Lecture 4 Lithography II

- **Resist types**

1. Optical negative resist

a. Polymer get cross link after exposure

b. Developer is usually solvent (xylene (二甲苯), toluene (甲苯), halogenated aliphatic hydrocarbons)

c. Example: Cyclized poly (cis-isoprene) type negative: resin is a synthetic rubber, sensitizer: bis-aryldiazide.

d. Resolution~3 μm (because large molecule), and swelling problem (from solvent developer) limit the use.=>replaced by high resolution, novalak type,aqueous-based developed positive resist in VLSI fabrication.

2. Optical positive resist

a. Better resolution (>50 nm), low molecule weight components

b. Do not form chain group, easy to be developed by base or alkaline.

c. Resin: base soluble phenolformaldehyde novolak resin matrix, sensitizer: diazonaphthaquinone dissolution inhibitor.

d. Process after exposure:
wolff rearrangement=>hydrolysis=>indene carboxylic acid

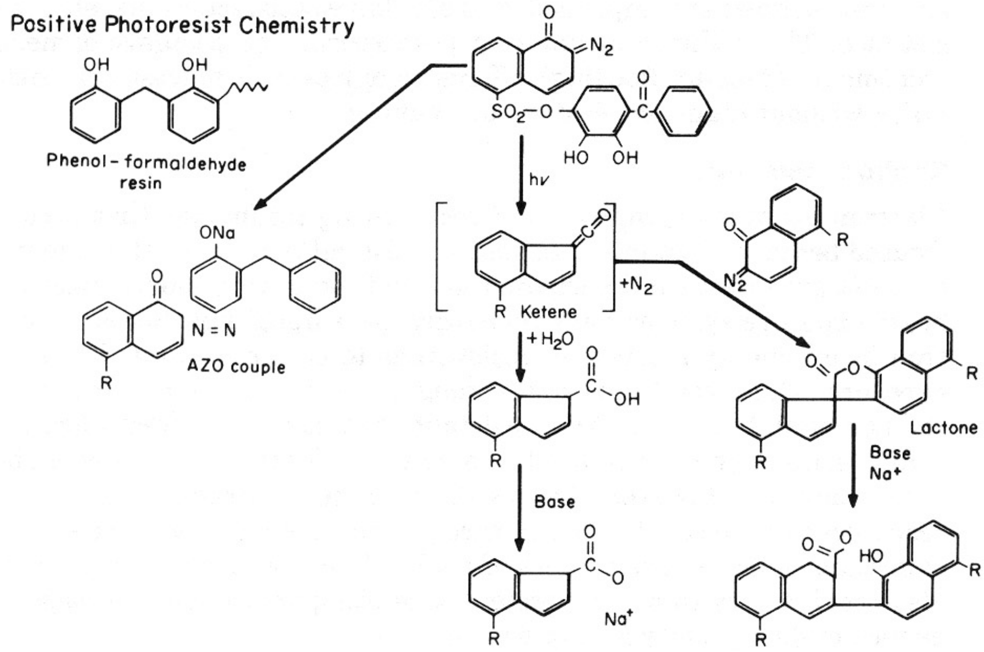


Figure 3.6 Positive novolak-type resist exposure reaction.[4]

3. Electron beam resist

a. Electron beam lithography: direct-writing using focus e-beam, high resolution.
b. Low through and plasma resistant chemistry
c. Positive resist: PMMA (Poly(methylmethacrylate), sensitivity is low), or PBS (poly-(butene-1-sulfone), high sensitivity).
d. Negative resist: COP (coplymer of glycidal methacrylate and ethyl acrylate)

4. x-Ray resist
a. using similar resist as electron beam uses, high resolution

5. Image reversal resist
a. add small quantity of monoazoline, imidazole, or triethanolamine to diazoquinone novolak resist. (AZ 5214)

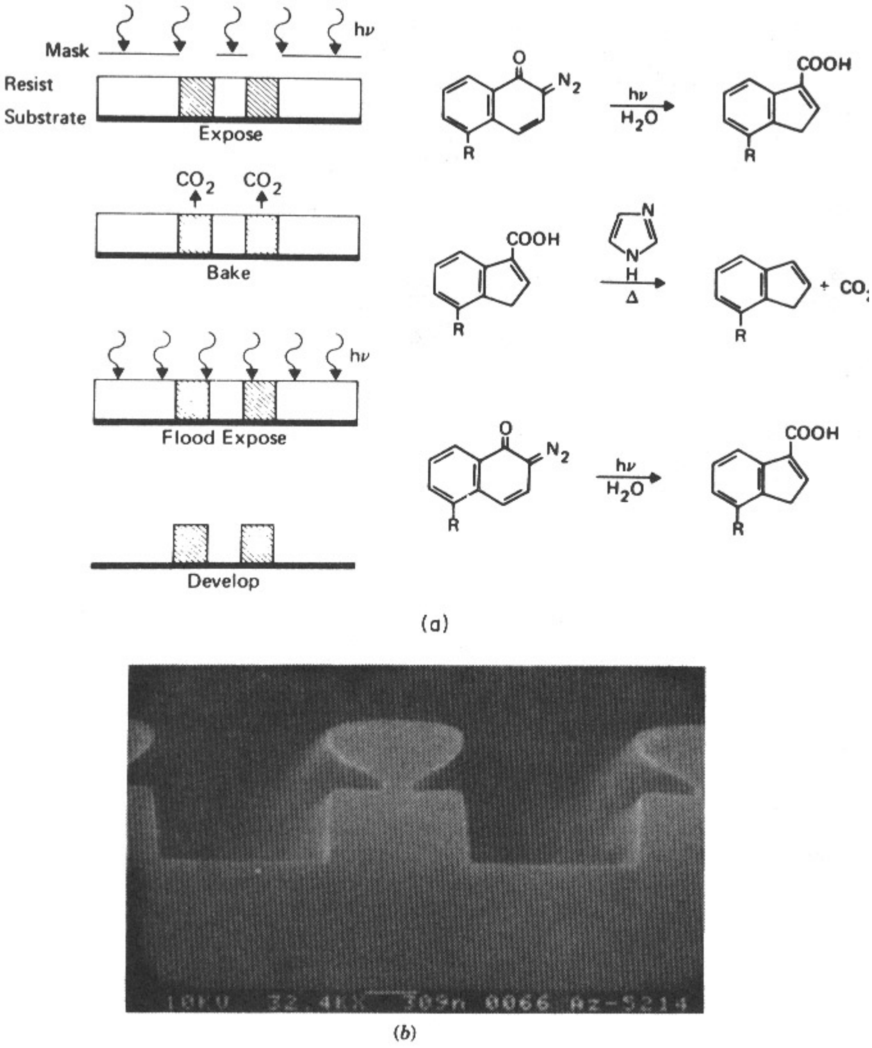


Figure 3.12 (*a*) Image reversal mechanism for positive photoresist and SEM of image.[7] (*b*) AZ-5214, image-reversal-processed, over etched thermal SiO_2 on silicon. (*Courtesy of I. Higashikawa, Toshiba.*)

- **Resist applications**
  1. **Etch mask**
  2. **Backside coating**
  3. **Dielectric insulation**
  4. **Lift off**
  5. **Implant masking**
  6. **Multiplayer imaging**
  7. **Micro structures (lens, mechanical parts, micro fluidic components…)**
  8. **Electroforming mask**

- **Concerns for resist selections**

1. **What kind of surface for the resist to apply?**
   (doping, irregularities, surface cleaning requirements, surface flatness, uniformity of surface properties, surface reaction with resist)
2. **What is the step heights?**
   (at least 0.2 μm thick is required for protection, least coverage for the whole wafer)

3. **What are the etchants to be employed?**
   (enough thickness for pinhole resistance, chemical compatibility, postbake time and etching temp、 time and concentration, etchant makes PR hard to strip,
4. **Minimum line and space**
   Usually aspect ratio for PR: less than 5.

5. **Economic, disposal aspects.**

- **The resists used in this course**

1. **<u>AZ5214 EIR</u>, positive or image reversal resist, 1~2 μm thick under 3000-6000 rpm, developer: AZ or AZ 400K, striper: AZ 300 T, Thinner: AZ 1500**
2. **<u>AZ4620</u>, positive resist, 5-20 μm thick under 3000-1000 rpm, developer: AZ or AZ 400K.**

- **Resist removal**
  1. **criteria**
     a. **Completely removed without residues, including metal components in resist (ie. Na…)**
     b. **No undesired etching on the bottom metal, silicon or oxide surface**
     c. **Cost efficient and safe process**
     d. **Environmental regulations**
     e. **Dissolution is preferred, no lifting or peeling to prevent redeposition**
     f. **Short removal time**

g. Free of metal ion (for IC process)

h. Simple method to detect the completion of process

Table for different stripping situations

TABLE 12.1 Applications and Requirements for Resist Stripping

Application	Special resist-removal requirements or problems
Lift-off process	Stripper must penetrate, swell, and lift a metal layer and provide a clean fracture.
Direct ion-implant resist masking	Highly baked resist is "chemically" reacted by the dopant ions at high temperatures, making the resist extremely insoluble in known strippers.
Etching noble and seminoble metals	Oxidizing acids react with resist images to form insoluble by-products. Resist must be lifted off at substrate interface and bypass insoluble surface species.
High postbake temperatures used to provide exceptional adhesion or etch resistance	Cross-linking (negative resists) or extreme hardening to form a bakelite-type product (positive resist) requires rigorous stripping chemistry.
Simple removal of misaligned resist patterns for reimaging after development and inspection	Positive resists and some negative resists leave a "memory," or ghost, image of the resist pattern, and microetching may be required to remove this memory.

2. Solvent type resist strippers

A. Ability to break down the structure of the resist layer

B. Three kind of structures hard to striped:

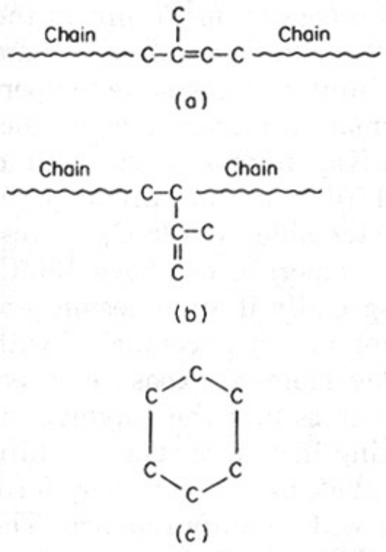


Figure 12.1 (*a*) Photoresist molecules in which the double bond forms part of the polymeric chain backbone require longer stripping times than (*b*) those with the bond external to the chain. (*c*) Hexagonal ring configurations strip even slower.[1]

C. Non postbaked positive PR is easier to stripped than hard baked ones, which can also be flood exposed and then developed

D. Organic stripper

1. Acetone

- **a. limited to non-postedbaked resist. Operated at room temp and prefer two bath system for 5 min in the first bath and 3-5 min for the second.**
- **b. hard bake temp > 120° C start to have residue. Adhesion promoter help on the residue remaining.**

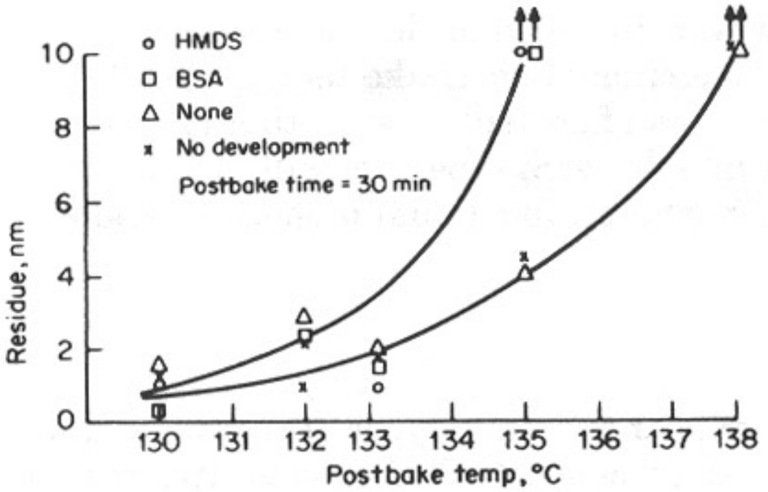


Figure 12.2 Residue thickness after acetone stripping as a function of postbake temperature.[2]

- **c. Post development exposure is recommended to ease the stripping.**
- **d. Good for lift off application with temp at 40° C, which leaves sharp metal edges.**
- **e. Low cost, good stripper for positive resist, but not good for negative resist (often use methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK))**

2. Trichloroethylene (TCE)

- **a. strip non-post bake negative resist, better to use in vapor state.**

3. Phenol-based organic strippers

a. for strip postbakeed positive and negative resist (up to 150-170 ° C).

b. Used at 90-100° C immersion in a two-bath system for 3-5 min in the first, 1-2 min in the second.

D. Inorganic stripper

1. **Usually sulfuric acid based (often called oxidizing strippers), for it oxidize the resist into carbon dioxide and water.**
2. **HNO_3+H_2SO_4=12:88, at 100° C for 5 min, for striping ion-implanted positive resist (baked at 400 ° C for 1 hour). Can attack metal!!**
3. **Chromic acid (chromium trioxide mixed in water) at 70-100 ° C, gentle to metal, but may causing electrical defects.**
4. **Caro's acid (Piranha), US patent 3900337 (1975), H_2O_2+H_2SO_4~10:90 at around 90-100° C, using both dehydration and oxidation, very efficient for hard baked positive resist, but not good enough for highly linked resist.**
5. **$K_2S_2O_8$+H_2SO_4=700g:2000ml, good for highly linked resist.**

E. Plasma resist stripping

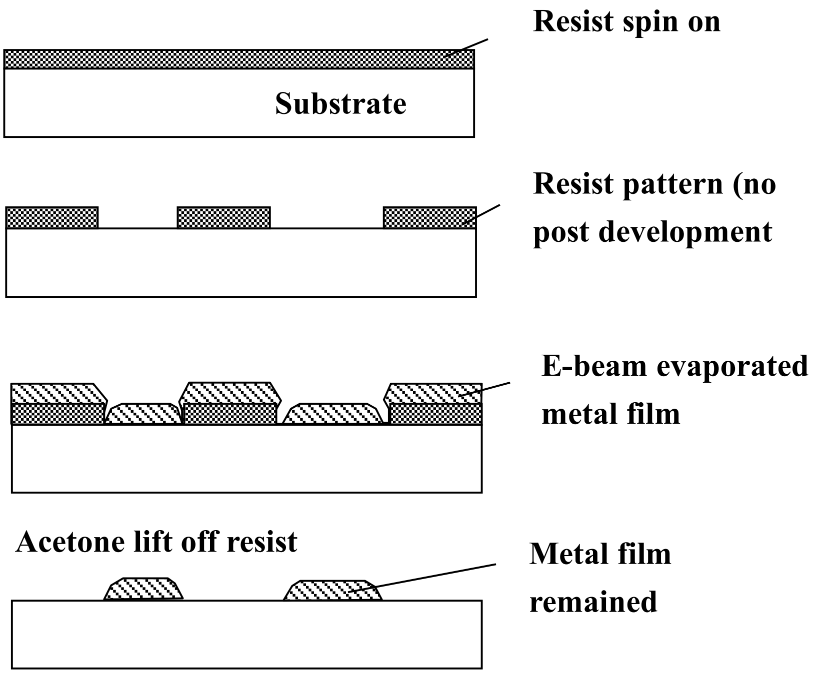
1. **safer, no metal, no attack on underlying surface, fewer processing step, controlled reaction**
2. **Rf power at 500 W and 14 MHz for more than 10 min.**

Oxidation reaction:

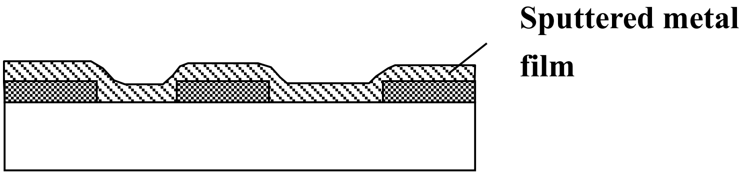
$$C_xH_y + active \quad oxygen = CO, CO_2, H_2O$$

- **Lift off process**

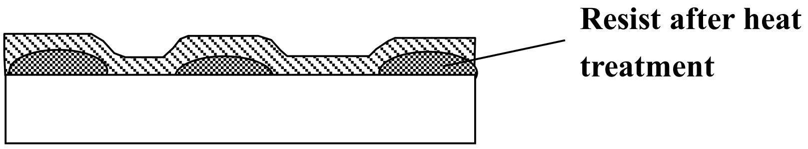
1. Lift off process:



2. Step coverage problem

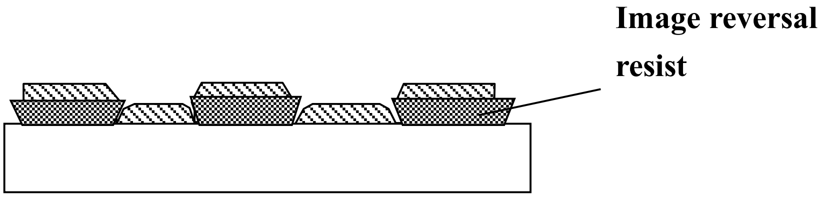


3. Thermal curing problem during postbake and evaporation

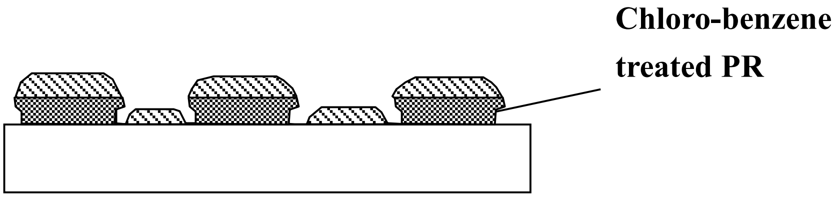


4. Using ultrasound to help on remove resist, but need to note the damage of micro structures.

5. Using image reversal to get negative slop for helping lift off process



6. Chloro-benzene treatment for 10 min after exposure for getting mushroom like resist top



Reference:

1. Integrated circuit fabrication technology, David J. Elliott, McGRAW-HILL international editions, 1989.