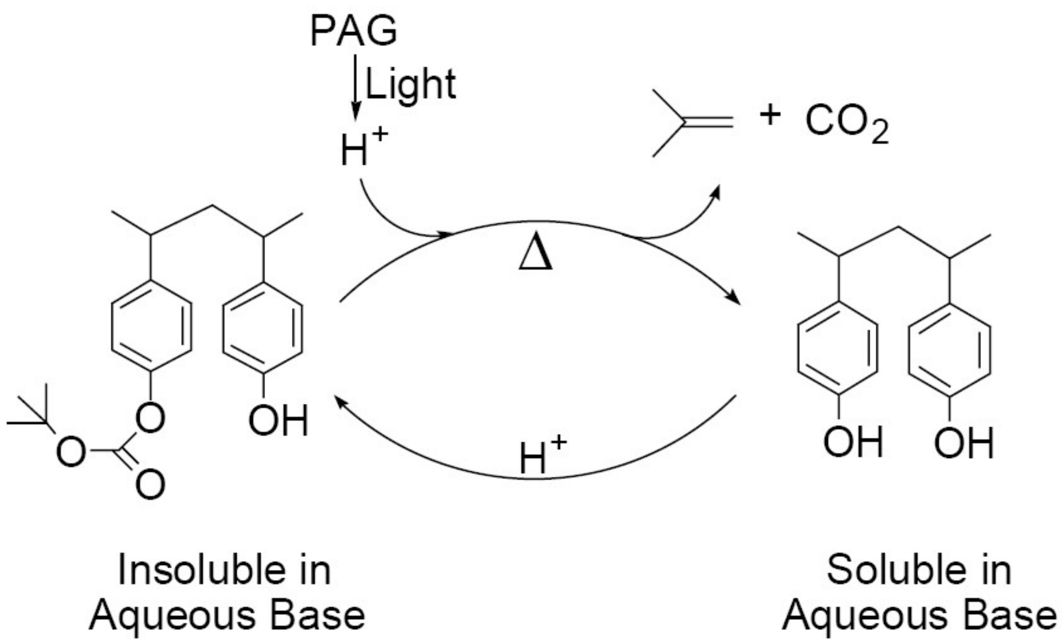
Resist base will neutralize the acid



Resulting line width → smaller than optically printed.

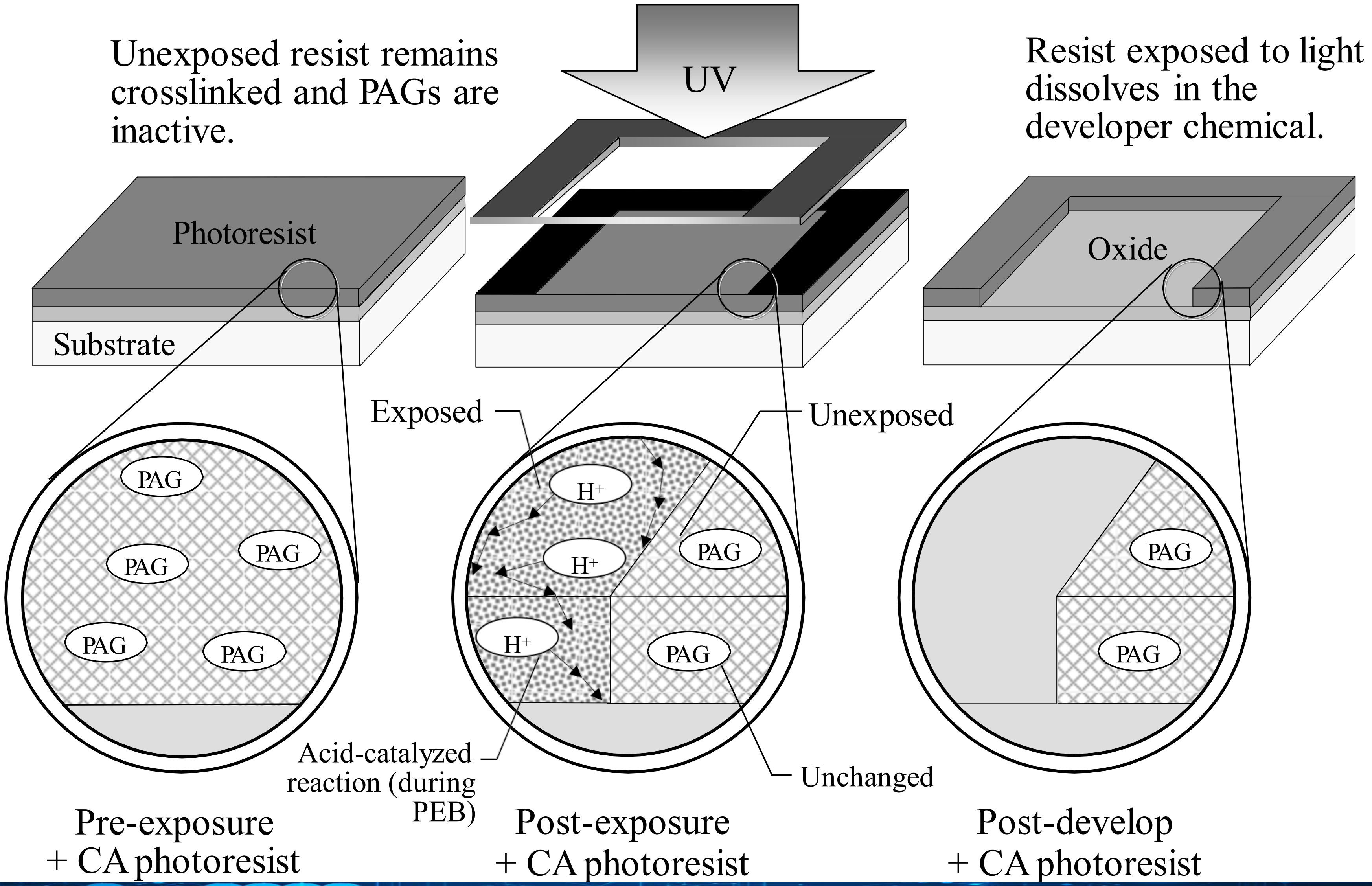
Photoresists during PEB

- Chemical amplification: deprotection catalyzed by protons
- High aromatic content => High etch resistance



- Before exposure, the phenol OH group of PHS is protected by the tBOC group. The base resin is insoluble in the developer solution such as tetramethylammonium hydroxide (TMAH) solution.
- An triphenylsulfonium salt salt acts as a photo-acid generator and generates the acid during the exposure.
- The acid-catalyzed reaction induces chain reactions and deprotects tBOC during the PEB.
- As a result, the phenol OH groups are generated in the exposed area and can be dissolved in the alkaline developer.

Chemically Amplified (CA) DUV Resist



Exposure Steps for Chemically- Amplified DUV Resist

1.	Resin is phenolic copolymer with protecting group that makes it insoluble in developer.
2.	Photoacid generator (PAG) generates acid during exposure.
3.	Acid generated in exposed resist areas serves as catalyst to remove resin-protecting group (t-BOC) during post exposure bake (PEB) step.
4.	Exposed areas of resist without protecting group are soluble in aqueous developer.

Metrics of Resist

Metrics of Resist

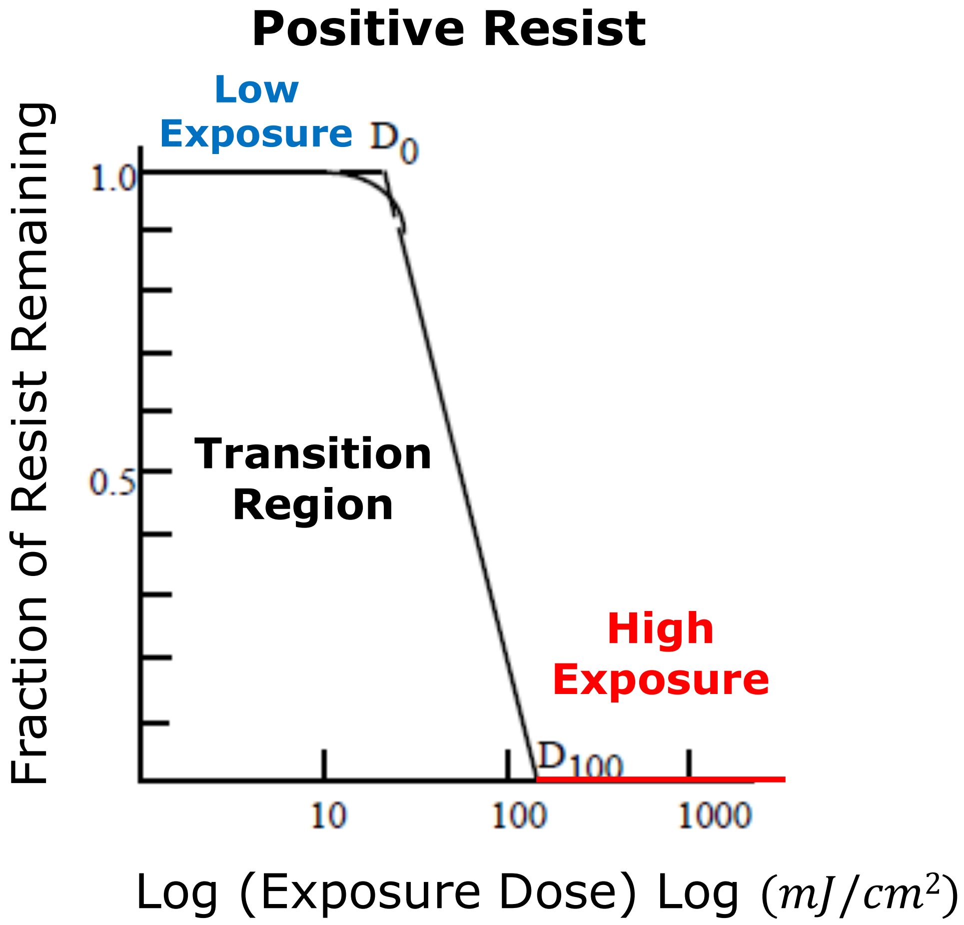
- Adhesion
- Photo activity
- Resolution
- Contrast
- Viscosity
- Sensitivity
- Etch resistance
- Thermal stability

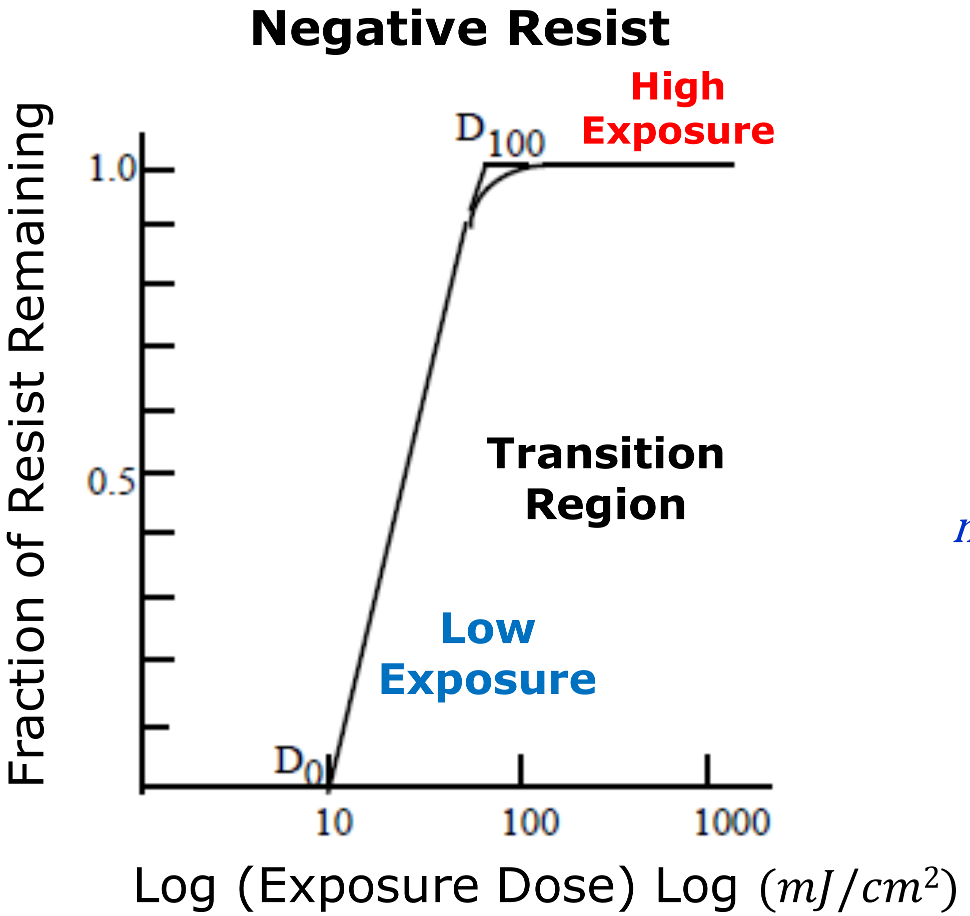
Resolution and Contrast of Resist

- Resolution: How fine a line the resist can reproduce from an aerial image
- Resolution of resist is determined by:
  - Contrast, thickness, and proximity effects
  - Swelling and contraction after development
- Contrast: Ability of resist to distinguish between transparent and opaque regions of the mask
  - Measured by exposing the resist of given thickness to varying radiation dose and measuring dissolution rate

Contrast Curve

- The contrast curve of the resist presents the fraction of remaining resist as a function of exposure dose (mJ/cm^2).





$$mJ/cm^2 = mW/cm^2 \times sec$$

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Contrast, γ, can be defined as:

$$\gamma = \left[log_{10} \frac{D_{100}}{D_0} \right]^{-1}$$

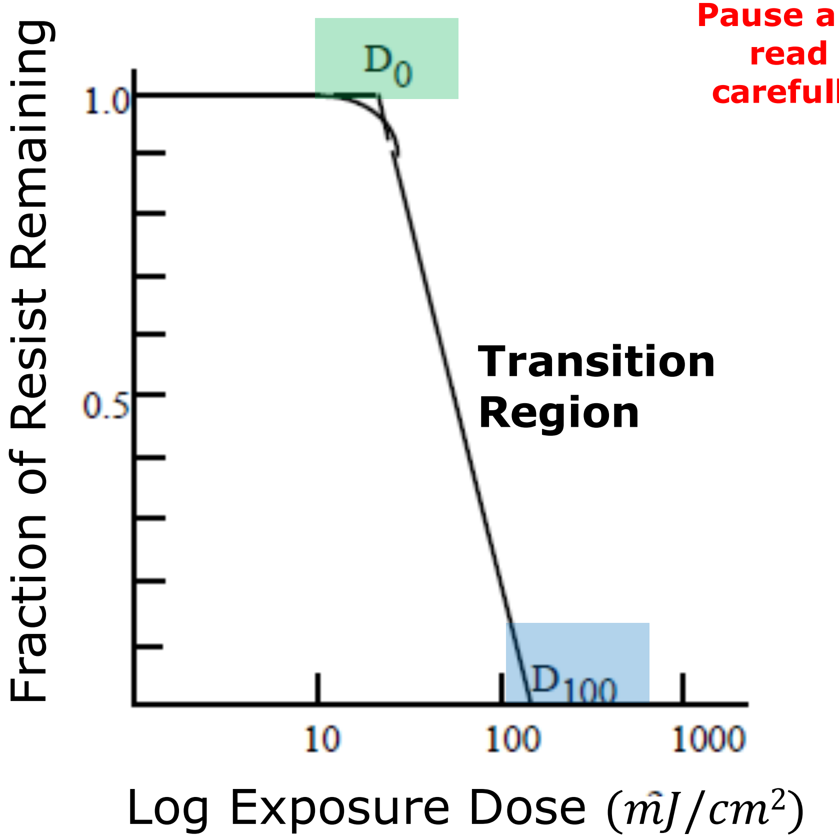
D_{100}: Lowest energy dose where **all of the resist is removed**

D_0: Lowest energy dose to **begin to drive the photochemistry**

Contrast

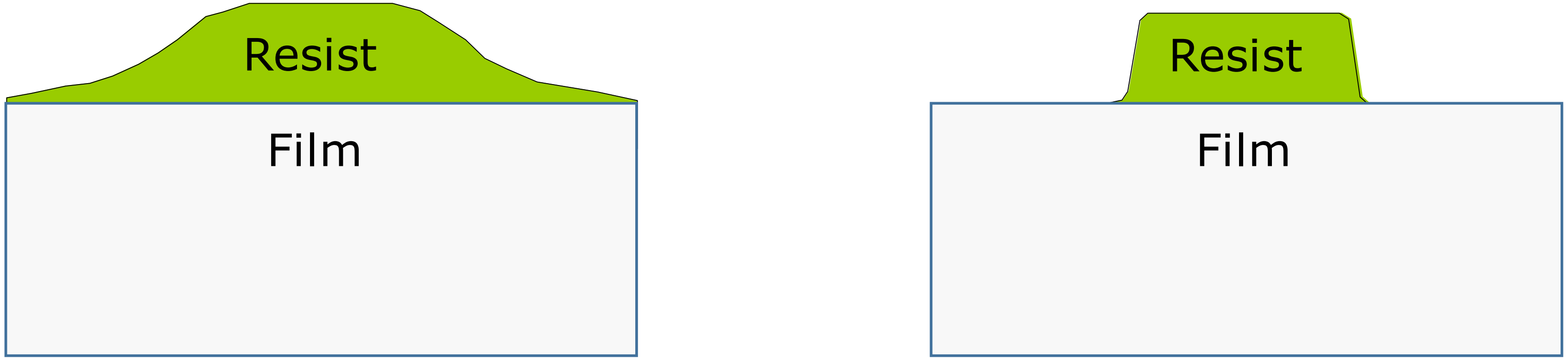
- Measures the **ability** of the resist **to distinguish** between **transparent** and **opaque regions** of the mask
- Higher ability to distinguish → **Higher contrast** → **Sharper edge**

Positive Resist



Pause and read carefully

Resist Contrast



Low Resist Contrast

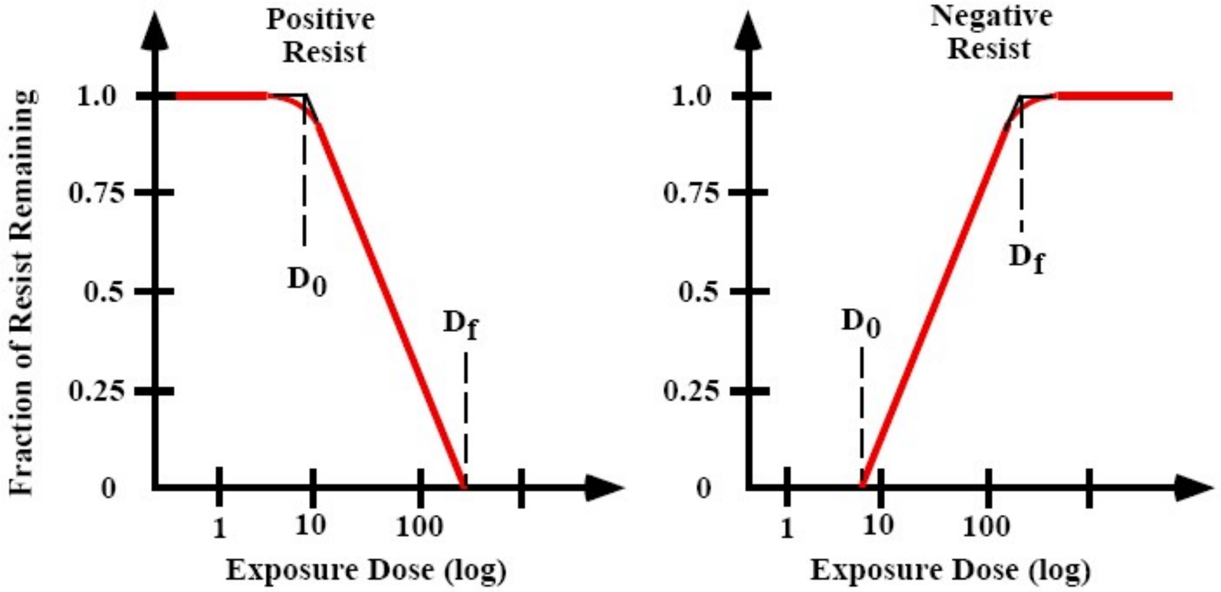
- Sloped walls
- Swelling
- Poor contrast

High Resist Contrast

- Sharp edges
- No swelling
- Good contrast

Contrast Curves

Positive Resist



Negative Resist

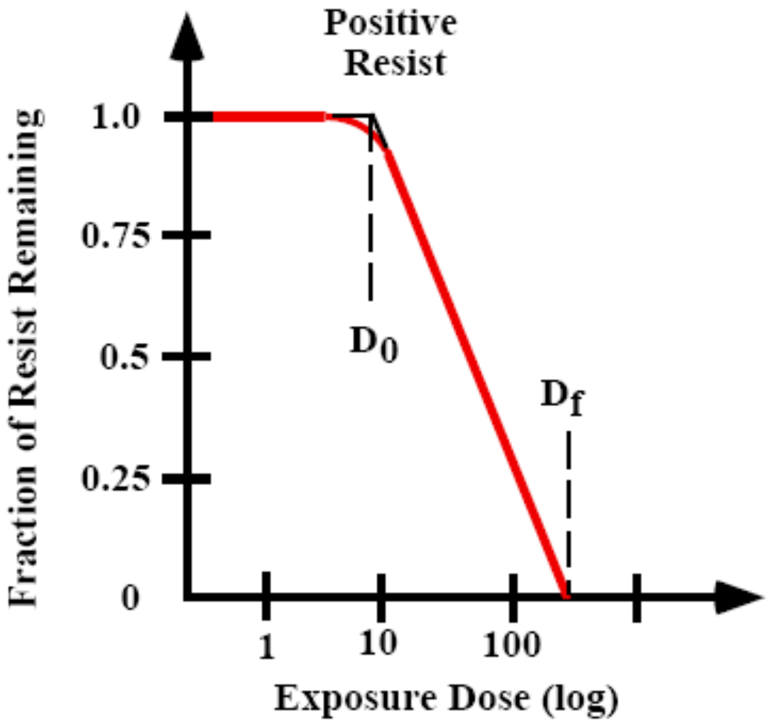
Resist Contrast

- D100 = exposure energy dose for complete resist removal
- D0= threshold exposure energy dose for resist removal
- Typical values
  - γ_p=2.2 & γ_n=1.5 under fixed developer conditions $\gamma = \left[\log_{10}\frac{D_{100}}{D_0}\right]^{-1}$

Resists with higher contrast result in better resolution because of more vertical resist profile

Sensitivity and contrast for resists

- Large sensitivity for CA DUV resists compared with conventional DQN resist: 20-40 $mJcm^{-2}$ compared to 100 $mJcm^{-2}$ typical for DNQs
- Post-exposure bake very critical in DUV resist technology (chemical reaction occurs)



Remaining photoresist against exposure dose

Sensitivity : D_{100} (D_f)

Chemical Contrast γ --- slope of curve defined as :

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

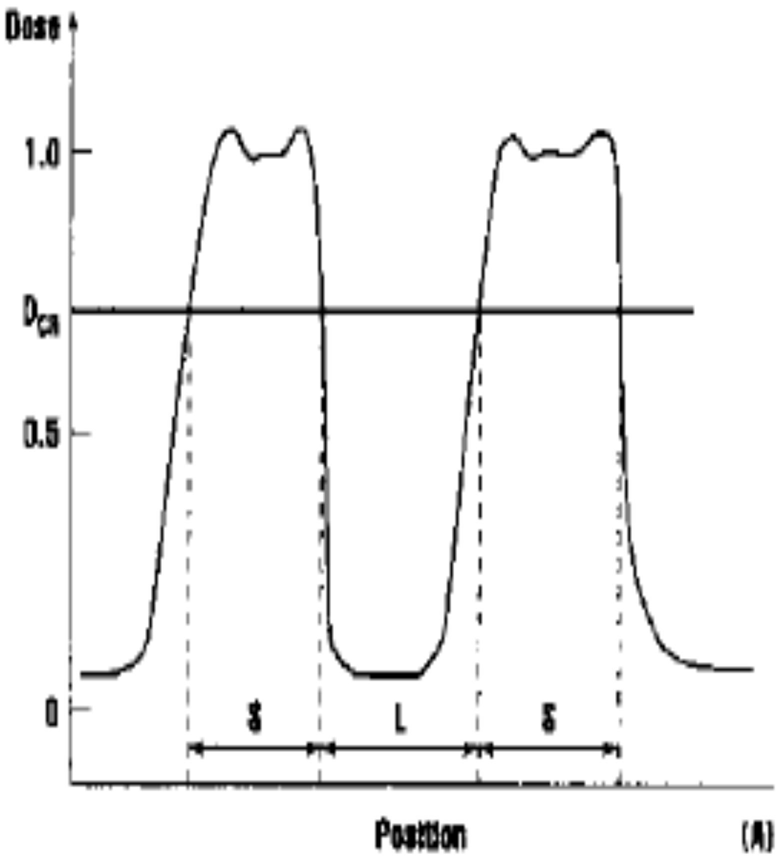
High γ → high resolution/contrast

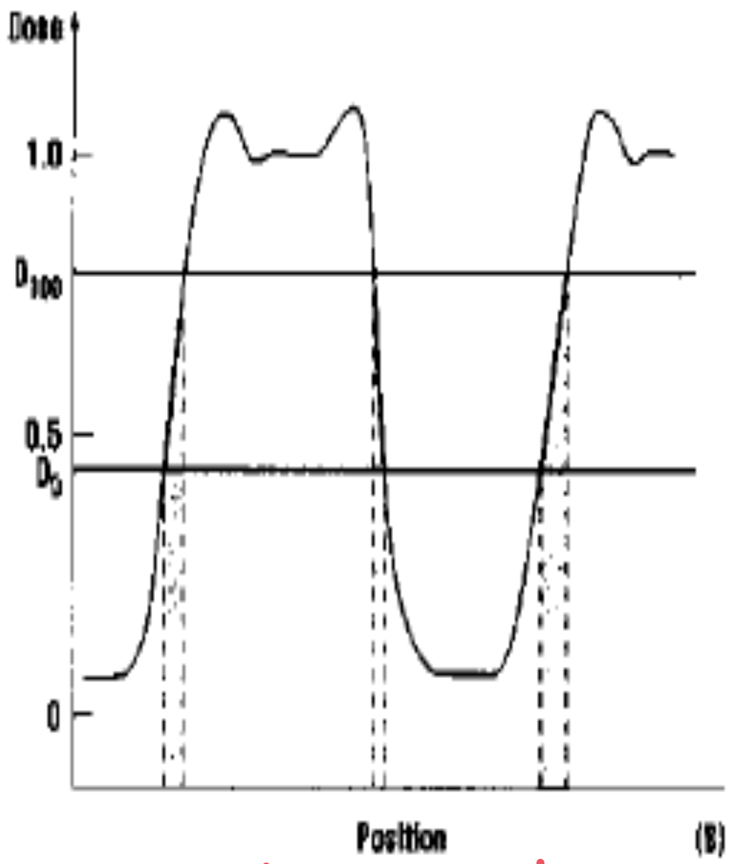
e.g.

DNQ g-line/i-line resist : γ = 2 - 3

DUV CA resist : γ = 5 - 10

Critical Resist Modulation Transfer Function(CMTF)





$$CMTF_{resist} = \frac{D_{100} - D_0}{D_{100} + D_0}$$

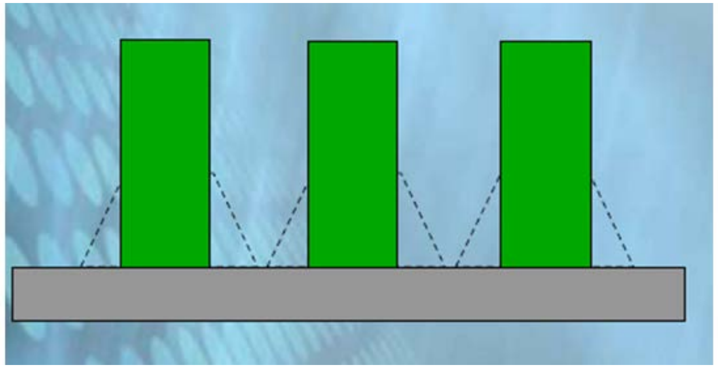
$$CMTF_{resist} = \frac{10^{1/\gamma} - 1}{10^{1/\gamma} + 1}$$

as high as possible　　as small as possible

In order to print lines : MTF$_{\text{exposure system}}$ ≥ CMTF$_{\text{resist}}$

Critical Resist Modulation Transfer Function(CMTF)

Ideal resist: vertical resist profile.

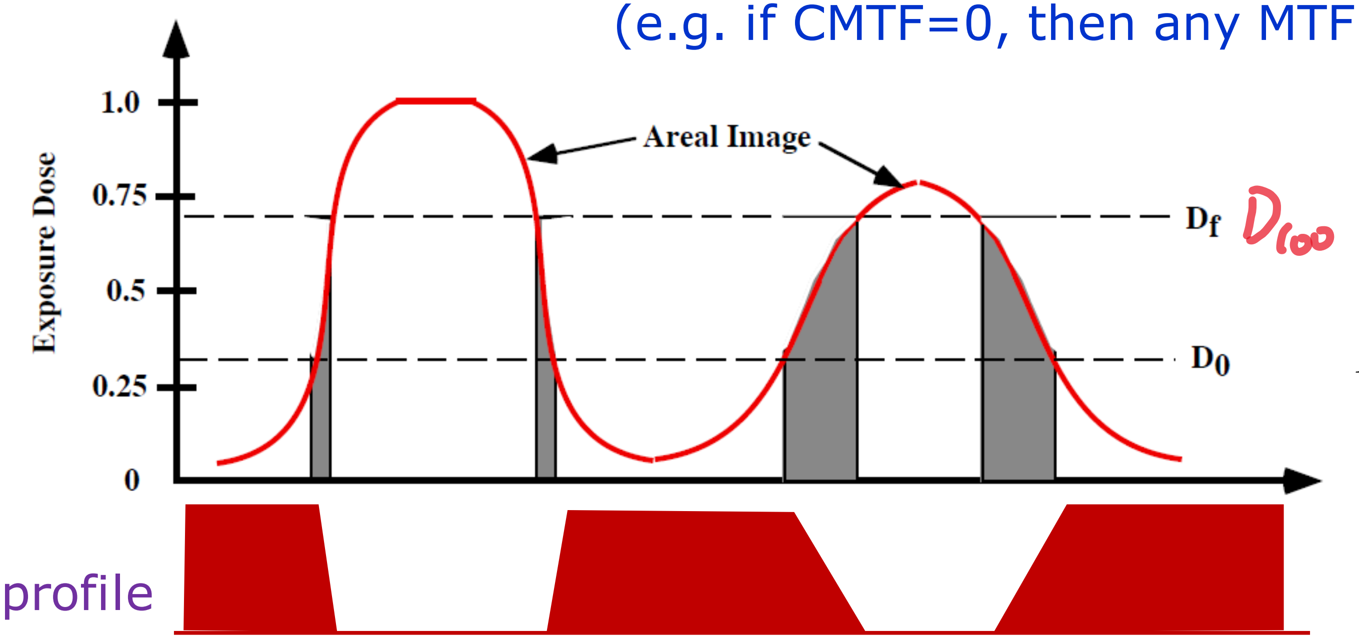


Typical CMTF values for g and i-line resists are about 0.4. Chemically amplified DUV resists achieve CMTF values of 0.1 - 0.2.

In general CMTF < MTF is required for the resist to resolve the aerial image.

(e.g. if MTF=1, then any D_{100}-D_0 is OK.)
(e.g. if CMTF=0, then any MTF is OK)

Non-ideal resist: for real situation with finite γ, the result is a tapered profile.



Positive resist profile

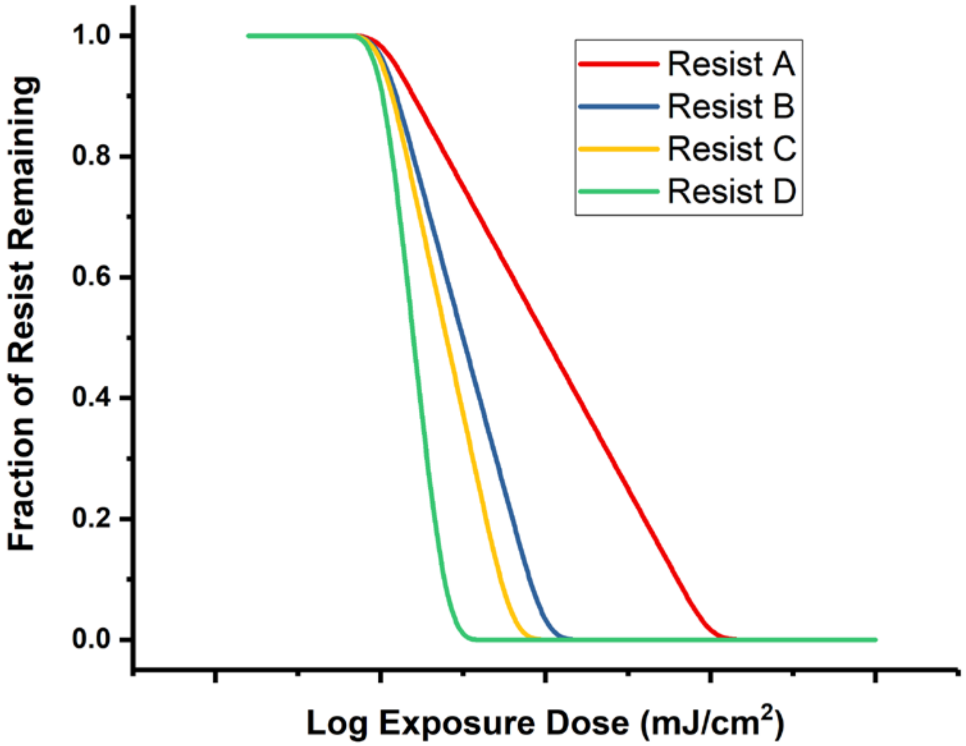
$$MTF = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}$$

Practice Question 1

The fabrication process of a device requires resist that is capable of **achieving sharp edges**.

Which of the following resists is the most suitable for this purpose?

Pause and try out this question

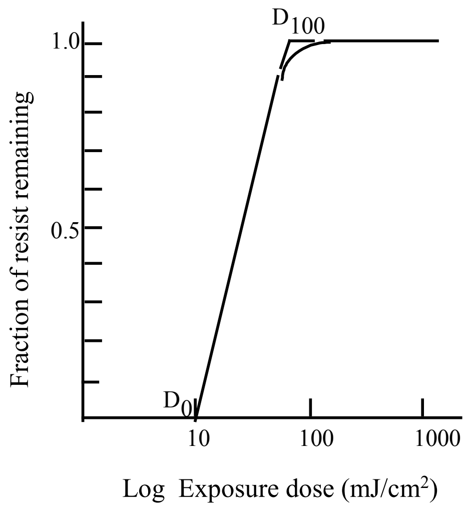


Resist D:

- It has the steepest contrast curve, indicating high contrast value.
- The high contrast value indicates ability to form sharp edges.

Practice Question 2

Figure shows a contrast curve of a photoresist.



Pause and try out this question

I) What type of photoresist is this?

II) Using the estimated values of D_0 and D_{100} from Figure 1, determine the contrast value γ.

III) What happens of the exposure dose is at a point between D_0 and D_{100}?

IV) Discuss whether the resist contrast should be high or low and explain why the contrast value might decrease at shorter wavelengths (higher photon energies) of the exposure light.

Practice Question 2

I) Negative Resist

II) $\gamma = \left[log_{10}\frac{D_{100}}{D_0}\right]^{-1}$ = 1/ $[\log_{10}\frac{90}{10}]$ = 1.05

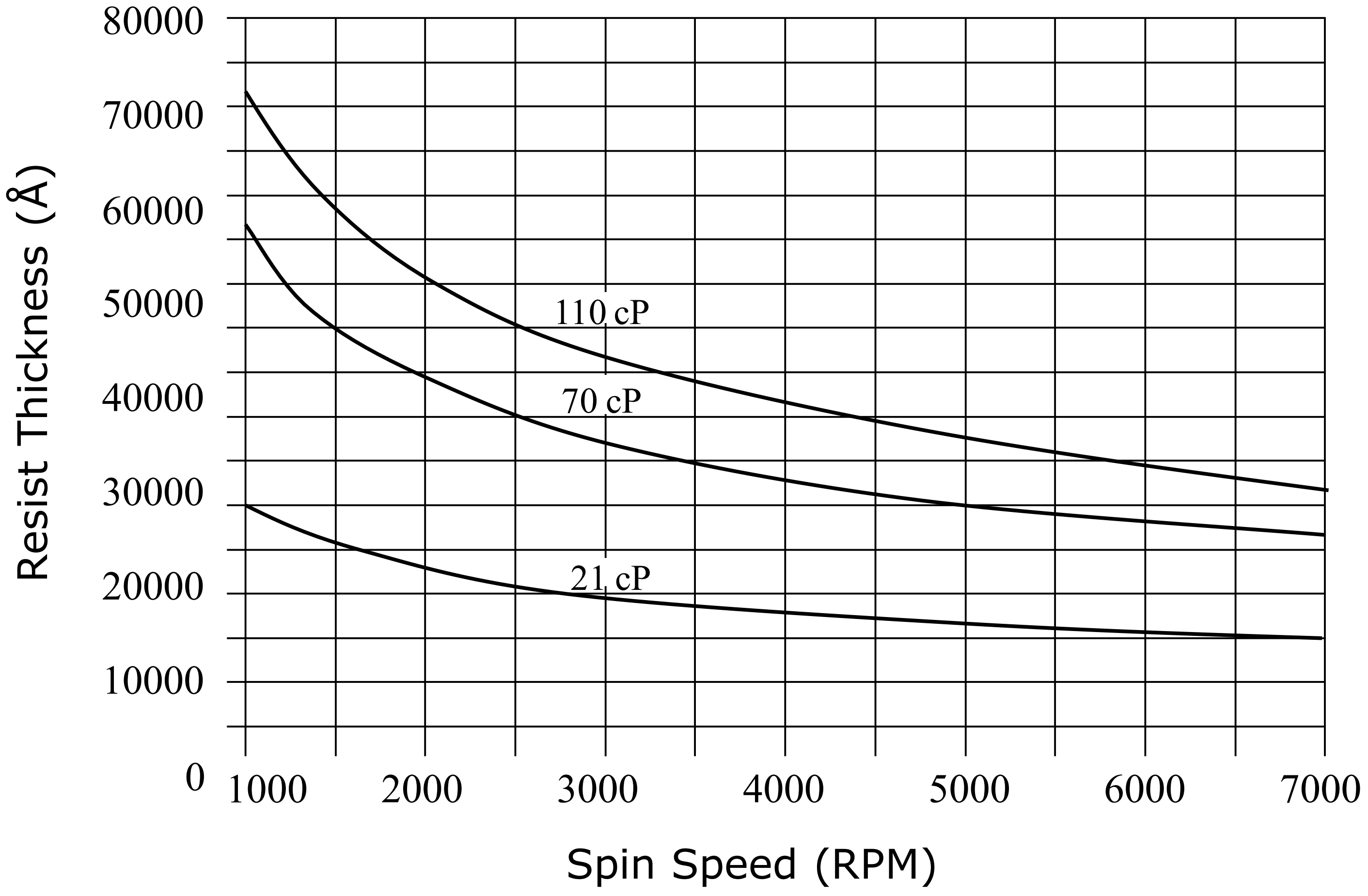
Pause and read carefully

III) Blurred (not sharp) pattern transfer

IV) The higher the contrast of the resist, the sharper the line edge. Resist contrast represents the sharpness of the transition from exposure to non-exposure in photoresists. The higher the contrast, the sharper the edge.

Resist Viscosity

Spin speed curve of IX300 (thick DNQ resist) for different viscosity.



Solvent:

- Keeps photoresist in liquid state
- Allows spin coating of the photoresist
- Solvent content determines resist viscosity and hence, the **thickness**

Thinner Resist

$$I_R \cong \left[\frac{viscosity \times solid\ content\ (\%)}{\sqrt{spin\ speed}}\right]$$

Higher Spin Speed

Practice Question 3

An experiment in a spin coating process shows that a final resist thickness of 320nm is obtained when spun at 3000 rev/min.

Pause and try out this question

a) Estimate the spin speed, if a 270nm thick coating of the same resist is required.

b) If the maximum practical spin speed is 4000 rev/min, how would you re-formulate the resist to meet the above required resist thickness of 270nm?

a) Resist Layer Thickness, $I_R \cong \left[\dfrac{viscosity\ \times solid\ content\ (\%)}{\sqrt{spin\ speed}}\right]$

$$270 = \frac{\sqrt{3000}}{\sqrt{spin\ speed_1}} x\ 320$$

Therefore new spin speed = 4214 rev/min

b) If the max speed is restricted to 4000 rev/min, the viscosity and/or the solid content of the resist need to be increased in value.

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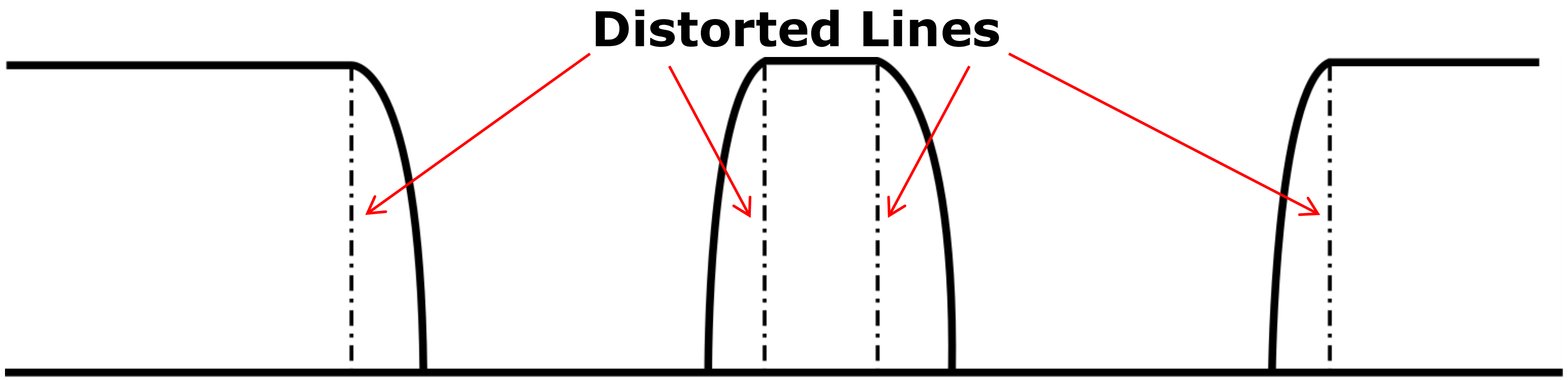
Advantages and Disadvantages of Positive and Negative Resist

Advantages and Disadvantages of Using Negative Resist

Advantages	Disadvantage
Well established	**Solvent-induced swelling** • Broadening of linewidth during development phase • Not suited to features $< 2\mu m$
Shorter exposure time as compared to positive resist, higher throughput	



Developed Negative Resist:

Dashed Lines Indicate Mask Pattern – Solvent-Induced Swelling

Advantages and Disadvantages of Using Positive Resist

Pause and read carefully

Advantages
Does not suffer from swelling
Better resolution
Thick resist available (for etching)

Disadvantage
Lower throughput: Requires much larger energy and longer exposure time

Etching will be discussed in the coming lecture

energy

rearrangement

Advantages and Disadvantages of Resists

Advantages	Disadvantage
Well established	**Solvent-induced swelling** • Broadening of linewidth during development phase • Not suited to features $< 2\mu m$
Shorter exposure time as compared to positive resist, higher throughput	

Negative Resist

Advantages	Disadvantage
Does not suffer from swelling	Lower throughput – requires much larger energy and longer exposure time
Better resolution	
Thick resist available (for etching)	

Positive Resist

Pause and read carefully

Resist Technology - Summary

Resist technology:

- Positive resist forms carboxylic groups after photochemical reaction with UV light, enabling it to be dissolved in the base developer.
- Negative resist forms polymer cross-linking after photochemical reaction with UV light, preventing it from dissolving in the organic developer.
- The important metrics of resist include resolution, contrast, and viscosity.

Quiz Question

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For the next nine statements, choose the type of photoresist, positive (+) or negative (-), that matches the accompanying statement.

Pause and try out this question

read carefully

a)	+	-	Undergoes a chemical change when exposed to UV light.
b)	+	-	The exposed regions become crosslinked and hardened.
c)	+	-	The exposed regions become soluble and soft.
d)	+	-	The resulting pattern is exactly the same as the mask.
e)	+	-	The resulting pattern is opposite of the mask pattern.
f)	+	-	Swells up during the develop process, which limits Critical Dimensions.
g)	+	-	Has the best resolution of the two types of resists/
h)	+	-	The dominant resist type for use in VLSI processing.
i)	+	-	The preferred resist for use in submicron lithography.

Practice Question

NANYANG TECHNOLOGICAL UNIVERSITY

An optical lithography system has an exposure power of 0.3 mW/cm^2. The required exposure energy for Resist A is 10mJ/cm^2, and for Resist B is 130 mJ/cm^2.

a) Compare the wafer throughput for Resist A and Resist B. Assume negligible time for setting up the wafers.

b) Identify the type of photoresists for Resist A and Resist B. State the reason for your answers.

Pause and try out this question

read carefully

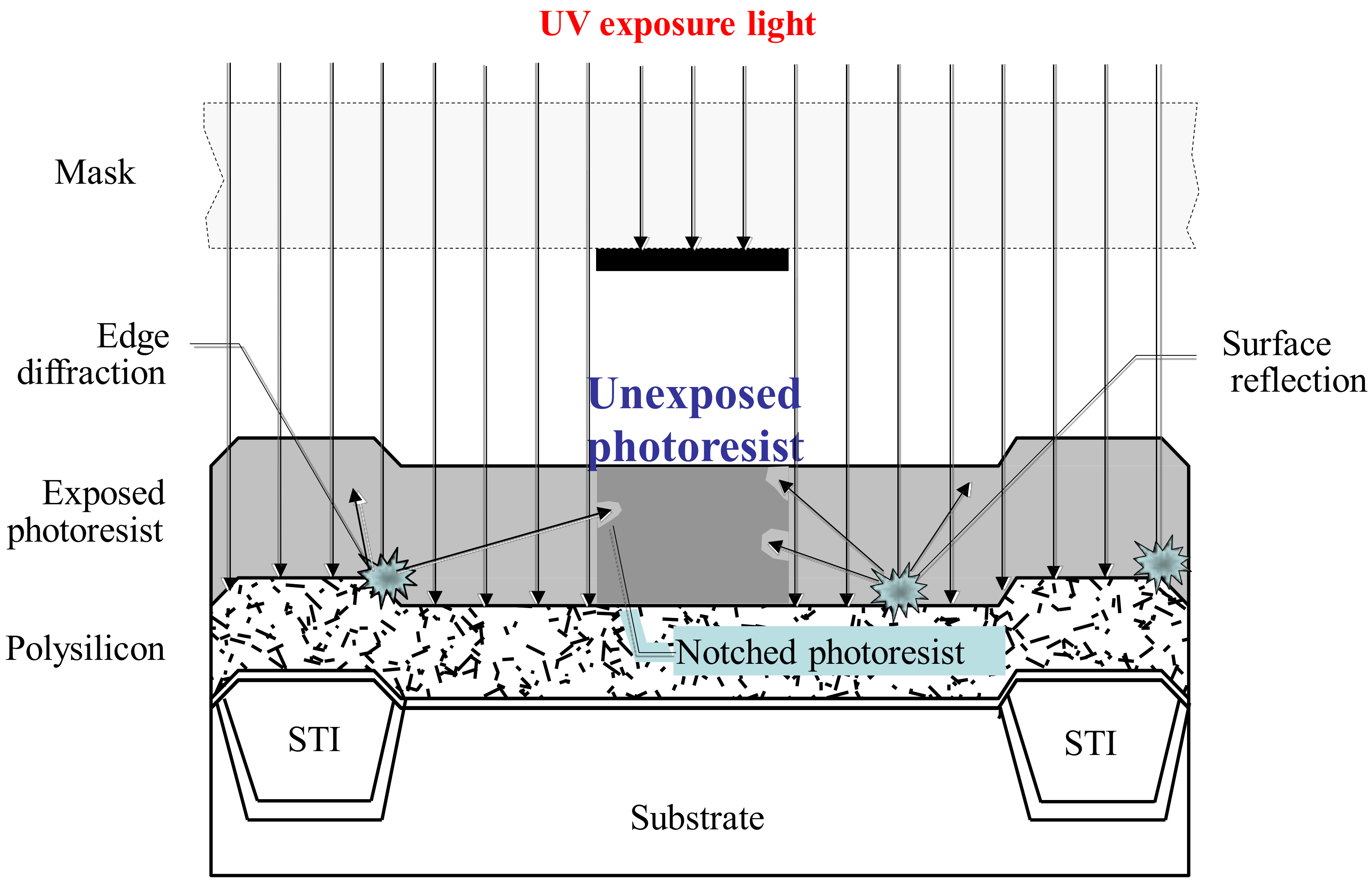
a) Time taken for Resist A = 10/0.3 = 33 sec – faster throughput

Time taken for Resist B = 130/0.3 = 433 sec – lower throughput

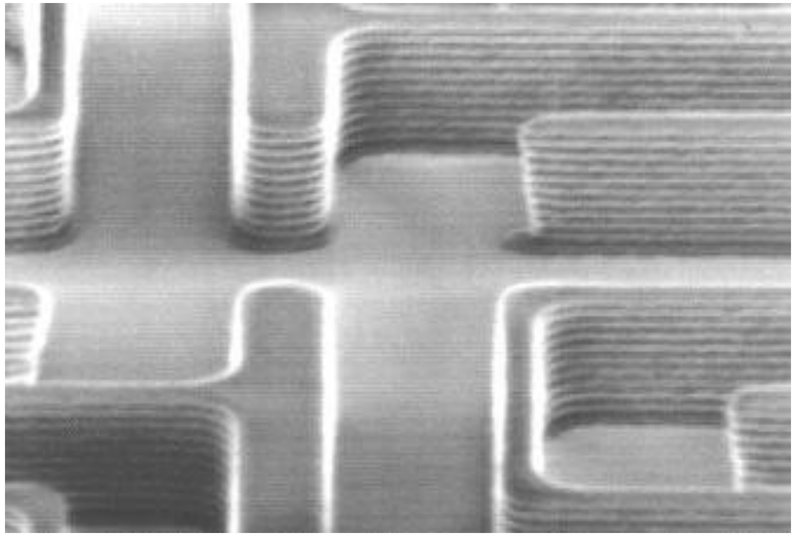
b) Resist B is likely to be a positive resist. Require much larger energy, and longer exposure time, thus lower throughput. Resist A is likely to be a negative photoresist.

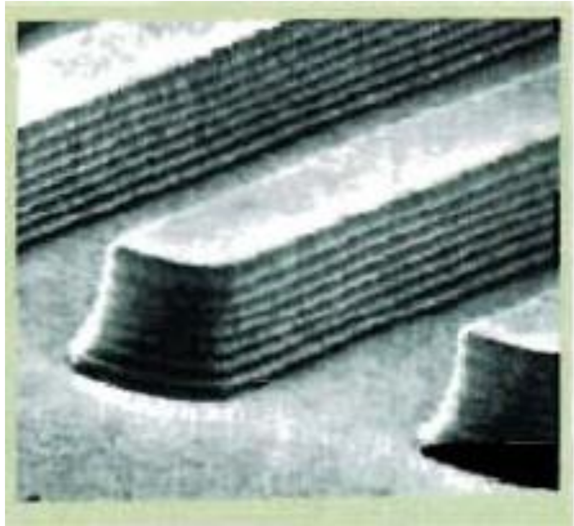
Problems with Reflective wafer surface

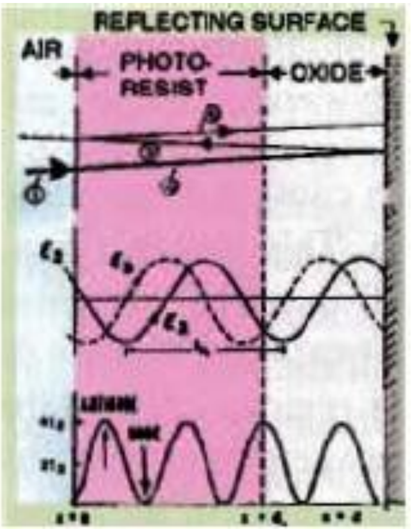
Photoresist Reflective Notching Due to Light Reflections from non-planarized surface



Standing Wave Effect in photoresist



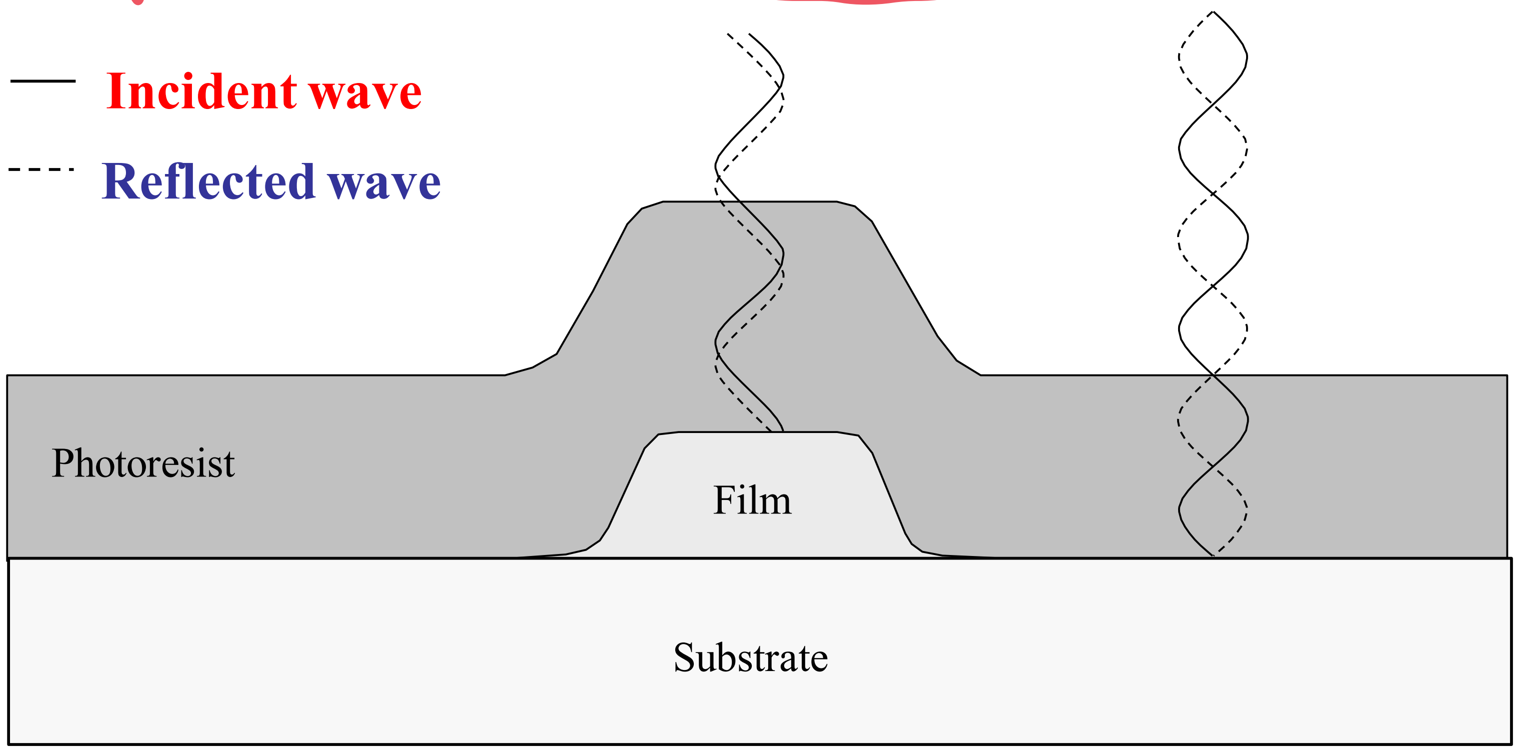




Standing wave effect causes modulation of the developed photoresist edges

Standing Waves Effect

Incident and Reflected Light Wave Interference in Photoresist 不一致.

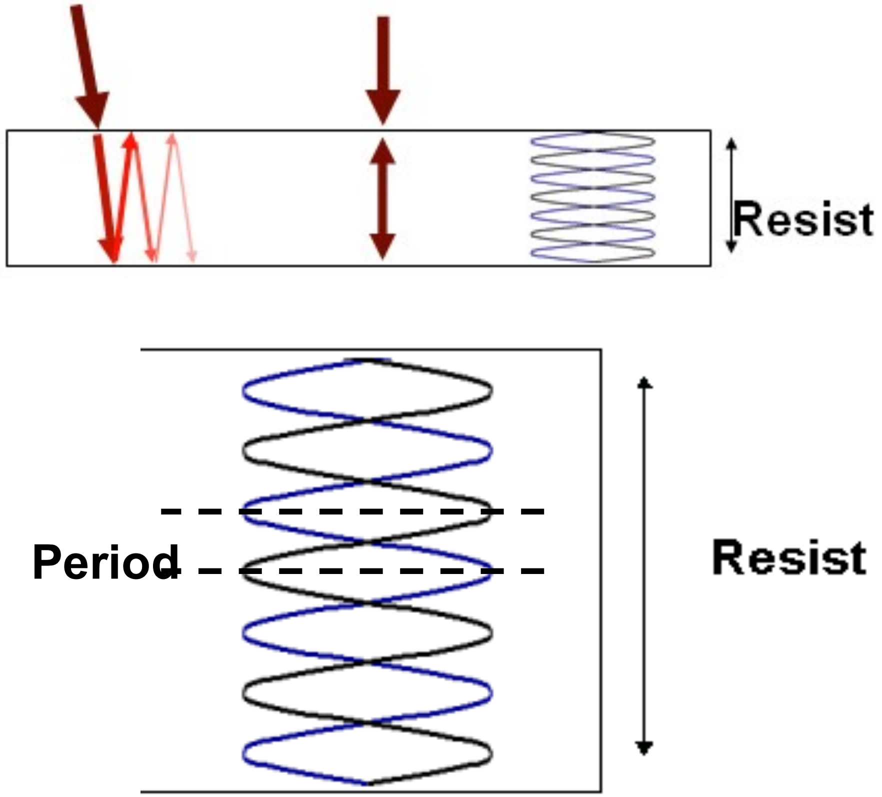


Reflected waves from reflective wafer surface cause standing waves and hence non-uniform exposure along the thickness of the photoresist film and over surface topology.

Cause of Standing Wave Effect

Light reflectance inside the resist cause standing waves:

Standing Wave intensity depends on:
- Resist thickness
- Resist absorbance
- Light incident angle
- The substrate film: reflectivity, refractive index



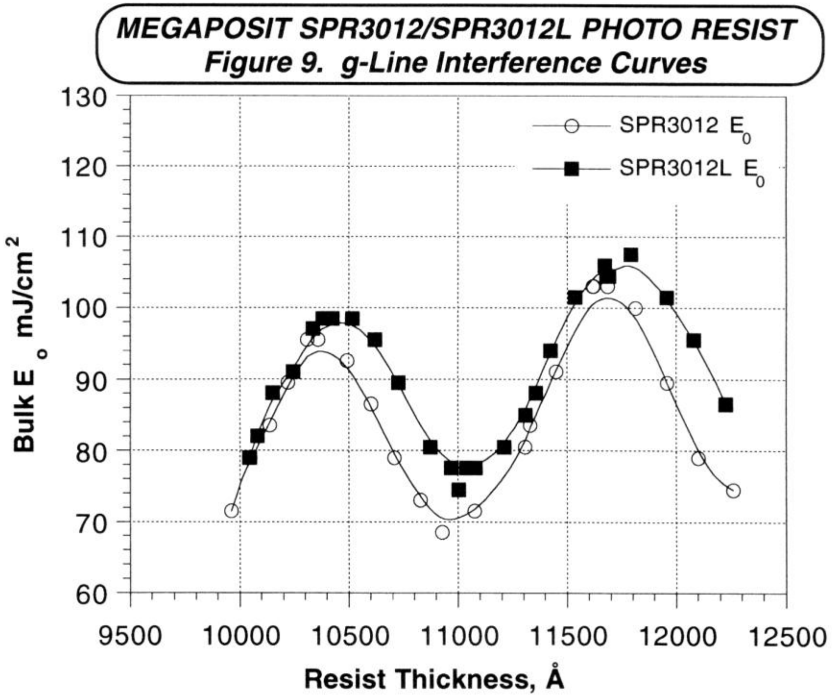
$$\text{Period} = \frac{\lambda}{2n}$$

n : Resist refractive index

Variation of Exposure Dose due to Standing Wave Effect

The interference standing waves may cause modulation in the exposure dose (total UV energy per unit area) for complete exposure of the photoresist to vary with the photoresist film thickness. The standing wave interference effect will also result in the variation in linewidth with changing photoresist thickness and such phenomenon is sometimes called the <u>Swing Curve.</u>

Swing Curve ---Variation of Exposure Dose modulation by g-line with resist film thickness



Thickness fine tuning done by swing curve chart.

Preferred resist thickness:

an extreme point of the swing curve to reduce line-width variation.

Reduction of Standing Wave Effect

- Reflected waves from wafer surface in particular those reflective layers such as metals causes reflective notching and standing wave effect
- Standing wave effect is a serious problem for fine line lithography when exposing on reflective surfaces

how

- Suppression of reflected waves :

a) Dyeing the photoresist to increase absorption on exposure and reduce reflected waves intensity

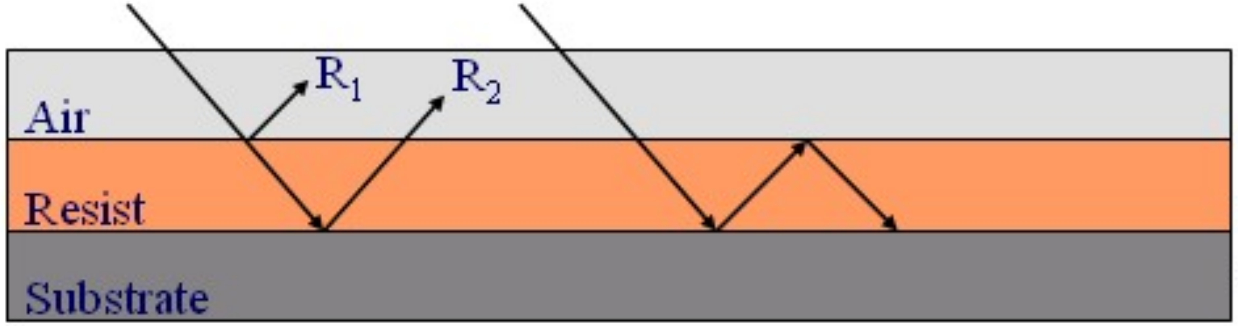
b) Post Exposure Bake (PEB)

c) Antireflective coating (ARC) to reduce reflection wave intensity --→

- Bottom ARC (BARC) prior to resist spinning
- Top ARC (TARC) after resist spinning

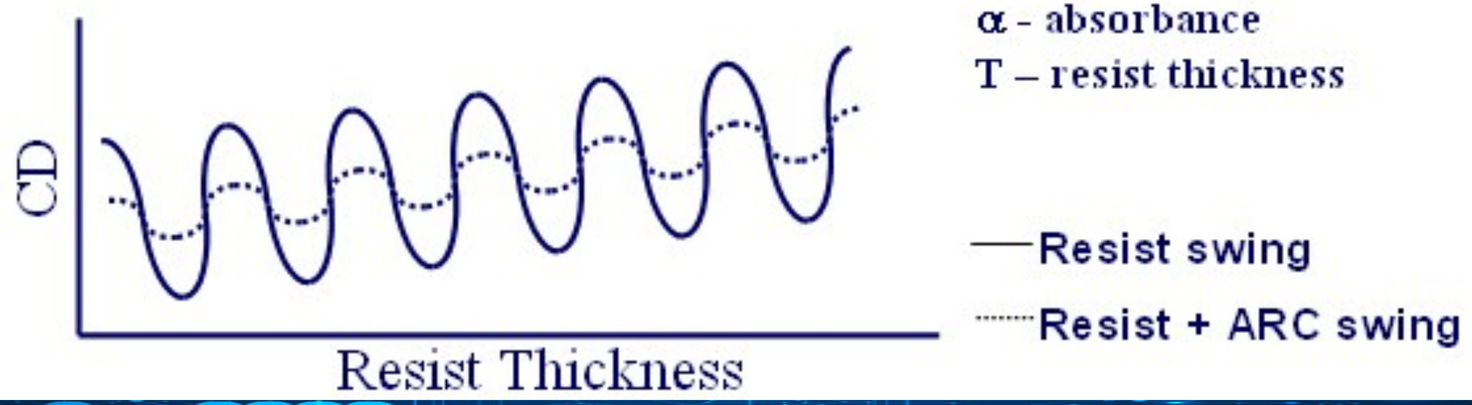
Reduction of Swing Curve Amplitude

- Increase absorption α by adding dye to the photoresist
- ARC – Anti Reflective Coating reduces reflection
  ➔ reduces reflection wave amplitudes (R1 – top, R2 – Bottom)



$$\text{Swing} = 4\sqrt{R_1R_2}\,\exp(-\alpha t)$$

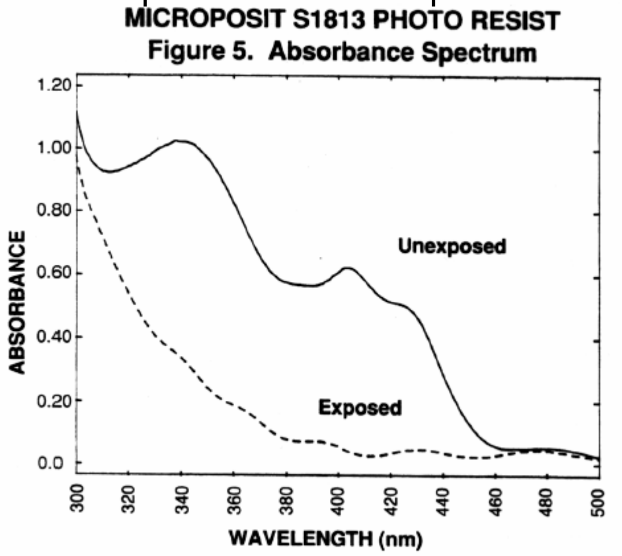
R – reflectivity
α - absorbance
T – resist thickness

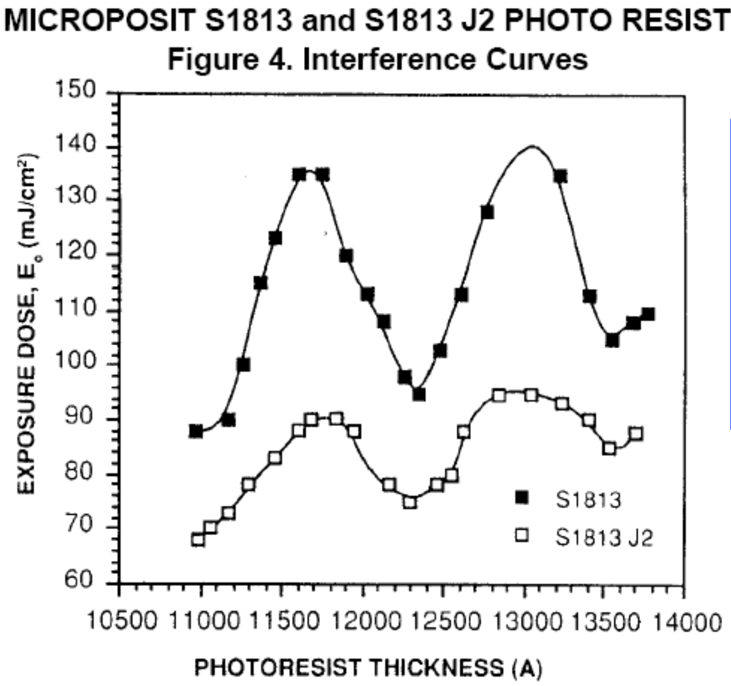


Reduction of Reflection by Dyed Resist

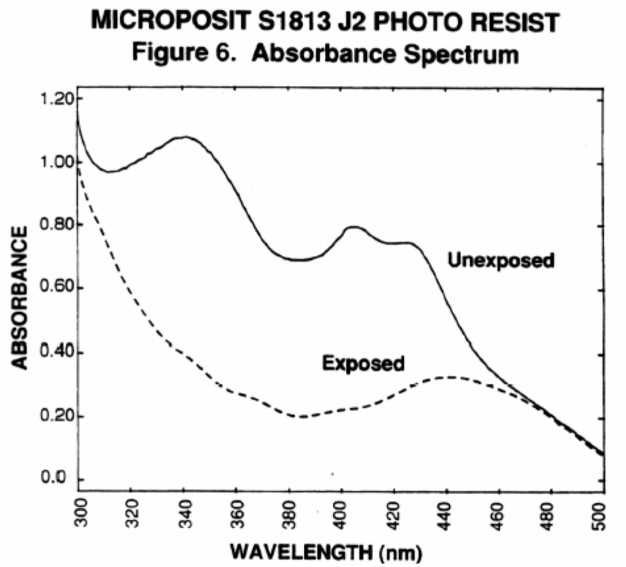
The exposure modulation can be partially compensated using dyed version of the photoresist by increasing the absorbance of the exposed photoresist and hence reducing the reflected UV light intensity from the reflective substrate.

Absorpbance of S1813 photoresist



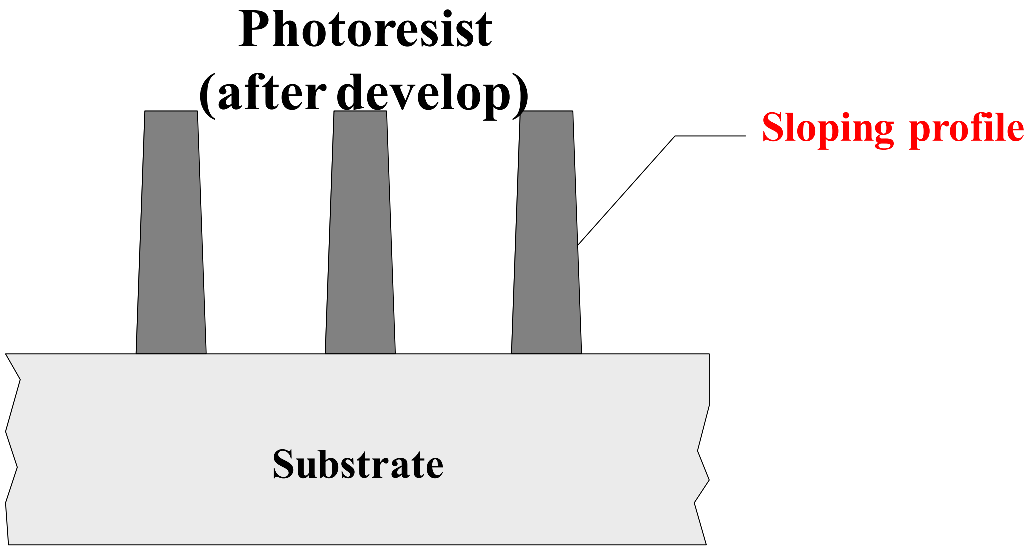


Reduction of Swing Curve amplitude with dyed photoresist

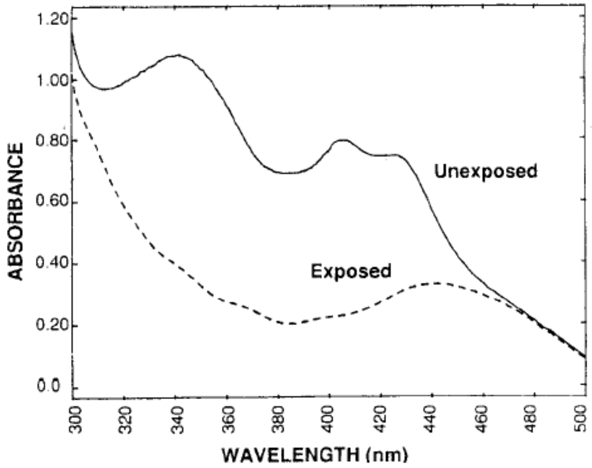


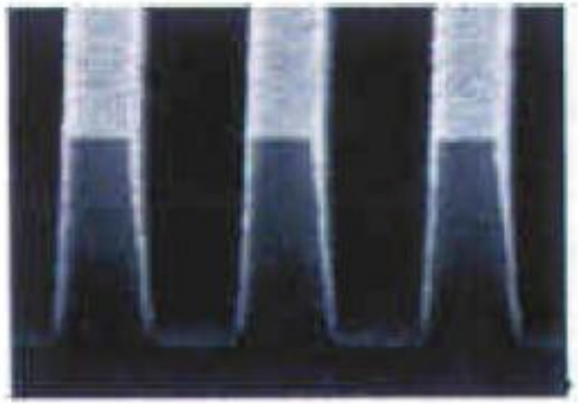
Increased absorbance of S1813J2 dyed version photoresist on exposure

1. The light intensity at the bottom of the resist is considerably less than that received at the top
2. To achieve straight-wall images, the resist absorption <20 % ---- new resist materials for DUV 248nm and 193nm



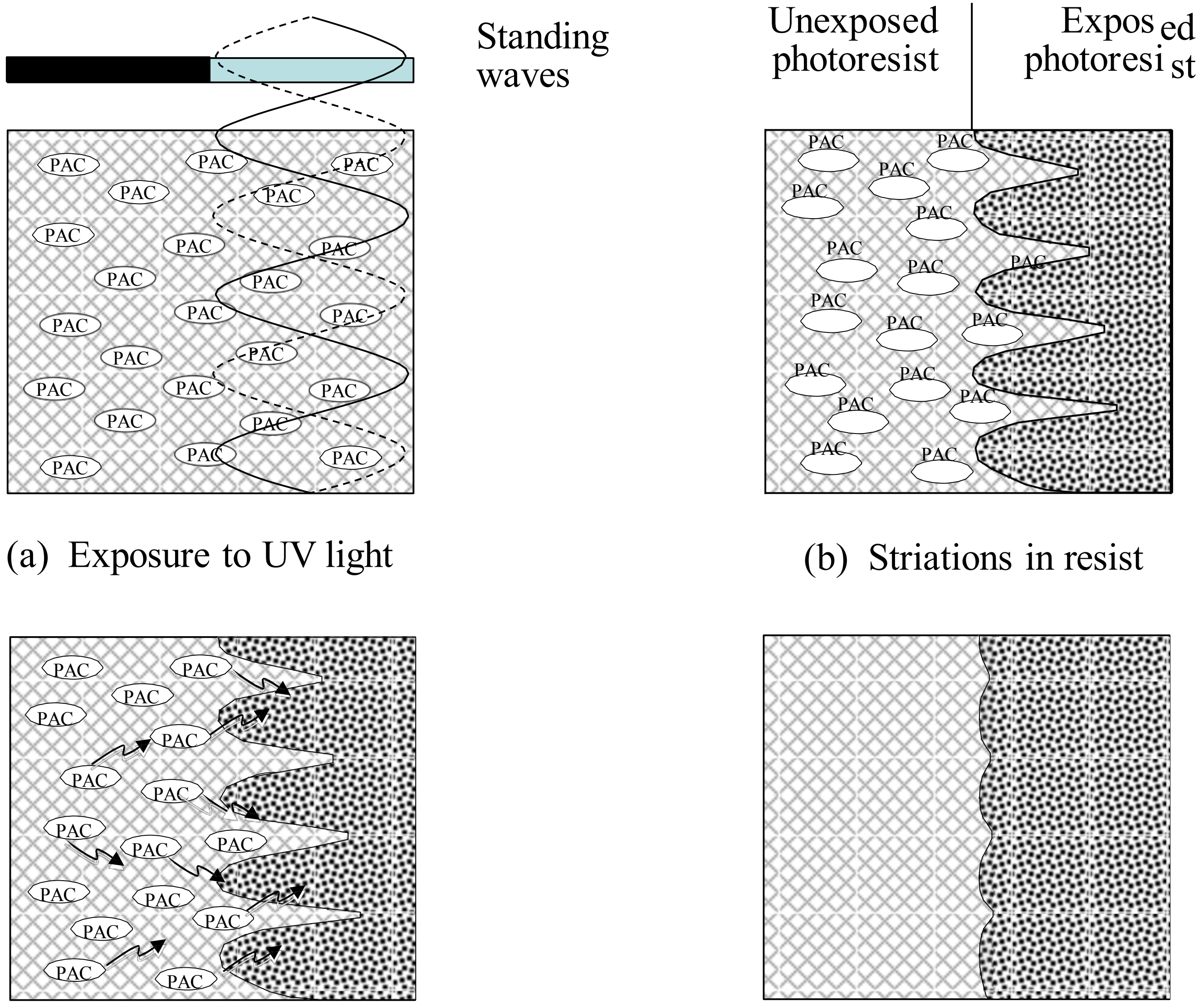
MICROPOSIT S1813 J2 PHOTO RESIST
Figure 6. Absorbance Spectrum





0.48 µm Lines/Spaces

Reduction of Standing Wave Effect by PEB



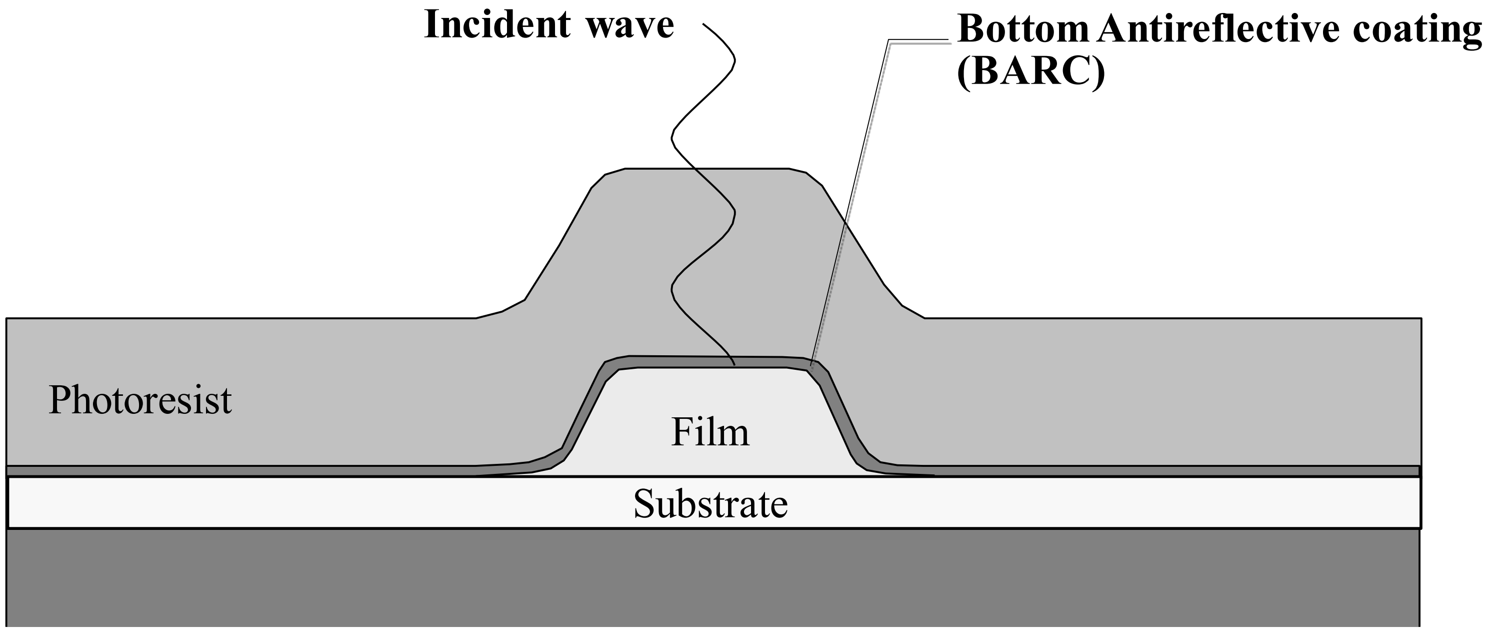
(a) Exposure to UV light

(b) Striations in resist

(c) PEB causes PAC diffusion

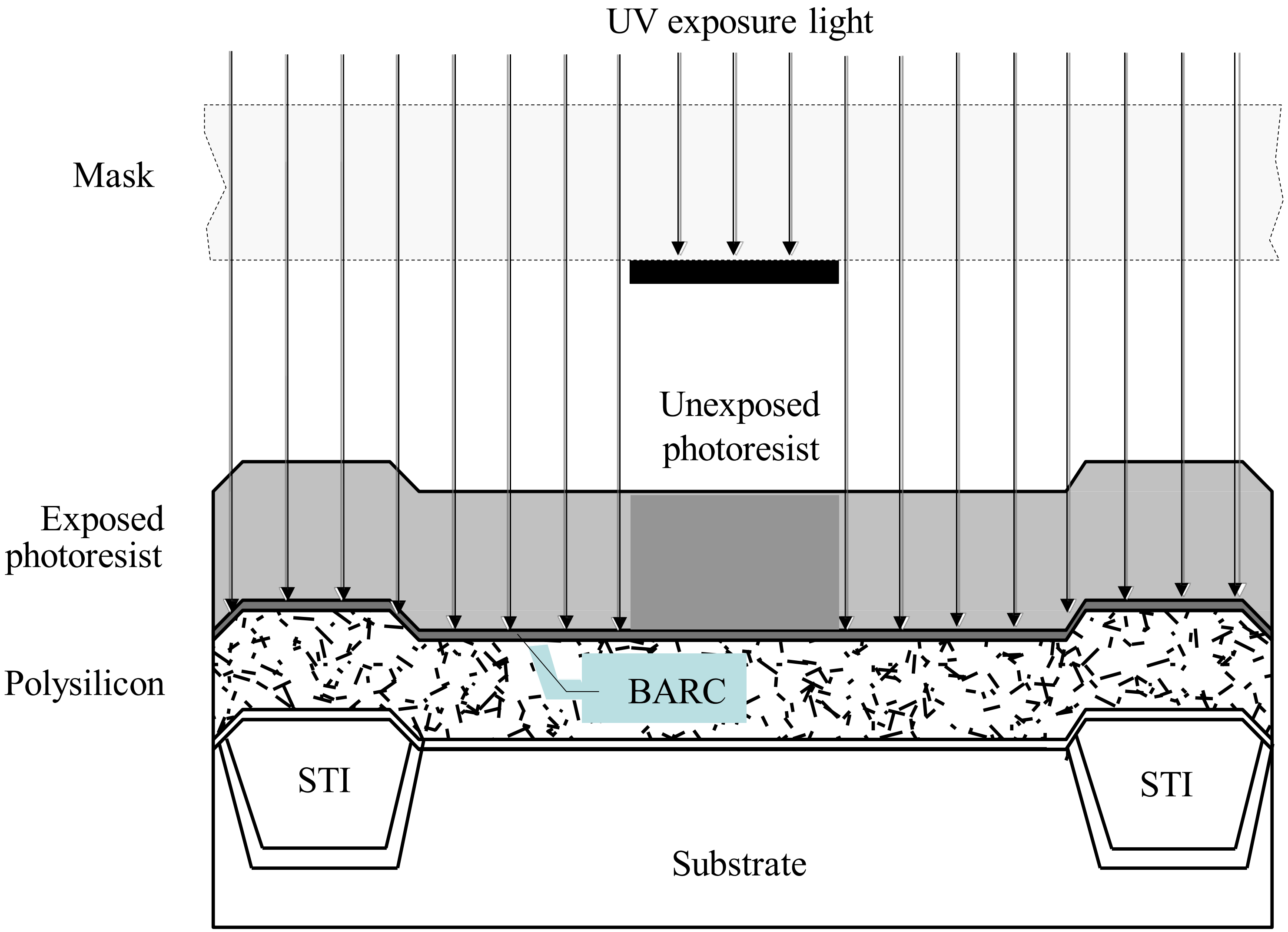
(d) Result of PEB

Suppression of Standing Wave Effect by BARC

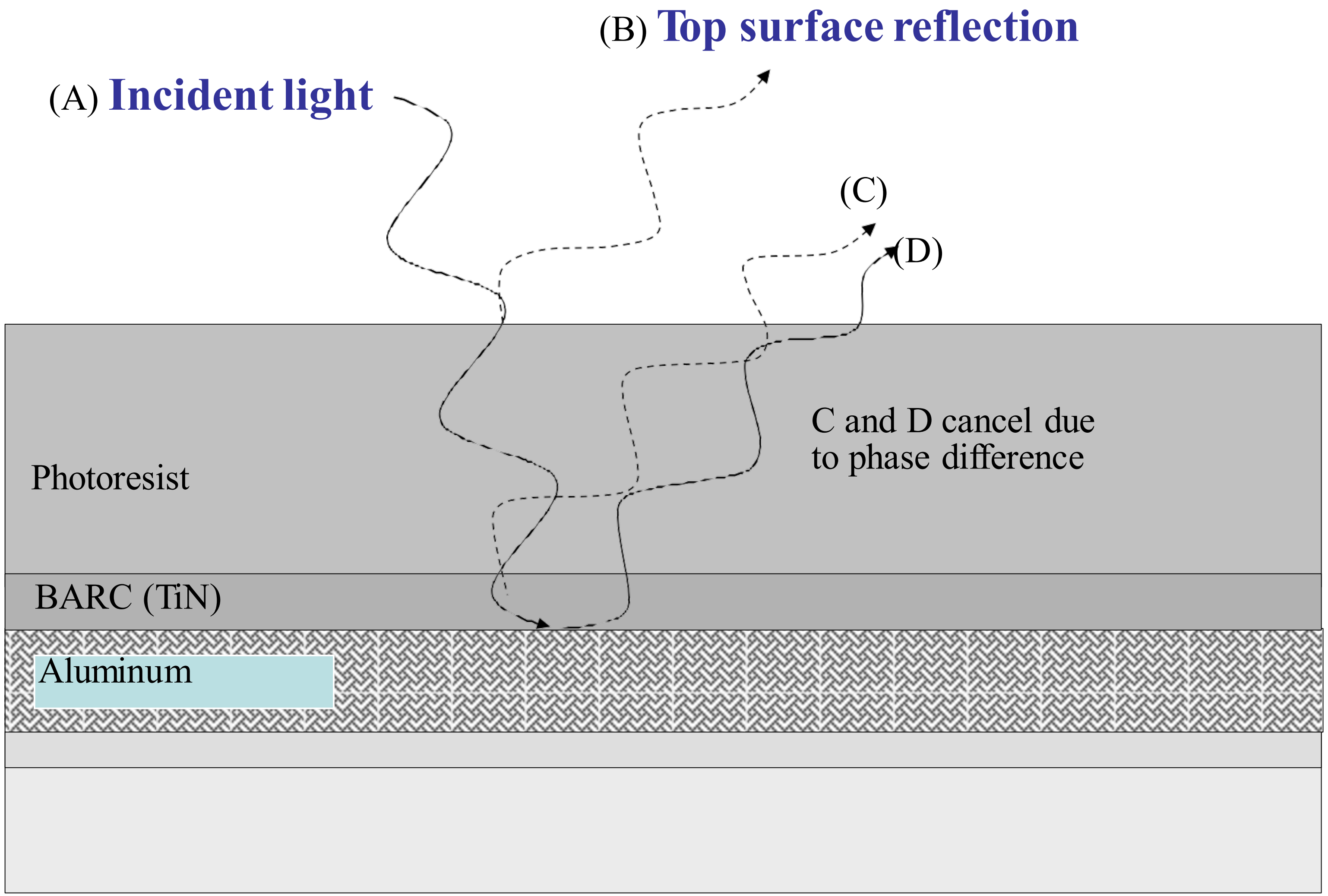


The use of antireflective coatings can help prevent interference by reducing the reflected wave intensity.

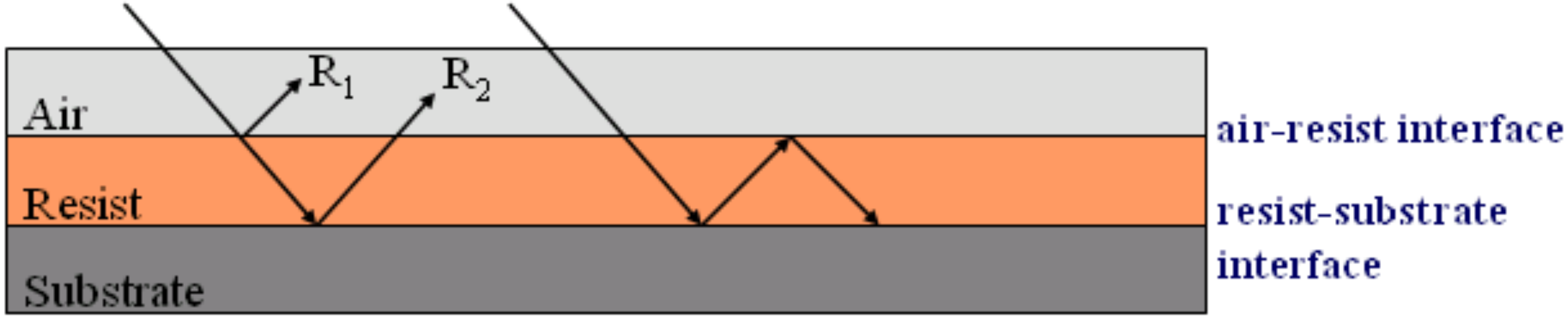
Suppression of Standing Wave Effect by BARC

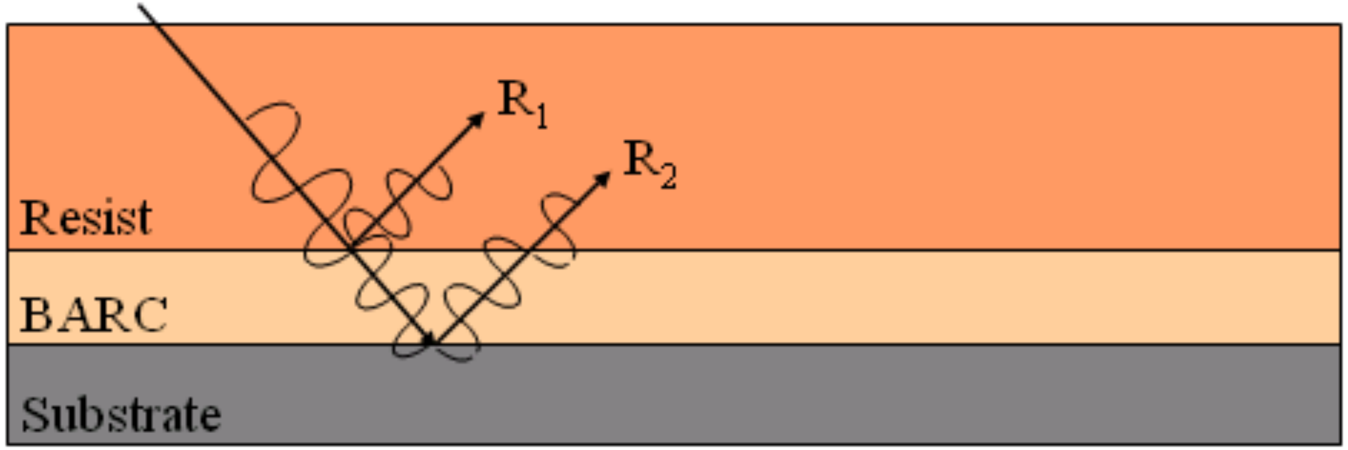


BARC Phase-Shift Cancellation of Light

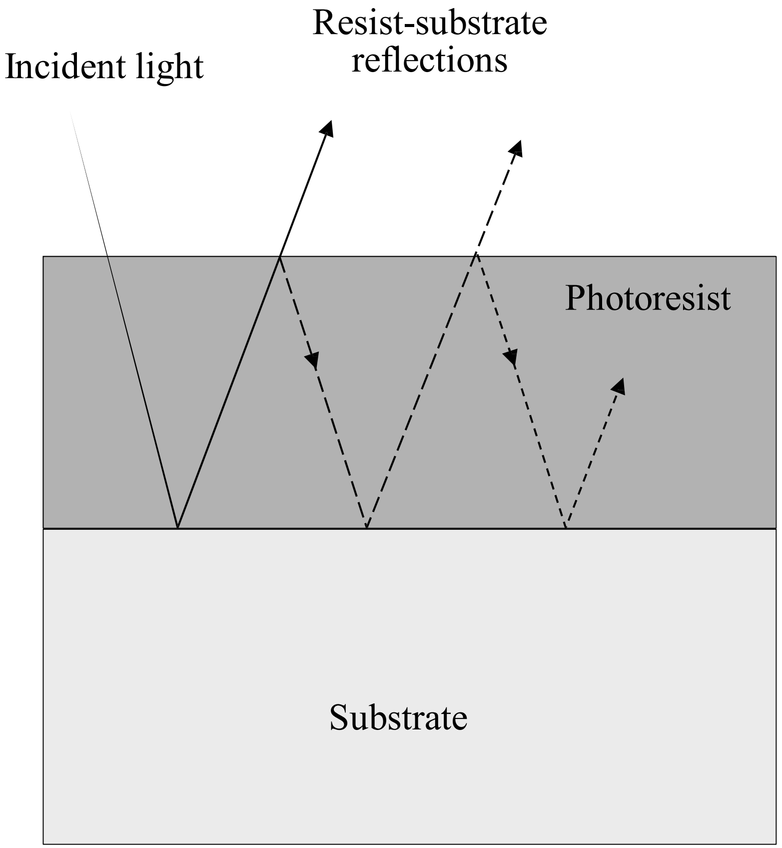


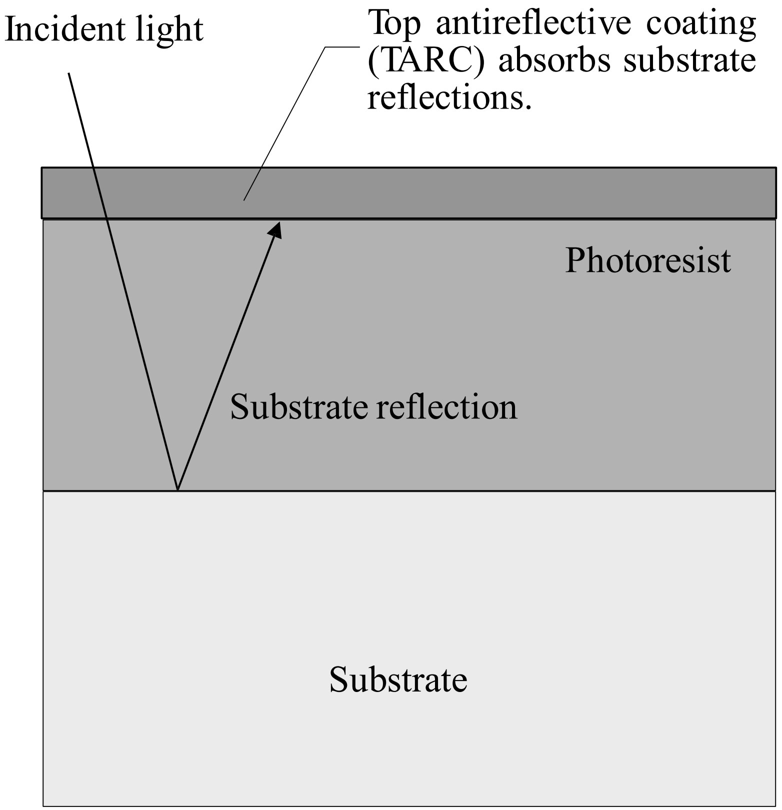
BARC Phase-Shift Cancellation of Light



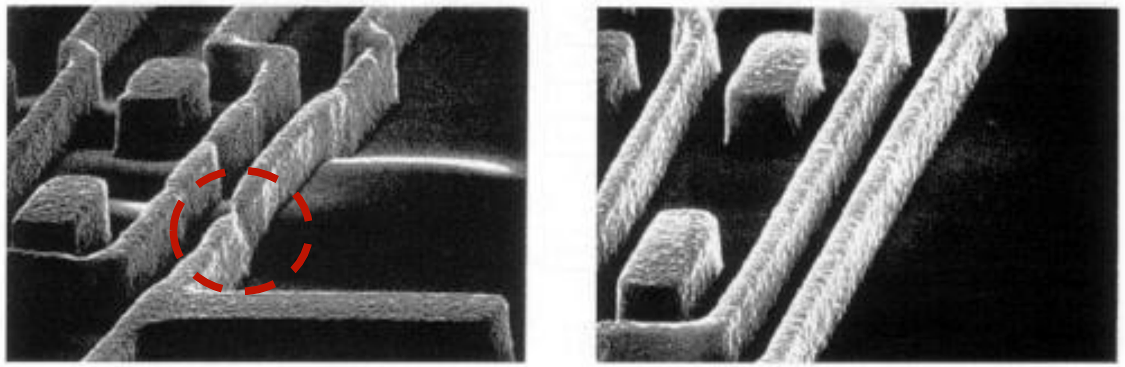


Suppression of Standing Wave Effect by TARC



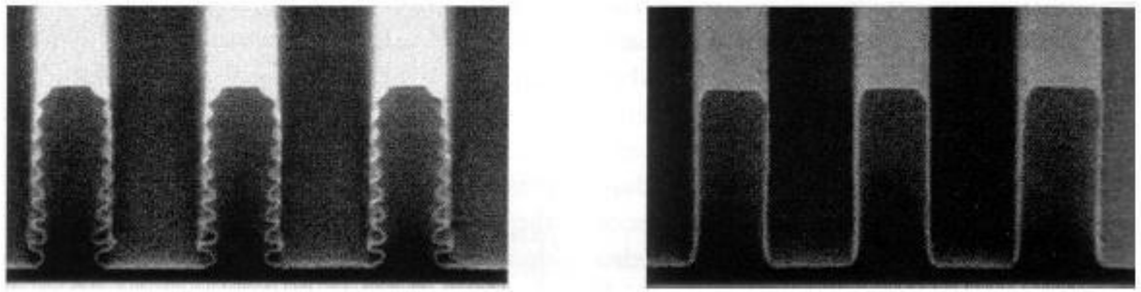


The use of BARC



SEM photographs showing that ARC process improves linewidth narrowing (right with BARC) at a step on a topographic substrate. Linewidth is 0.25µm.

Post Exposure Bake (PEB)



SEM photographs of resist image of 0.35 µm pattern in 0.98 µm thick i-line resist developed with (right) and without PEB (left).