

Chapter II

Theory

2.1 Resists

Resists are polymers which used for resistance to etching in lithographic steps. Lithography has been associated with the printing industry. However, the manufacture of printed circuit boards, microelectronic chips, and other photofabricated products also involves the use of photosensitive polymers to form images. Each industrial application requires a specific set of polymers, sensitizers, and developers, but the fundamental concepts of image formation and image transfer remain the same.

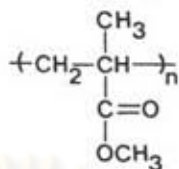
2.2 Classification of Resists

From steps in microlithographic process, an important material used is a resist which protects the surface of the substrate during the lithographic steps. The resists are divided into two classes depending on their behavior under irradiation.

2.2.1 Positive resists

Usually, positive resists become more soluble in the irradiated area relative to the unexposed area. By the other method, polymers with being less soluble in appropriate solvent become more soluble in appropriate solvent after irradiation, due to the changing of the functional group on polymer chain into the different one. Positive resists, which require

facile chain scission, are frequently vinyl polymer such as poly(methyl methacrylate) (23)

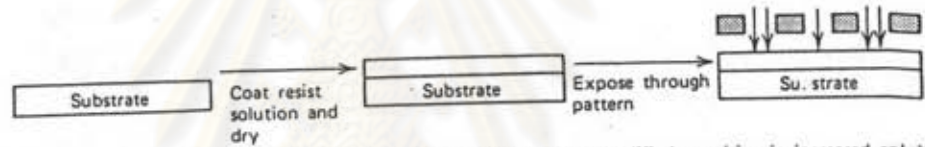
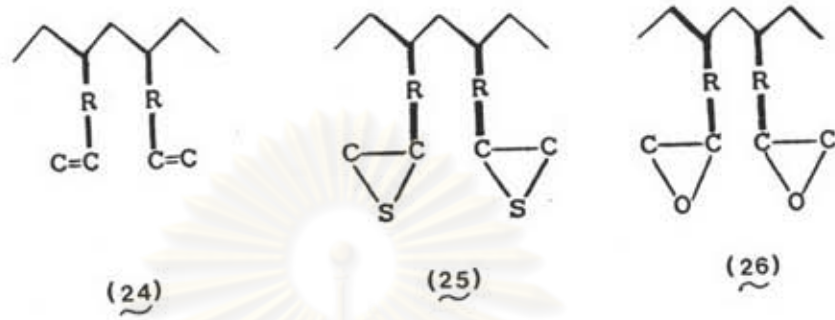


(23)

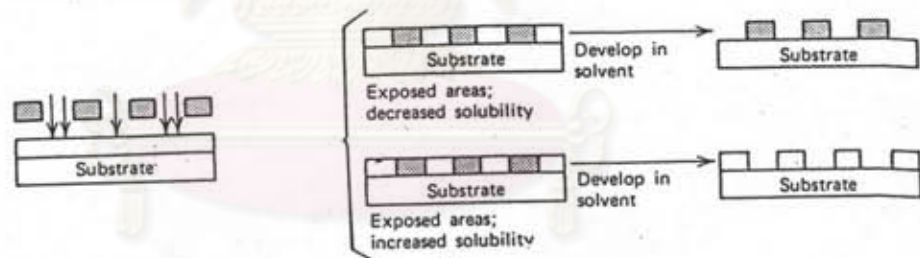
2.2.2 Negative resists

Usually, negative resists become less soluble in the irradiated area than in the unexposed area. By the other method, polymers with photofunctional group, either pendant or admixed with, being more soluble in appropriate solvent become less soluble in appropriate solvent after irradiation, because of changing in polarity of functional groups. Negative resists, which require ease of crosslinking, are polymers bearing double bonds or other reaction groups, e.g : vinyl (24), episulfide (25) and epoxide groups (26) (Figure 2.1)

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The exposed areas can cross-link, resulting in insolubility, or be modified, resulting in increased solubility



The cross-linked system is termed negative-working

The modified system is termed positive-working

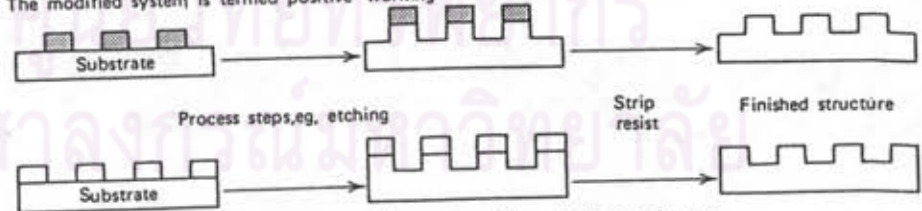


Figure 2.1 Schematic outline of photoresist use.

2.3 Characteristic Parameter of Resists

Since this research is focussed on the negative resists, only characteristic parameter of negative resists will be mentioned. There are three main functional characteristics that polymeric resist system must possess in order to be useful in a microlithographic application.

2.3.1 Sensitivity

The sensitivity expresses the aptitude of a resist to undergo structure modification under irradiation. In order to define this parameter, it is necessary to introduce the incident dose "D". In the case of an electron-beam exposure "D" is expressed as

$$D = \frac{I \times t}{S} \quad \text{C/cm}^2$$

where "I" is the beam current in amperes, "t" is the exposure time in seconds and "S" is the area exposed in square centimeters. For electron-beam irradiations exposure dose is given in C/cm^2 (C = coulombs), for X-ray exposures in J/cm^2 (J = Joule) and for UV and visible light in J/cm^2 .

The sensitivity of a polymer is determined by plotting the normalized thickness of resist layers after development (e_r/e_0 = crosslinked thickness/ initial thickness), as a function of dose, (Figure 2.2)

For a negative resist, the ratio c_r/c_0 increases with the dose up to a value of $i = 1$, for which the total thickness of the layer is referred to as the gel dose D_g^1 . The sensitivity of a negative resist is usually taken as the dose $D_g^{0.5}$ or $D_g^{0.7}$ required to crosslink the film so that respectively 50% or 70% of the initial thickness remains after development.

2.3.2 Contrast

The pattern resolution attainable with a given resist is determined by the resist contrast (γ). For negative resist, it is defined as

$$\gamma_{0.5} = \frac{0.5}{\log \frac{D_g^{0.5}}{D_g^1}} \quad \text{or} \quad \gamma_{0.7} = \frac{0.7}{\log \frac{D_g^{0.7}}{D_g^1}}$$

the contrast appears to be an important requirement for high resolution that is characterized by the minimum of the lines developed in the resist layer (number of lines per millimeter after irradiation and development)

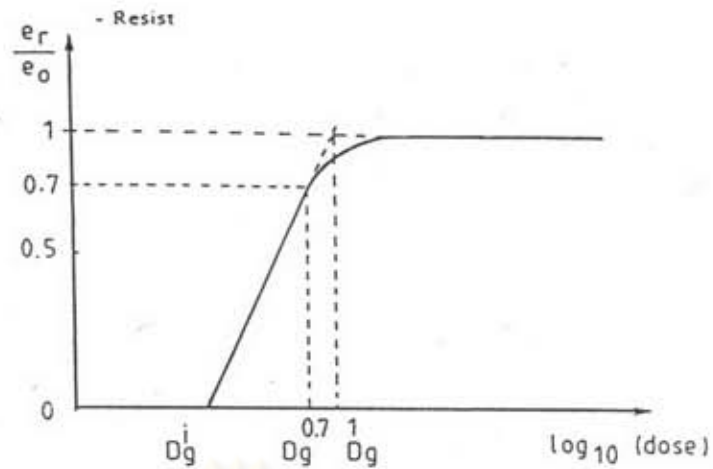


Fig. 2.2 Sensitivity and contrast for negative resist.

2.3.3 Etch resistance

A third characteristic that resists must possess is the resistance to the processes used to transfer the resist image into the inorganic substrate. This is a crucial process step in device manufacture. Common image transfer processes include both wet and plasma etching and ion implantation. Polymer properties, such as adhesion to the wafer surface, glass transition temperature, solubility, resistance to various plasmas, etc., determine the suitability of resists for various application.

For photosensitive negative resists, they are polymers which are sensitive to light. The new lithographic processes that integrated-circuit makers are looking at include those based on deep-ultraviolet (less than 300 nm), electron-beam, and X-ray irradiation. Until now, the near - uv region has been satisfactory, such as at 436-, 404-, and 366- nm lines of mercury sources. So the resists used have to be sensitive.

2.4 Suitable Conditions for a Good Resist

2.4.1 Spin coating

It is generally accepted that a thickness of the resist layers between 0.6 and $1.5 \mu\text{m}$ shows a few defects. But a resolution of $0.1 \mu\text{m}$ needs a lower thickness. Actually, the sensitivity is dependent on the molecular weight of the polymers. The higher the molecular weight, the better the sensitivity will be. However a compromise has to be found because a high molecular weight induces a too high viscosity prejudicial to the formation of a film of good quality and uniform thickness. (Figure 2.3)

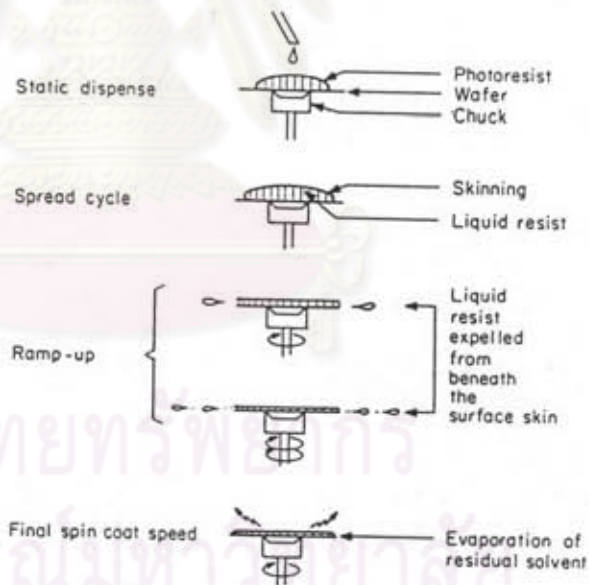


Fig.2.3 Spin coating environmental and physical factors that affect final film thickness on the wafer.

2.4.2 Adhesion

The resist should have adequate adhesion during spin coating, development and wet etching of SiO_2 . Usually it seems to be beneficial to add an adhesion promoter.

Poor adhesion leads to marked undercutting of the patterns and loss of resolution. If wet etching is replaced by a dry etching technique, less adhesion is required to maintain perfect image transfer.

2.4.3 Sensitivity

A high sensitivity allows a reduction in the time of irradiation. The following values have to be reached, in order to reduce the time of irradiation below one minute

- for electron-beam irradiation : $10^{-6} - 10^{-7}$ C/cm² under 20 keV
- for X-ray irradiation : 2-7 mJ/cm²
- for UV and visible : 5-20 mJ/cm²

2.4.4 Contrast

Resolution is partly linked to the contrast of the resist. A value at least equal to 2 seems necessary to obtain a 0.5 μm resolution.

2.4.5 Resolution

The resolution is characterized by the minimum width of the lines developed in the resist layer. It is measured by the number of lines per millimeter after irradiation and development.

The parameters which affect the contrast and also the resolution are :

- swelling during the development
- diffusion in the case of an electron-beam irradiation

during an X-ray exposure ($\lambda < 50 \text{ \AA}$) the diffraction and diffusion phenomena may be neglected and the resolution may be better. The present aim is to obtain features as fine as $0.1 \mu\text{m}$. The swelling of an organic polymer in a solvent proceeds in two steps :

- the swelling of the polymer when the solvent diffuse in the matrix
- the transformation of swollen polymer into a real solution. The importance of the swelling is determined by : the molecular weight, the structure of the polymer, the glass transition temperature and the solvent.

2.4.6 Etch resistance

The requirements on the polymer depended on whether wet or dry etching processes are to be employed. The most common method by far is wet chemical etching. Buffered hydrofluoric acid solution are used, for example, to etch SiO_2 . Since lateral penetration of the chemical etchant can be significant for thick substrate films, new more unidirectional etching methods have been developed, including ion milling plasma etching, and sputter etching. Each of these methods places its own requirement on the resist material, and while a material may be a perfectly adequate resist for one etching process, it may be completely unacceptable for another. As will also be shown, high radiation sensitivity, especially in the case of positive resists, is often coupled with low dry etch resistance, due to the fact that upon absorption of both high and low energy particles the same chemical reactions are initiated. Aromatic compounds being only weakly damaged by radiation exhibit high dry etch resistance.

2.4.7 Other properties

The synthesis of the polymers must be easy and reproducible and the monomers must have low toxicity.

2.5 Energy Exposure Used for Negative Resists

2.5.1 Electron-beam resists

when a negative resist is irradiated by an electron-beam, crosslinking occurs causing the formation of a three-dimensional network, which is insoluble in the solvent for the original linear chain polymer. The minimum incident dose D_g^1 (C/cm^2) required to produce this network is given by the relation.

$$D_g^i = \frac{50 q \rho z N}{EG(x) \bar{M}_w}$$

in which :

- q : charge on electron
- ρ : density of the polymer
- z : thickness of the film
- N : Avogadro's number
- E : energy absorbed in the resist. layer per incident electron
- \bar{M}_w : weight average molecular weight of the polymer
- G(x) : number of crosslinks produced per 100 eV of absorbed

Thus, a resist having a high molecular weight and $G(x)$ will need energy, a lower incident dose and therefore will be more sensitive. The contrast of a negative resist will be better described by the two following parameters:

- 1) The molecular weight distribution
- 2) The effect of scission probability.

The rate of gel formation decreases as the molecular weight distribution widens. This will induce a decrease of the contrast. Therefore, a high contrast demands a narrow molecular weight distribution.

Actually, both crosslinking and degradation occur simultaneously. A polymer behaves as a negative resist providing the ratio of crosslinking to degradation is greater than a critical value. The effect of a significant scission probability will reduce the amount of gel formed and decrease the contrast. Compared to the number of studies made in the field of positive resists, much less has been done in the field of negative resists. The sensitivities of a crosslinkable polymer is enhanced by the introduction of chemical groups sensitive to crosslinking upon an electron-beam irradiation. These groups are the following :

- double bond : $-CH=CH_2$
- epoxide group : $-CH-O-CH_2$
- epithio group : $-CH-S-CH_2$
- carbon-halogen bond : $-C-Cl$, $-C-Br$

2.5.2 X-ray resists

The use of X - ray ($\lambda < 50 \text{ \AA}$) allows a decrease in the diffusion and diffraction phenomena. Indeed these phenomena limit the resolution in photo - and electron microlithography. It is generally supposed that organic polymers (those containing carbon, hydrogen, oxygen and/or nitrogen) have the same sensitivity (G) to X - ray and electron irradiation. A correlation between their sensitivities has been made evident by Thompson [35]. This is not surprising since the fundamental mechanism resulting from the absorption of X-rays by organic materials is the ejection of electron whose energy has values between 1 and 3 KeV depending on the wavelength of the X-rays. These electrons induce in the polymer, identical reactions to the ones observed where irradiating with an electron-beam. The same chemical intermediates are obtained:

- secondary electrons
- cations, anions
- neutral radicals
- electronically excited species

Under these conditions, it seems obvious that the resists used for electron-beam irradiation are suitable for X-ray irradiation. When a negative resist is irradiated by an X-ray beam, crosslinking occurs causing the formation of a three-dimensional network, which is insoluble in the solvent for the original linear chain polymer. The minimum absorbed dose (δ_{abs})_i required to produce this network is given by the relation :

$$(\delta_{\text{abs}})_i = \frac{50 \rho N}{G(X) \bar{M}_w}$$

where ρ : The density of the polymer

$G(x)$: number of crosslinks produced per 100 eV of absorbed energy

N : Avogadro's number

\bar{M}_w : Weight average molecular weight of the polymer.

Spear and Smith have linked the incident irradiation dose ΦT_{irrad} to σ_{abs} , the minimum incident dose ΦT_{irrad} or D_g^i is given by the relation :

$$D_g^i = \frac{50 N}{G(x) \bar{M}_w \left(\frac{\mu}{\rho} \right)}$$

Where μ/ρ : mass absorption coefficient at a given wavelength. Thus, a resist having a high molecular weight and $G(X)$ will need a lower incident dose and therefore will be more sensitive. Moreover, as for electron-beam resist, high contrast demands a narrow molecular weight distribution.

The techniques of X-ray lithography have been less extensively studied than those of photolithography or electron-beam lithography, but many advantages that can be derived from this process make it a very promising field of research.

2.5.3 Photoresists

Negative photoresists were used to make images as early as 1826 when camera images were made by exposing Syrian asphalt coated on a metal plate. Light caused the resin to crosslink and harden, and solvent dissolution of the uncrosslinked, unexposed polymer produced a negative image, which

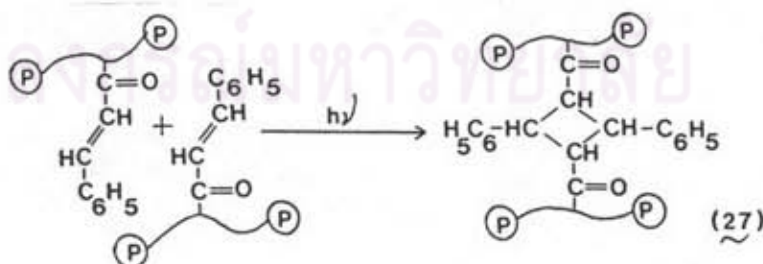
could be etched into the metal substrate. This technology was refined for making deep-etched printing masters and printed circuit boards. The physical chemistry of crosslinking reactions is expressed by

$$D_g^i = \frac{z \rho}{A \bar{M}_w \Phi}$$

where : D (g) is the gel dose exposure as the amount of energy needed to produce a critical crosslink density.

- Z is the coating thickness
- ρ is the coating density
- A is the useful absorbance
- \bar{M}_w is the weight-average molecular weight.
- Φ is the quantum yield

The crosslinking reaction may be a selective dimerization, as seen for cinnamate, or a nonselective reaction such as the reaction of a bisazide-derived nitrene with an olefin containing polymer. Cinnamate esters undergo a 2+2 photodimerization to form truxinate or truxillate (27) esters when exposed to appropriate radiation as following.



The dimerization of cinnamate esters attached to separate polymer chains crosslinks the two chains. Later dimerizations create a net work that can not be dissolved by developing solvent. Some 2+2 photoadditions of small bifunctional monomers are reversible by exposure to shorter wavelengths.