10 Photo resist materials

From Wolf Chapter 12
and Campbell chap 8.
"Campell"

2 functions

a. precise pattern formation

b. protection of the substrate during etch or ion implant

Materials Parameters

- Optical properties – index, absorption coefficient, photo sensitivity
- mechanical properties – viscosity, solids content, etch resistance,
- processing / safety properties – toxicity etc.

(do next page on PR components first)

Sensitivity – Related to quantum yield and Abs. $\alpha(\lambda)$

$$\Phi = \frac{\text{number of photo-induced events}}{\text{number of photon abs.}}$$

[# of photons absorbed related to $\alpha(\lambda)$

* use λ w/ large α
* keep α for off-peak λ (i.e. background light) minimized.]

Sensitivity is important for determining the dose need to fully expose the resist.

Photoresist Components

3 - Components

(1) matrix material → Resin

- Binder, establishes mechanical properties of the film.
- usually inert to radiation

(2) Photo Active Compound (PAC)

→ active ingredient

→ causes photochemical changes in the resist

(3) Solvent

→ solubilizes resist so that it can be spun coat onto wafers

→ eg. propylene-glycol-monomethyl ether (PGME)

(high boiling points w/ favorable solvent properties of alcohols, etc.

Move on specific chemistry later...

10 Resolution - Contrast

Diffraction → Optical Intensity profile not uniform = contrast is ability of P.R. to distinguish between light and dark portions of the mask

Contrast influences
- resolution
- resist wall angle
- line width

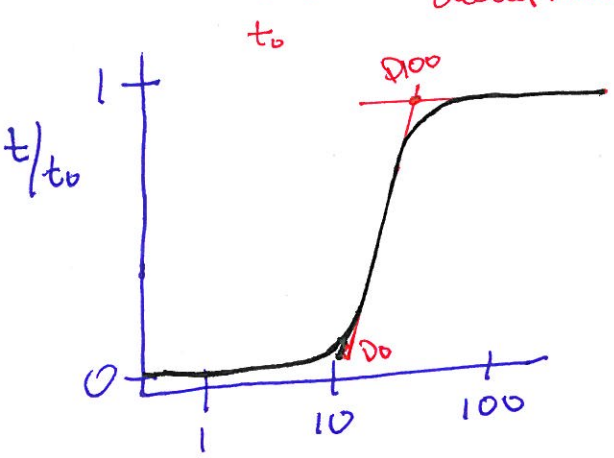
$\equiv \boxed{\gamma}$

γ Negative Resist → rate of crosslinking per change in dose

γ Positive Resist → rate of chain scission/solubility per change in dose

Response / Sensitivity Curves

t = film thickness after exposure and development

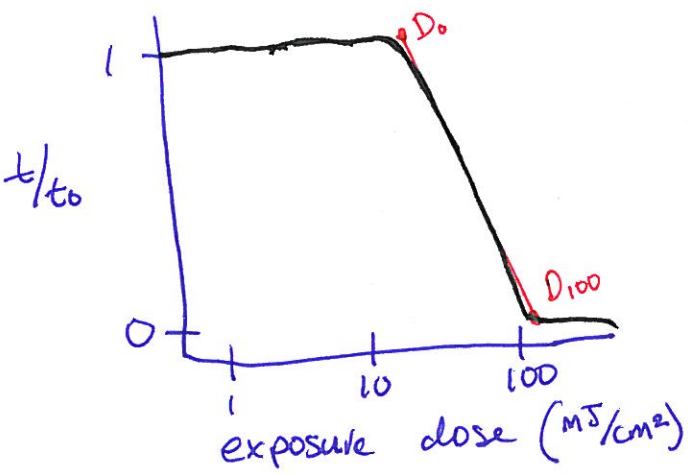


D_0 → ~~nothing has reacted yet,~~ lowest dose required to start driving photochemistry

D_{100} → minimum dose for which all photo resist is reacted

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

= Slope of the line on the semi-log plot.

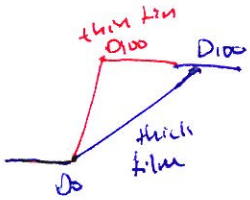


inside photoresist, light intensity will decrease by

$$I(z) = I_0 e^{-\alpha z}$$

I_0: initial intensity; α: absorbtion coefficient; z: depth

D_0 is independent of resist thickness



D_{100} is inversely proportional to Absorbance, so gets larger for thicker films

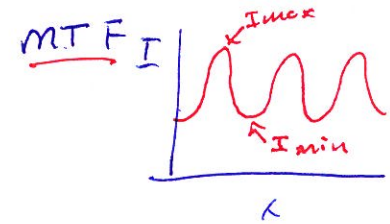
$\Rightarrow$ this leads to $\gamma = \dfrac{1}{\beta + \alpha T_R}$

T_R: film thickness; α: absorbtion coefficient; β: another process constant

$\rightarrow$ thinner films have larger γ, better contrast. $\rightarrow$ but worse step coverage and worse etch resistance.

Critical Modulation Transfer Function

[* minimum optical modulation needed for pattern transfer]



$$CMTF_{resist} = \frac{D_{100} - D_0}{D_{100} + D_0} = \frac{10^{1/\gamma} - 1}{10^{1/\gamma} + 1}$$

if MTF of optical image < CMTF

No Pattern!

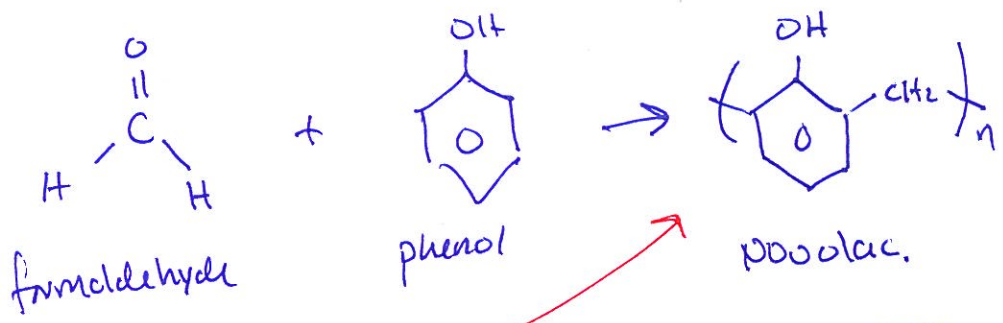
Photoresist Chemistry

(1) Positive Optical Resists

g and i line ⇒ DNQ / Novolac Resists

A. Novolac ⇒ matrix resin. From "new lacquer". – mainly used as adhesives in plywoods

phenol – formaldehyde Resins



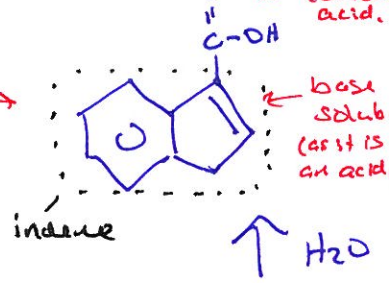
Base Soluble!

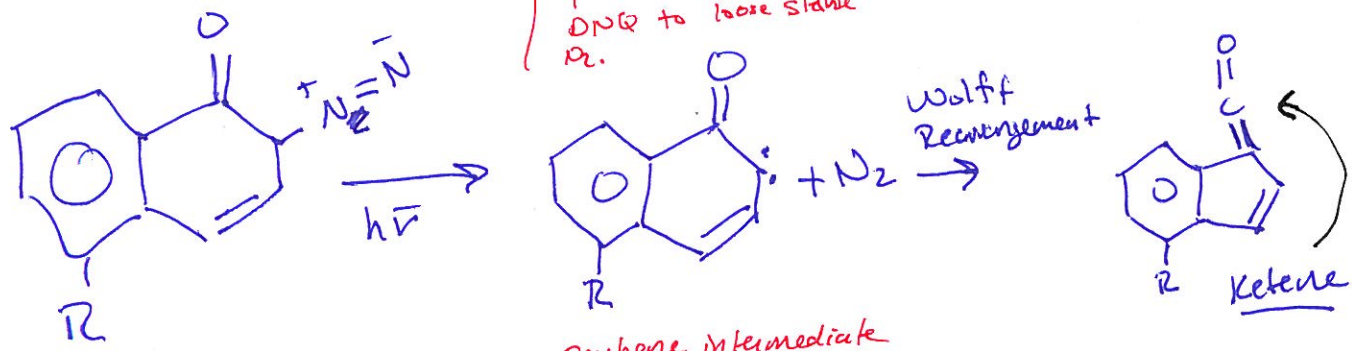
$n = 10-20$

B. DNQ = diazonaphthoquinones

→ PAC = photosensitizer

enhances dissolution of novolac





photons cause DNQ to loose stable N2.

Carbene intermediate

Base insoluble

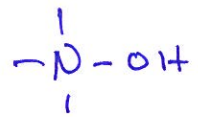
makes Novolac also insoluble! (likely through an H-bonding mechanism)

Positive DNQ / Novolac Resists, cont.

Solvents → PGME → high BP (ie >100°C) reduces safety concerns due to flash point

→ good solubility

Developer → typically 0.26 N TMAOH in H_2O



(2) Negative Optical Resists → used extensively in early days of IC fab.

→ lower resolution due to (>2 μm) swelling during development.

– cheaper / less sensitive to process conditions

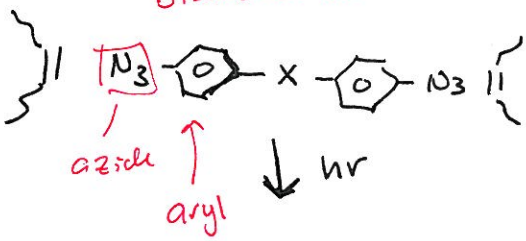
Resin = Cycloized synthetic rubber resin → irradiation insensitive, soluble in non-polar solvents

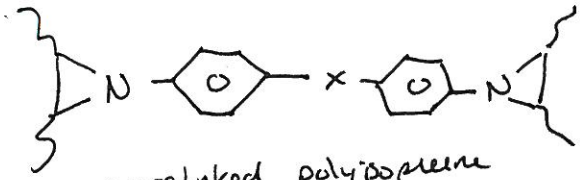
(poly isoprene) (double bonds on substituents connected together)

e.g. (toluene)

PAC = bisarylazide

aryl bisazide sensitizer





crosslinked polyisoprene

Crosslinking Chemistry

$R\text{-}N_3 \xrightarrow{h\nu} R\text{-}N: + N_2$

nitrene + nitrogen gas

$R\text{-}N: + R\text{-}N: \rightarrow R\text{-}N{=}N\text{-}R$

$R\text{-}N: + H\text{-}\overset{|}{C}\text{-} \rightarrow RNH\text{-}\overset{|}{C}\text{-}$

$R:N: + \| \rightarrow N\text{-}N$

etc.

Note exposure to O_2 can quench the nitrene reactive precursors.

→ Chemically Amplified Deep UV Resists

→ novolac resin absorbs strongly in deep UV → can't use anymore

CA → chemical amplification

① → hν causes decomposition of PAG (photo acid generator)

② H^+ catalyzes cascade of chemical reactions in the resist (x-linking or bond breaking)
negative positive

③ 500 – 1000 chemical reactions per photon!

④ RXNs happen during post exposure baking

→ high resolution possible as deep UV light can be used.

Problems: Reproducibility

1. very sensitive to bases at ppb levels in air
   - must filter w/ Activated charcoal,

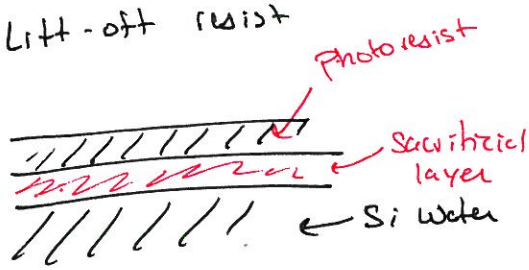
2. 3-4x more expensive than DNQ / Novolac Resists

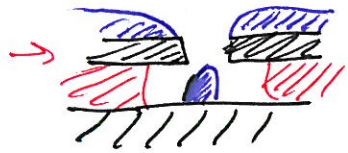
3. at very small feature size (<30nm) diffusion of the protons becomes a problem and limits process.

Multilayer Resist Processes → Seperate photo resist layer (imaging function) from etch resistance, planarization, reflection suppression, etc.

Lift-off resist

A.



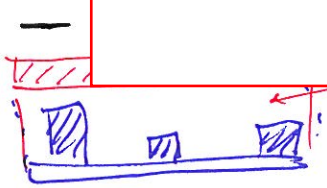


assists w/ lift off
no metal touching features

B. Si CARL process – Silicon-Chemical Amplification of Resist Lines

"planarization"

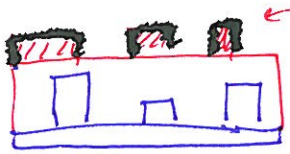
Skipped



↓ important for achieving high resolution on non planar surface

↓ expose/develop

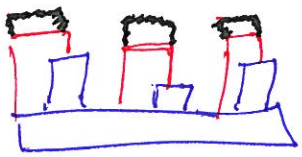
↓ silylate (adhesion layer)



amino silane treatment: reacts w/ carboxylic acid in DNQ.

↓ O_2 plasma

→ selectively etches the organics resist, but does not etch the SiO_2



Contrast Enhancement Layers

→ CEL

1. → spin CEL onto resist coated wafer (100nm-300nm)

→ material starts opaque, but bleaches when exposed to light.

→ windows in CE act like perfect contact mask
↓
thus high resolution

→ thinness of resist lead to inherently better contrast

→ →

improve squareness of pattern

Advantages → improved resolution

Disadvantages → increased process complexity, longer exposure times, longer development times

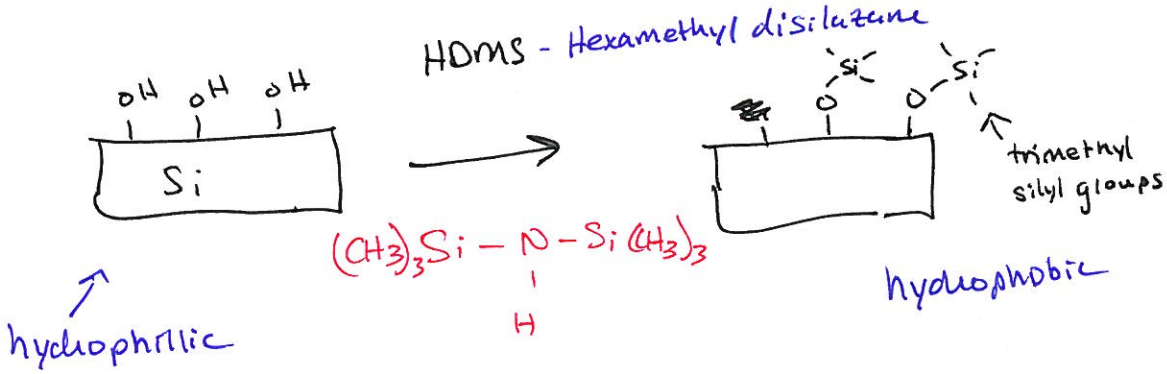
Photoresist processing: Basic Steps

1. Dehydration Baking and Priming

a. bake (200–400°C) to remove surface H_2O immediately before resist coating. Makes surface more hydrophobic.

b. priming: pre-resist coating to improve adhesion

HDMS - Hexamethyl disilazane



→ usually applied via vapor priming for ~10 min @ 100°C

→ also directly applied as liquid via spin coating.

2. Spin Coating of Resist

3 stages

1) dispense resist onto wafer center
2) accelerate wafer to final ω
3) spin at constant speed to establish desired thickness and to dry the film
   → 2000 - 6000 RPM for 20-30 s

→ thickness of resist $\propto \dfrac{\text{viscosity (\% solid in solution)}}{(\text{spin speed})^{1/2}}$

4) edge-bead removal (key for contact lithography!)

2. Spin coating

- film thickness is relatively flat ± 1 nm !

- balance between centrifugal forces controlled by spin speed / viscous forces controlled by solvent viscosity

→ physics complicated by evaporative processes and the formation of surface "skins"

* to minimize defects: clean wafer (no particles), clean resist, no air bubbles, not excessive exhaust (leading to excessively fast evaporation rates)

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3. SoftBake (or pre-bake)

→ after spin coating resist layer is still "tacky" w/ 65-85% solvent.

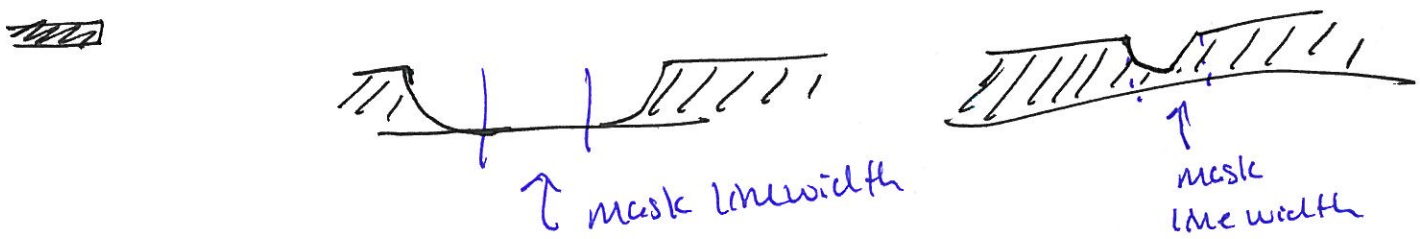
→ heat to 100-120°C for a couple minutes

→ solvent content drops to 10-30%

Precise soft bake parameters affect subsequent exposure step and resist contrast (γ) etc. !

3.4 Exposure → expose through mask with controlled dose of radiation.

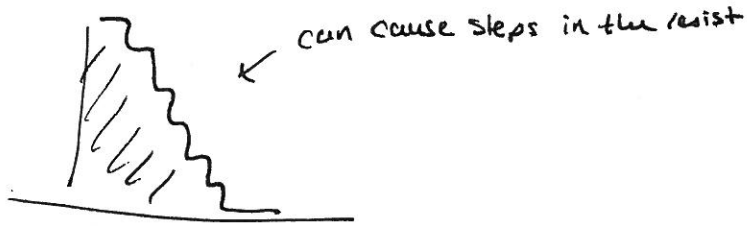
overexposure ⟷ underexposure



must optimize exposure dose for feature size, resist, underlying substrate etc.

Complications

A. → standing waves – hi / low exposure separated by $\lambda/2n$ (n = index)



B. Reflectivity of resist varies w/ the thickness of the layer (due to changes in interference)

C. Thickness of Resist changes at step edges

3. Exposure Continued.

Routes to address complexities

- Anti reflection Coatings → ~~index~~ match index to minimize reflections.
- add Dyes that don't bleach (increase α so that standing waves and reflections are damped)

4. Post exposure bake

a. → DNQ / Novolac positive resist – bake

(I have never done this) → causes diffusion of DNQ and can get rid of ~~fa~~ features due to reflections etc

b → DUV-CA Resist → essential to drive catalytic image forming reactions.

5. Development → dissolve soluble parts of resist.

a. positive DNQ/novolac Resist → Basic TMAOH solution in H_2O

b. negative resists → organic solvents

used instead of inorganic bases because "metal ion free"

Ideal process: unexposed regions not etched, development time should be short, should cause minimum pattern distortion or swelling,

Development time must be optimized to fully dissolve exposed resist, but not unexposed resist

6. After-Develop inspection

a. — line width variation

b. — line width measurements etc...
(too small / big)

- Process is still 100% reversible at this point!

Photoresist can easily be stripped in solvent, and process can be repeated

7 Post-development Bake.

a. — hardens patterned resist prior to etch or implant process

b. ~150°C → improves adhesion to SiO_2
(important for wet etching, eg., w/ HF)

8 Photostabilization

$\lambda < 320$ nm + 110°C for 60 sec

→ strongly crosslinks the resist → very good etch resistance
(important for dry etching features in inorganics)

disadvantage = resist stripping more difficult → must use O_2 plasma.