Photoresists

• general properties of polymers
• photoresist types
• photoresist characterization (dissolution behavior, sensitivity, contrast, resolution, etching resistance)
• resist materials
  – general characteristics
  – negative resists
  – positive resists
• photoresist processing
Generic properties of polymers

- Polymers are long chain, usually organic (C, O, H) molecules with high molecular weights (1000 → >1,000,000)

- **Thermoplastic** polymers -- chains are free to move past each other at high temperatures, and become entangled at low temperatures
  - *linear chains* (LDPE) ↔ *branched chains* (HDPE)

- **Thermoset** polymers -- chains are crosslinked together to form a three-dimensional network (example: epoxy resins)

- The properties of a polymer are determined by its chemical constituents, its molecular weight (and M.W. distribution) and the degree of cross-linking
Important polymers in photoresists

\[ \text{m-cresol} + \text{formaldehyde} \rightarrow \text{novolac polymer} \]

(novolac = “new lacquer”)
Important polymers in photoresists

- **cis-isoprene**
  
- **poly (cis-isoprene)**

- **methyl methacrylate**
  
- **poly(methyl methacrylate) (PMMA)**
Mechanical properties of polymers

- The mechanical properties of polymers (which are important to photoresist processing) strongly depend on the long chain nature of these materials and both intra- and inter-chain reactions.
- The *glass transition temperature* $T_g$ is an important parameter:
  - $T < T_g$ -- only short-range motions of the polymer chain are possible $\rightarrow$ *elastic* behavior
  - $T > T_g$ -- long-range motions of the polymer chain are possible $\rightarrow$ *viscous* behavior
- Both the *chemical structure* (crosslinking versus chain scission) and the *physical environment* (temperature and strain rate) will play an important role in the elastic versus viscous characteristics of a typical photoresist.
Positive versus negative resists

- Positive-tone resist
- Negative-tone resist

Photoresist

Substrate

Mask

Development

Positive-tone resist

Negative-tone resist
Positive versus negative photoresists

• **Positive** photoresist -- exposure to light *increases* the solubility of the polymer (opening in mask $\rightarrow$ opening in resist)

• **Negative** photoresist -- exposure to light *decreases* the solubility of the polymer (opening in mask $\rightarrow$ closed area in resist)

• Both positive and negative resists are used, depending on device design, process flow, and the demands of the lithographic process (examples and reasons will be given…)
There are a few common characteristics of all photoresists that are used to gauge their performance:

- dissolution behavior
- sensitivity
- contrast
- resolution
- etching resistance

The choice of a particular photolithography process (optical system + photoresist system) will depend on compromises between these (and other!) factors.
Photoresist dissolution behavior

- Photoresist dissolution must be determined for each combination of exposure system, photoresist, and development system
- Dissolution curves give an operational definition of PR performance

Figure 2. Dissolution curves for positive resists after exposure. The doses are designated by the numbers accompanying the traces. A stronger dose leaves a thinner film at a fixed development time.
Photoresist sensitivity -- “contrast curves”

- $D_o$ = *incipient dose*: minimum dose required for a given process to emerge (note -- varies with process and development conditions)
- $D_{100}$ = *completion dose*: dose at which the resist is completely dissolved (positive resists) or at which the resist is completely inert (negative resist)
Photoresist sensitivity -- “contrast curves”

- The **contrast** is defined as

\[
\gamma = \frac{1}{\log_{10} \frac{D_{100}}{D_0}}
\]

- **Contrast** is the ability of a photoresist to distinguish between light and dark portions of the mask
- In general, the **higher** the contrast, the **sharper** are the edge profiles of developed lines (**highly desirable**!)
- Contrast can be varied by adjustment of the resist processing parameters
Photoresist resolution

- **Resolution** is the ability of a resist to resolve fine lines in the final printed pattern
- Resolution depends strongly on the chemistry of the resist and the developer system
- Other factors can affect resolution
  - Exposure hardware (Chapter 7)
  - Resist deformation from thermal flow during processing
- If a resist is heated above its glass transition during processing, thermal flow may distort the exposed pattern
  - plasma etching
  - doping
  - high-temperature deposition
After the photoresist is exposed, it is exposed to corrosive or physically-abusive environments in subsequent processing

- **Wet etches** → strong acids or bases
- **Dry etches** → oxygen plasma “ashes” organic materials; chlorinated (for metals) and fluorinated (for silicon) plasmas are very corrosive to photoresists

**Etching resistance** is the ability of a resist to withstand the conditions necessary to transfer the pattern

- Etching resistance is a strong function of resist chemistry
- **Adhesion** to the substrate is very important (adhesion promoters may be applied prior to PR application)
Resist materials -- overview

- A polymer-based photoresist must meet rigorous requirements:
  - high sensitivity
  - high contrast
  - high $T_g$
  - good etch resistance
  - good resolution
  - easy processing
  - long shelf life
  - minimal solvent use
  - reasonable cost

*not your basic Tupperware!*
Resist materials -- negative resists

- Negative resists were the first to be used in semiconductor device fabrication
- Polymer matrix + organic sensitizer
  - matrix: poly(cis-isoprene) -- a synthetic rubber
  - sensitizer: bis(aryl)azide

Mechanism -- the sensitizer loses nitrogen under $h\nu$ and generates a highly reactive nitrene; this reacts with the polymer to crosslink it and lowers its solubility by organic solvents (like vulcanization)
Problems with negative resists

- Resolution in negative resists is limited by swelling in the exposed crosslinked areas caused by solvent uptake:

  - Line width of negative resists limited to ~3 μm
  - Organic solvents a problem (environment-safety-health)
  - Advantages: greater process latitude, much lower cost
  - Negative resists dominate in low-cost, high-volume chips
Resist materials -- positive resists

- Positive resists have gained popularity because of their superior resolution, better etching resistance, and thermal stability
- Polymer matrix + organic sensitizer
  - matrix: novolac resin (cresol/formaldehyde polymer)
  - sensitizer: diazoquinone (DQ)

 Mechanism -- upon photolysis, the DQ sensitizer loses nitrogen and is converted into a carboxylic acid; the irradiated areas of the resist can be dissolved in a strong base (KOH, NaOH)

the specific organic group R plays only a secondary role in the resist exposure process
Specific reaction mechanism of DQ

1. $\text{DQ} \xrightarrow{h\nu, -\text{N}_2} \text{carbene}$

2. $\text{carbene}$

3. Wolff rearrangement

4. indenecarboxylic acid (ICA)

$\text{H}_2\text{O}$
Photoresist processing

This will be repeated 15 to 30 times during the processing of a given wafer -- all lithography steps must be aligned to each other.

These steps are being performed on highly value-added wafers -- any error will negate (trash) all of the prior work.
**Wafer preparation**

- The substrate must be *atomically clean* and *free from contamination* for a successful lithographic process. *Dirty substrates* → *poor adhesion, pinholes, opaque spots*

- **Problem** -- what surface needs to be cleaned?
  - metal (aluminum, metal silicide)
  - semiconductor (Si, GaAs)
  - insulator (SiO₂, Si₃N₄)

- **Problem** -- what kind of contamination is present?
  - organic films
  - inorganic films
  - particulates

  All have different surface chemistries, and all need different analytical methods.

  All can come from different sources, will be process-dependent, and will require different methods for complete removal.
Examples and sources of common contaminants

**ORGANIC FILMS**
- **oil or grease (low MW)**
  - lubricants from air handling or other machinery; vacuum pump fluids
- **polymeric (high MW)**
  - plasma deposited from sputtering systems; deposits from previous resist processing

**INORGANIC FILMS**
- **oxide films**
  - air oxidation; excessive heating; $O_2$ in deposition equipment
- **salts**
  - airborne chemicals; storage containers; contaminated cleaning reagents
- **water**
  - improper or incomplete drying from wet cleanups; humidity

**PARTICULATES**
- **organic**
  - residual resist; contaminated chemicals; dirty spin coaters; human “debris”
- **inorganic**
  - airborne “dirt”; contaminated deposition, baking and/or storage equipment
Adhesion promoters

- Adhesion promoters encourage the adhesion of the resist to the substrate (Si, SiO₂, Si₃N₄, GaAs, Al₂O₃, etc.)
- Common promoters lower the surface energy of the substrate surface by reacting with it
  - → trimethylsilydiethylamine (TMSDEA)
  - → hexamethylcyclotrisilazane (HMCTS)
  - → hesamethyldisilazane (HMDS)
- Promoters are usually applied from the gas phase
- One monolayer on the surface is sufficient
Resist application

- The goal of resist application is to create a *uniform*, *adherent*, *defect-free* polymeric film over the *entire* substrate.
- Spin coating is the universal method that is used:
Resist application

- Resist application follows the following steps:
  1) mount the wafer onto a vacuum chuck
  2) apply resist to a wafer
  3) accelerate to a desired RPM
  4) spin at constant RPM to near dryness
  5) stop rotation and remove wafer
- Only about 1% of the dispensed resist remains on wafer
- For a given system with constant molecular weight, solution concentration, etc., the film thickness depends only on the spinning parameters

\[ T_R = k \omega^\alpha \Rightarrow \log T_R \propto \alpha \log \omega \quad \alpha \approx -\frac{1}{2} \]
Effect of spin speed on resist application

Figure 10 Resist film thickness as a function of spinning speed (in RPM) for three different molecular weights of the same polymer. The solution concentration is constant for all samples.

Figure 11. Resist film thickness as a function of spinning speed for three solutions of different concentrations. The polymer composition and molecular weight are constant for the three samples.
Softbake

- After spin-coating and air-drying, the polymer film has two important characteristics:
  - it contains about 1% to 3% residual solvent
  - the film may have built-in stresses
- Residual solvent will effect both exposure and developing
- Stresses can cause loss of adhesion and erratic etching

Softbaking seems trivial, but it is very important in order to ensure reproducible processing

- Typical condition -- 30 minutes at 90°C (above $T_g$, but not high enough to crosslink the polymer)

⇒ Next step – exposure of the pattern
Develop cycle

- Development is a critical step because it exerts a great influence on pattern quality
- Usually performed by spray or immersion in solutions
- Important parameters include developer strength, agitation, pH, temperature and humidity
- All parameters affect the rate of dissolution of both the exposed and unexposed regions, as well as polymer swelling and distortion
- Positive resists $\Rightarrow$ alkaline solutions (KOH + H$_2$O)
- Negative resists $\Rightarrow$ organic solvents
- The process of polymer dissolution is complex -- modeling is difficult, so most processes must be determined “empirically”
Hardbake

• The hardbake (a.k.a. postbake) performs several functions:
  – remove residual solvent
  – anneal the film to promote adhesion
  – improve edge profiles
• Since there is no latent image to preserve, the temperature used can be much higher than that used in softbake (but not too high...)

Post-development treatments

• “Plasma descumming” -- the development process is not perfect, so defects may be present:
  – residual resist on the substrate surface
  – ragged and non-uniform edges
  – A mild plasma etch (O₂ or O₂-CF₄) at low power for short times can “clean up” the resist pattern

• Substrate treatment -- [*wet or dry etching, or additive processes*]

• “Resist stripping” -- removes developed photoresist after the substrate is processed
  – inorganic wet strip -- HNO₃, H₂SO₄, H₂O₂
  – organic wet strip -- acetone, trichlorethylene
  – plasma strip (“ashing”) -- O₂ or O₂-CF₄
“Odds and ends” – The critical modulation transfer function

• In discussing the far-field image of a diffraction grating we introduced the *modulation transfer function* of the optical system

\[
MTF = \left( \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{max}} + I_{\text{min}}} \right)
\]

• A similar *critical modulation transfer function* can be defined for a photoresist:

\[
\text{CMTF}_{\text{resist}} = \left( \frac{D_{100} - D_0}{D_{100} + D_0} \right) = \left( \frac{10^{1/\gamma} - 1}{10^{1/\gamma} + 1} \right)
\]

• If the MTF of an image is less than the CMTF the image **will not** be resolved; if the MTF > CMTF the image **will** be resolved
Multilevel resists

*The problem* -- surface topography can cause variations in photoresist thickness, leading to linewidth variations.
Multilevel resists

*The solution* -- apply a thick planarizing layer that a thin imaging layer can coat uniformly.

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[Diagram showing the process of applying a thick planarizing layer followed by a thin imaging layer, followed by development and plasma etch.]
Multilevel resists

- A relatively thick (1 μm to 4 μm) planarizing resist layer (often PMMA) is applied over surface topography
- A thin (0.3 μm to 0.5 μm) imaging resist is applied over the planarized surface
- A very thin (~0.05 μm) isolation layer (often SiO₂) is sometimes deposited between the two resist layers
- The imaging layer is exposed and developed; it can then serve several functions:
  - a mask for wet etching of the planarizing layer
  - an exposure mask for exposing the underlying planar resist
  - a mask for plasma etching of the planarizing layer
Advantages and disadvantages of multilevel resists

• Advantages
  – depth of focus problems in projection printing are minimized
    \[ \sigma = \frac{\lambda}{(\text{NA})^2} \]
    with a NA of 0.4 and \( \lambda = 436 \text{ nm} \), \( \sigma = 2.7 \text{ \( \mu \)m} \)
  – linewidth variations due to resist thickness are reduced
  – variations due to non-uniform reflectivity are reduced

• Disadvantages
  – extra processing steps increased cost, complexity, and possibility of killing defects
Contrast enhancement layers

- Contrast enhancement uses a photobleachable layer (CEL) on top of a standard resist
- Exposure to UV light changes the thin top layer from opaque (diarylnitrone) to transparent (oxaziridine)

initial exposure of CEL by both primary and diffracted light

bleaching of the CEL restricts the lateral extent of PR exposure

final resist profile is less affected by diffracted light
Chemically-amplified resists (CAR)

- The *quantum yield* of the diazoquinones used in positive resists is typically 0.2 to 0.3, requiring three to four photons to transform a single molecule of sensitizer.
- In *chemical amplification*, a single photon initiates a cascade of chemical reactions (just like AgI photographic emulsions).
- CARs contain a photoacid generator (PAG) that “unzips” a polymer chain and can attack chains repeatedly.
- The chemistry of CARs is very complex — a common PAG is poly-(4-hydroxystyrene) blocked with *t*-butyloxycarbonyl groups (PBOCST).
Figure 4-46. Acid catalyzed cleavage reactions useful in lithography.
Advanced and Future Lithography

Since the minimum feature size is $k\lambda/\text{NA}$, the long term solution to obtaining smaller device sizes is to lower $\lambda$.

Changes must be made in current systems:
- Efficient small wavelength sources must be developed
- Reflective optics and masks must be developed
- Resists responsive in the extreme UV range must be developed
- Cost issues must be addressed

**Extreme Ultraviolet Lithography**
- 13.4 nm wavelength
- Use for 70 nm ~ 2005 timeframe

Figures extracted from Cahners MDR Microprocessor Forum 2000, October 11, 2000,
Xtreme Semiconductor Process Technology, Charles (Chuck) W. Gwyn, Program
Director Intel Corporation & EUV LLC
Advanced and Future Lithography

Other companies/universities are taking the approach of using X-Rays or Electrons for lithography:

X-Rays:
Advantages:
• Very small wavelength (1.5 Angstroms or shorter)
• Can be performed in air, but particles are a problem
Disadvantages:
• Bright sources of X-rays exist, but are still not bright enough for high throughput.
• Polished mirrors are very difficult and expensive to make and maintain.
• Shares all of EUVL problems.

Electron Beam Lithography:
Advantages:
• Extremely small wavelength (<0.01 Angstroms or shorter)
• Viable solutions for 10 nm features are available TODAY.
• No mirrors required.
• Limited need for optics.
Disadvantages:
• Bright sources do not exist resulting in very limited throughput.
• Vacuum based technology.