

## Chapter I



### Introduction and Theory

#### 1.1 General

Astonishing progress has been made in very large scale integrated (VLSI) electronic devices in the past decade. These advances are placing increasing demands on microlithography, the technology used to generate the high resolution circuit elements characteristic of today's integrated circuits. In 1976, state-of-the-art devices contained a few thousand transistors with minimum features of 5-6  $\mu\text{m}$ . In the comparison, today's devices contain over 1 million transistors and minimum features of 0.9  $\mu\text{m}$ . Within the next 10-15 years, some new form of lithography will be required with a capability of routinely producing features of  $< 5 \mu\text{m}$ . The alternatives to conventional photolithography are short-wavelength photolithography, scanning electron beam lithography, X-ray lithography, and scanning ion beam lithography. No matter which of those technologies become dominant, new resists and processes will be required. In addition, the necessity to accommodate the effect of topographical features on the wafer surface that is exacerbated by the continuous decrease in feature size will demand some form of "multilevel" scheme. In the simplest multilevel scheme, resist is required to function as both a radiation-sensitive imaging material and a pattern-transfer mask for the reactive ion etching of the thick planarizing layer.



Astonishing progress has been made in microelectronics, especially in the technology of lithography used to generate the high resolution circuit elements characteristic of today's integrated circuits. In 1976 the state-of-the-art dynamic random access memory (DRAM) device was capable of storing 4000 bits of data and had 5-6  $\mu\text{m}$  minimum features. These devices were patterned by photolithography using either contact printing or, the relatively new, 1:1 projection printing. Today, devices with one million bits of storage capacity are commercially available with minimum features of 0.9  $\mu\text{m}$ . Surprisingly, photolithography is still the technology used to fabricate microelectronic chips. Step-and-repeat 5x or 10x reduction cameras or highly sophisticated 1:1 projection printers are the dominant printing tools. There is perhaps no better example than lithography to illustrate the uncertainty associated with predicting technological direction and change. In 1976, it was generally believed that photolithography would not be able to produce features smaller than ca. 1.5-2.0  $\mu\text{m}$  with high chip yields in a production environment. The current belief is that conventional photolithography will be able to print features as small as 0.5  $\mu\text{m}$  and will remain the dominant technology well into the first half of the 1990s. The same basic positive photoresist based on a diazonaphthoquinone photoactive compound and novolac resin that has been in pervasive use since the mid-1970s will likely still be the resist of choice. The cost of introducing a new technology and the cost associated with development and implementation of new hardware and resist materials are strong driving forces pushing photolithography to its absolute resolution limit and extending its commercial viability.



The technological alternatives to conventional photolithography are largely the same as they were a decade ago, i.e., short-wavelength photolithography, scanning electron beam lithography, X-ray lithography, and scanning ion beam lithography. It is not intended of this thesis to discuss the various lithographic technologies in detail; however, each will be briefly summarised so that the resist can be better appreciated. No matter which technology becomes dominant after photolithography has reached its limit, new resists and processes will be required, necessitating enormous investment in research and process development. The introduction of new resist materials and processes will also require a considerable lead time, probably in excess 3-6 years, to bring them to the performance level currently realized by conventional positive photoresists.

A modern integrated circuit is a complex three-dimensional structure of alternating, patterned layers of conductors, dielectrics, and semiconductor films. This structure is fabricated on an ultrahigh-purity wafer substrate of semiconducting material such as silicon. The performance of the device is to a large degree governed by the size of the individual elements. As a general rule, the smaller elements, the higher device performance. The device structure is produced by a series of steps used to precisely pattern each layer. The patterns are formed by lithographic process that consists of two steps: (1) delineation of the patterns in a radiation sensitive thin-polymer film, and (2) transfer of the pattern with an appropriate etching technique. A schematic representation of the lithographic process is shown in Figure 1.1. Each types of resist will be



discussed in detail in the latter.

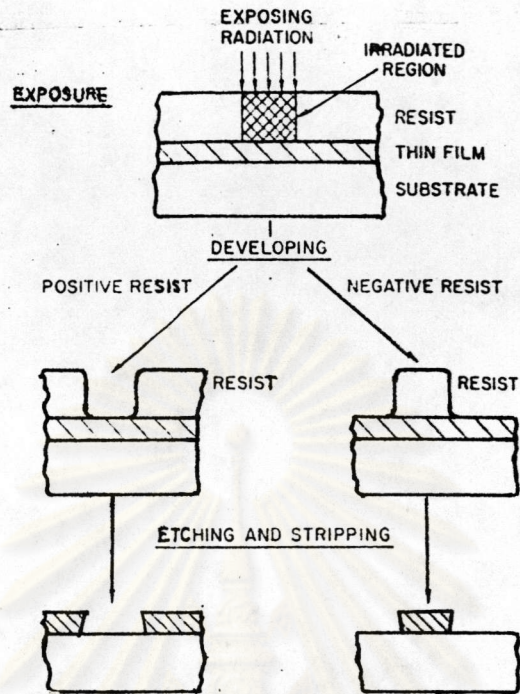


Figure 1.1 Scheme of the lithographic process.

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## 1.2 Microlithography

Figure 1.2 illustrates a typical procedure employed in the production of integrated circuits.

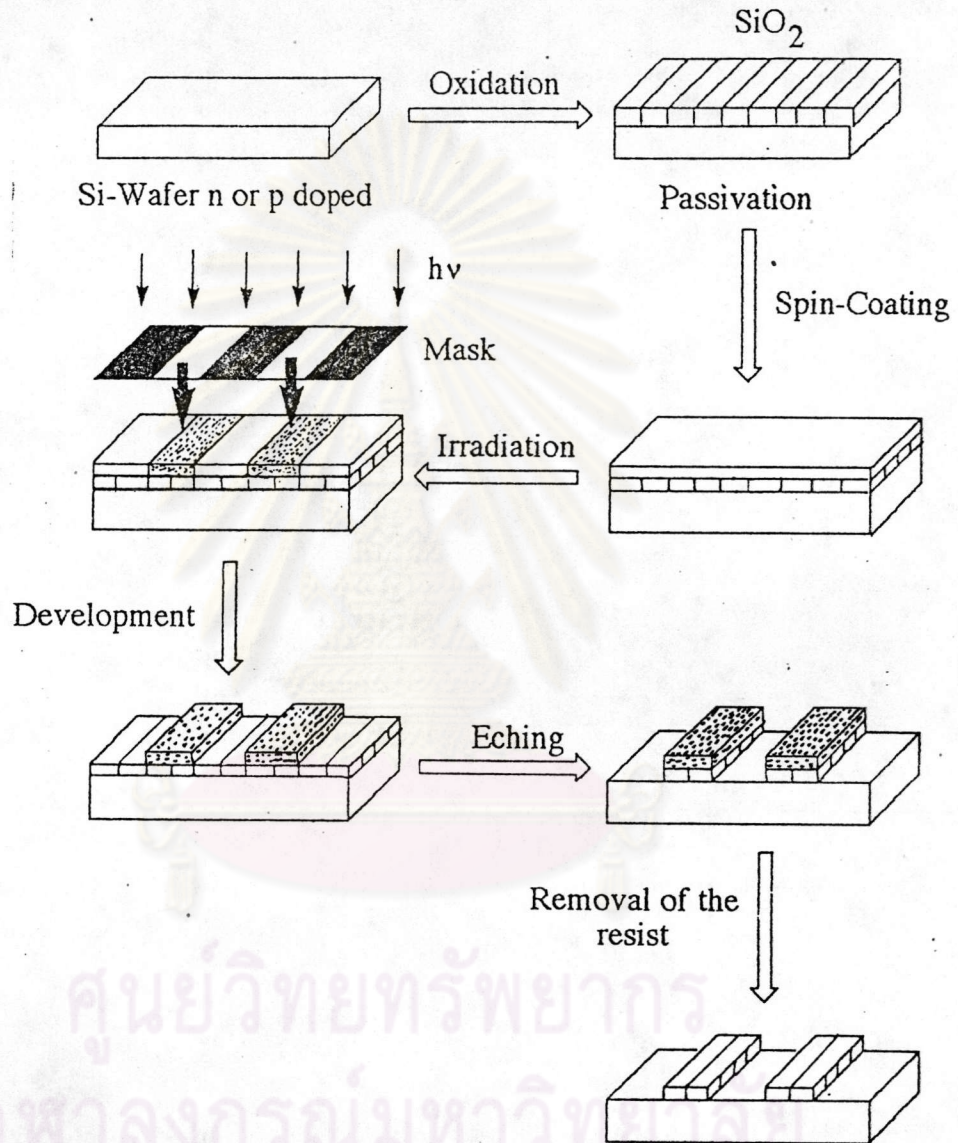


Figure 1.2 Photolithography using positive resist.

### 1.2.1 Passivation

In order to protect the surface of silicon and to dope it only at the desired positions, the silicon wafer is covered



with a thin layer of  $\text{SiO}_2$  ( $0.1 \mu\text{m}$ ). This oxide is impermeable to boron atoms and to impurities like oxygen. Silicon dioxide can be stripped by hydrofluoric acid (silicon itself is not attacked). Therefore, to strip selectively the oxide layer and to obtain the design of a circuit, given positions have to be protected.

#### 1.2.2 Coating

The passivated silicon surface is spin-coated with a polymer of about  $1 \mu\text{m}$  thickness which is suitable for high resolution. The step is followed by an annealing to remove the solvent and favor the adhesion of the resist on the substrate. To obtain a uniform thickness, the resist and wafer have to be clean.

#### 1.2.3 Irradiation

Subsequently, the polymer film is irradiated using a mask. The irradiation induces a modification of the polymer linked to the energy absorbed by it.

#### 1.2.4 Development

Areas of the resist layer which are exposed to light become detected in the subsequent development process. Depending on whether the irradiated or the non-irradiated regions of the polymer remain on the substrate after development, the polymer are classified as negative or positive working.



### 1.2.5 Removal of SiO<sub>2</sub>

In the non-protected zones, the silicon dioxide layer is etched away by hydrofluoric acid or by plasma.

### 1.2.6 Removal of the resist

The resist is removed and the substrate is only partially covered by the silicon dioxide layer. "Windows" have been opened which make the silicon substrate accessible for further treatment such as doping.

The manufacture of a transistor needs at least four lithographic steps. But often, up to twelve lithographic steps are necessary for more sophisticated circuits. Therefore, the precision of superposition is of great importance. The resists used must have very particular properties because the sharpness of the designs and these sizes will be dependent on the quality of these resists and on the radiation used.

## 1.3 Types of Microlithography

### 1.3.1 Short-Wavelength Photolithography

The major advances in this technology in the past decade are improved quartz lenses and high-output light sources for projection cameras. Several step-and-repeat 5x and 10x reduction systems that use excimer laser sources have been designed and/or built. Systems using refractive optics require a very narrow bandwidth light sources ( $<0.001 \text{ \AA}$ ) since it is



not practical to correct for chromatic aberrations in quartz lenses. Laser sources provide narrow bandwidths with enough intensity to accommodate resists with 50-150  $\text{mJ cm}^{-2}$  sensitivities, enabling a rather wide choice of resist chemistries. Some work is also being done on 1:1 refractive projection systems using conventional, wide bandwidth Hg arc sources in the 200 - 260 nm region. However, since the intensity of these sources is less than that of laser sources, more sensitive resists ( $<20 \text{ mJ cm}^{-2}$ ) will be required for high throughput.

### 1.3.2 X-ray Lithography

Early work in X-ray lithography followed the general strategy of conventional 1:1 optical projectors and used electron beam bombardment X-ray sources. The power from such sources is limited by thermal considerations, and in order to minimize the penumbral shadowing, the distance between the sources and mask-wafer combination must be relatively large, making the incident reflux on the wafer small. These two limitations necessitate resists with sensitivities of  $<10 \text{ mJ cm}^{-2}$ . This extremely high sensitivity requirement substantially limits the chemistries available for resist design, and only negative materials have been repeated with satisfactory sensitivity. Although able to demonstrate submicron resolution, these negative resists are limited to features of at least  $0.5\mu\text{m}$  or larger. More recent work in X-ray lithography have been directed towards step-and-repeat systems that utilize high-intensity synchrotron radiation sources. Storage rings capable of producing X-ray in the wavelength region of interest are now



smaller and cheaper than those available 10 years ago, and when compared to other lithographic hardware options with submicron capabilities, they are within economic reach. In addition, the brightness of synchrotron sources is sufficiently high so as to permit the use of resists with  $50\text{-}200\text{ mJ cm}^{-2}$  sensitivities, thus allowing a wider choice of chemistry to design resists having resolution and submicron process robustness.

### 1.3.3 Electron Beam Lithography

This technology is the most mature of all of the alternatives to photolithography. Electron beam lithography has been investigated at many industrial laboratories for well over a decade. This form of lithography utilizes a focused beam of electrons that is scanned under computer control across the resist - coated substrate. Early system operated at a modulation rate of 10-40 MHz and utilized a Gaussian, round beam,  $0.5\text{-}2.0\text{ }\mu\text{m}$  in diameter. This machine requires approximately 1 hour to write a pattern into a 4-inches diameter wafer utilizing a tungsten emitter as a source of electrons and a resist of sensitivity  $1\text{-}3\text{ }\mu\text{Ccm}^{-2}$ . Newer systems employing either  $\text{LaB}_6$  or field emission electron sources, shaped beams, and modulation frequencies of  $> 400\text{ MHz}$  have a capability of producing 10-30 wafers per hour and require resists with sensitivities of  $1\text{-}5\text{ }\mu\text{C cm}^{-2}$  at 20 kV. Electron beam lithography offers high resolution ( $< 0.1\text{ }\mu\text{m}$ ) and extraordinary registration accuracy, which is important when writing VLSI patterns directly. The major disadvantages of electron beam lithography are the high cost, low throughput, and physical size of the hardware.



#### 1.3.4 Scanning Ion Beam Lithography

This is the newest technology and is similar to scanning electron beam lithography in that it utilizes a finely focused beam of ions that are scanned under computer control onto the wafer. The ions either may be directly implanted into the substrate or used to expose the resist. Ion beam lithography is many years away from industrial use as a lithographic exposure method. Interest continues to be shown, however, since it is devoid of proximity effects. In addition, it is capable of implanting a wide range of atoms directly into a semiconductor material, thus eliminating the need for a resist.

In above mention the resist requirements of the different lithographic options, it is clear that new resists should be sensitive to the exposure radiation and are compatible with advanced processing requirements. Further, the necessity to accommodate substrate topography will likely demand some form of "multilevel" resist technology. This technology utilizes two or more discrete layers, each of which imparts a specific function. Considerable work is under way to develop suitable multilevel resists and processes. In particular, there have been numerous reports on metal containing polymers suitable for "bilevel" applications, which are the simplest multilevel schemes. Since all the alternatives to conventional wavelength photolithography employ rather high energy radiation, the resists are very similar, with a given chemistry finding application to most new lithographic technologies.



## 1.4 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 involve 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.

## 1.5 Chemistry of Resists

There are four types of resist chemistry, which are single-level resist chemistry, non-conventional resist chemistry, multilevel resist chemistry and gas-phase functionalization.

### 1.5.1 Single-Level Resist Chemistry

The resists are divided into two classes depending on their behavior under irradiation.

#### 1.5.1.1 Negative Resists

Polymers that become less soluble after exposure to irradiation are potential candidates for use as negative resists.



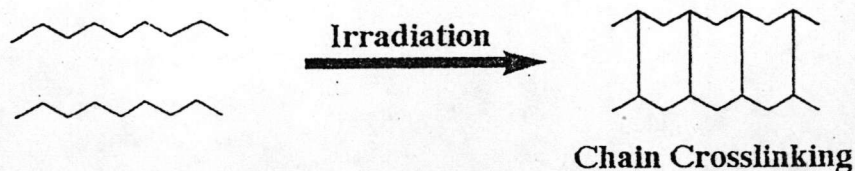


Figure 1.3 Chemical reaction occurring during irradiation of negative resist.

Figure 1.1 exhibited that the irradiated regions of the negative resist remain after development in a suitable solvent. Most negative-acting resists become insoluble through some type of irradiation-induced cross-linking reaction as shown in Figure 1.3. The most common negative resists are soluble in organic solvents, which, in turn, are used as developers. Since polymer dissolution occurs first by swelling of the matrix followed by chain disentanglement, it is critical to select a developer that minimizes swelling of the cross-linked regions, thereby facilitating high resolution. The ideal developer should be a kinetically good, but thermodynamically poor solvent for the resist. This ensures that developer will dissolve the unexposed regions of the film while minimizing the swelling volume of the irradiated regions in a given development time.

The sensitivity of negative resists is generally higher than that of positive systems since fewer events per chain are required to achieve differential solubility. In addition, in some negative systems, a chain reaction occurs yielding even higher sensitivities. Negative resists are



generally characterized by good adhesion and plasma-etching resistance.

Single-component resist systems have found broad application as resist for the higher energy lithographic techniques such as electron beam and X-ray lithography and to some extent deep-UV lithography. Three classes of cross-linking polymers have been reported as useful negative resist (such as epoxy-(glycidyl-), vinyl-, and halogen-containing materials (Figure 1.4)), and the radiation sensitive unit is an integral parts of the polymer. Cross-linking of the radiation-sensitive moieties frequently occurs via chain mechanisms that lead to

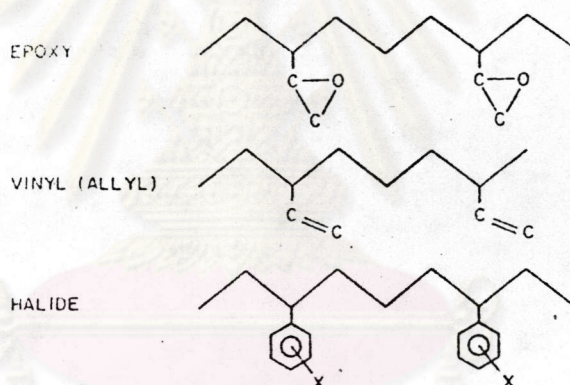


Figure 1.4 Radiation-sensitive groups use in negative, cross-linking resist systems.

high cross-linking efficiency and high resist sensitivity.

Polymer molecular properties such as molecular weight and molecular weight distribution have a profound effect on the lithographic behavior of these single-component, negative resists. As exemplified by studies on the electron beam sensitivity of poly(chloromethylstyrene) (PCMS) resist, an



increase in polymer molecular weight by a factor of 10 results in about a tenfold increase resist sensitivity (Figure 1.5) [1,2]. Though resist contrast remains unaffected, resist resolution decreases with increasing molecular weight due to

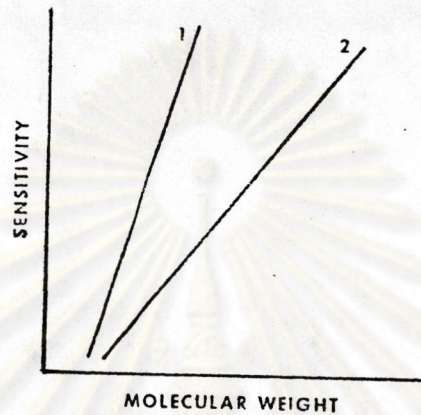


Figure 1.5 Effect of polymer molecular weight on resist sensitivity.

increased swelling during development. Alternatively, resist contrast is affected by the molecular weight distribution. Decreasing the dispersity leads to increased contrast (Figure 1.6) and improved resolution.



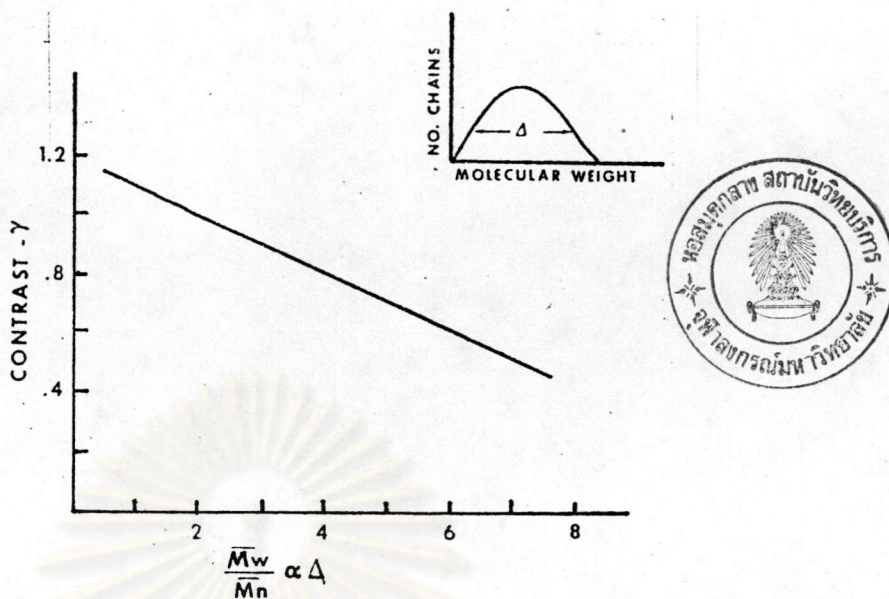


Figure 1.6 Effect of polymer molecular weight dispersity on resist contrast.

It is well-known that unsaturated carbon-carbon bonds typically undergo radiation-induced polymerization or cross-linking reaction, and this chemistry has been extensively utilized in the design of negative radiation-sensitive resists. One example of such a material is poly(allyl methacrylate-co-2-hydroxyethyl methacrylate). Cross-linking occurs through the unsaturated side chain, and high electron beam sensitivity has been reported. The chain mechanism of this reaction, however, results in post-irradiation reaction that leads to low resist contrast and resolution. Due to its aliphatic nature, this material exhibits marginal dry etching resistance. Poly(diallyl o-phthalate) (PDOP) is another example of a vinyl-containing resist. However, this material has not been used extensively due to its poor contrast and rather poor shelf life.



The epoxy moiety is well-known to undergo efficient cross-linking reaction under high energy radiation via a chain mechanism whereby radiation generates a reactive oxygen species that readily reacts with the epoxy moiety on a neighboring polymer chain, resulting in formation of a cross-link and corresponding propagating radical. This chain reaction mechanism leads to highly sensitive resists with high cross-linking efficiencies. However in a vacuum, a post-exposure curing reaction similar to that observed with the vinyl-substituted systems is also observed. In the vacuum environment of an electron beam exposure system such reaction results in a growth of feature size that is dependent upon the time the material remains in vacuo after exposure. Since this reaction is diffusion controlled, the extent of reaction is also dependent on the glass transition temperature ( $T_g$ ) of the resist and may be minimized by using resists with high  $T_g$ 's.

The incorporation of halogen groups into acrylate- and styrene-based polymer has been found to facilitate radiation-induced cross-linking with high cross-linking efficiency. The mechanism involves radiation induced cleavage of the carbon - halogen bond to generate a radical that may undergo rearrangement, abstraction, or recombination reaction leading to the formation of a cross-linked network. The mechanism has been extensively studied by Tabata and Tagana[48]. The localized nature of the cross-linking reaction in these polymers, as opposed to the chain propagation mechanism found in the epoxy- and vinyl-containing resists, eliminates the curing effects common to the vinyl and epoxy materials.



### 1.5.1.2 Positive Resists

Materials that exhibit enhanced solubility after exposure to the radiation are defined as positive resists. The mechanism of positive resist action in most of these materials involves either chain scission or a polarity change. Positive photoresists that operate on the polarity change principle have been widely used for the fabrication of VLSI devices because of their high resolution and excellent dry-etching resistance. Ordinarily the chain scission mechanism is only operable at photon energies below 300 nm, where the energy is sufficient to break main-chain bonds. The chemistry associated with positive resists is described below.

#### 1.5.1.2.1 Chain Scission Resists

The "classic" positive resist that undergoes chain scission upon radiation is Poly(methyl methacrylate) (PMMA). PMMA was first reported as an electron

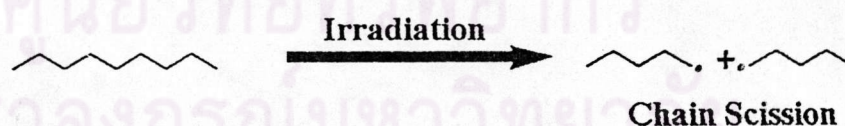


Figure 1.7 Chemical reaction occurring during radiation of positive resist.

beam resist by Hatzakis [4], and it is still considered to be one of the highest resolution materials available. The



accepted mechanism involves radiation-induced cleavage of the polymer backbone, resulting in reduction in polymer molecular weight and enhanced solubility of the exposed regions (Figure 8). Choice of an appropriate developer such as methyl isobutyl ketone allows selective removal of the radiated areas with minimum swelling of the remaining resist.

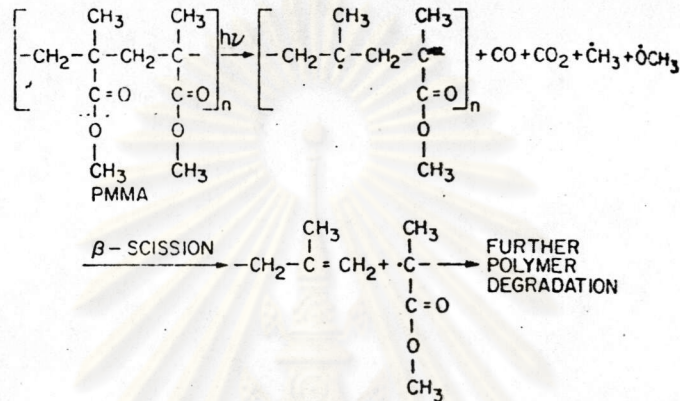


Figure 1.8 Mechanism of PMMA degradation.

The other class of "chain scission" positive resist is the poly(olefin sulfones). These polymers are alternating copolymers of an olefin and sulfur dioxide having the general structure shown in Figure 1.9. The relatively weak C-S bond is readily cleaved upon irradiation, and several sensitive resists have been developed based on the chemistry. One of these



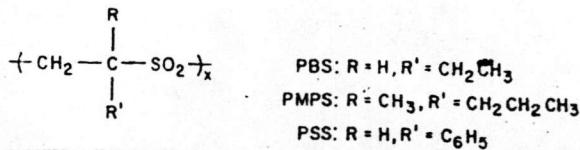


Figure 1.9 Structure of the poly(olefin sulfone) resist materials.

materials, poly(1-butene sulfone) (PBS) have been made commercially available for mask making.

#### 1.5.1.2.2 Solution Inhibition Resists

This class of resists operates via a dissolution inhibition mechanism and is typically composed of two components. The major component in most resists of this type is an alkali-soluble resin that is rendered insoluble in aqueous alkali solutions through incorporation of a hydrophobic, radiation sensitive material. Upon irradiation, the hydrophobic moiety may be either removed or converted to an alkali-soluble species, allowing selective removal of the irradiated portions of the resist by an alkali-developer.

The best known dissolution inhibition resist is "conventional positive photoresist", a photosensitive material that uses a novolac (phenol-formaldehyde) polymer with a diazonaphthoquinone photoactive dissolution inhibitor (PAC). The novolac matrix resin is a condensation polymer of a substituted phenol (often cresol) and formaldehyde. These resins are soluble in organic solvents, facilitating spin coating of uniform, high quality, glassy films. In addition, they are



soluble in basic solution such as aqueous sodium hydroxide (NaOH) or tetramethylammonium hydroxide (TMAH). The novolac is rendered insoluble in aqueous base through the addition of 10-20 wt % of the PAC. Upon irradiation, the diazoquinone undergoes a Wolff rearrangement followed by hydrolysis to generate a base-soluble indenecarboxylic acid (Figure 1.10).

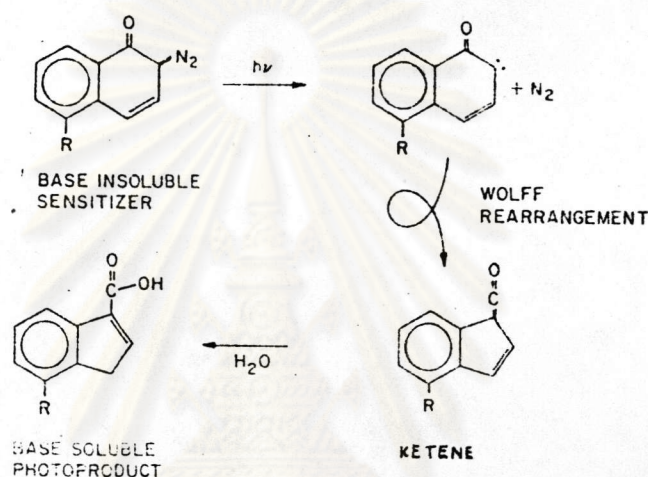


Figure 1.10 Photochemically induced radiation of a typical substituted diazonaphthoquinone dissolution inhibitor.

The exposed regions of the film may then be removed by treatment with aqueous base.

While the basic components of all conventional photoresists are the same, the precise performance characteristics depend on the substitution pattern on the novolac resin and/or PAC.



### 1.5.2 Non-conventional Resist Chemistry

Through creative chemistry and resist processing, schemes have been developed that produce positive-tone images in positive photoresist. One embodiment of these "image reversal" processes requires addition of small amount of base additives such as monazoline, imidazole, or triethanolamine to diazoquinone-novolac resists. The doped resist is exposed, and finally developed in aqueous base to generate high-quality negative-tone images. The chemistry and processes associated with this system are shown in Figure 1.11[5]. Thermally induced, base-catalyzed decarboxylation of the

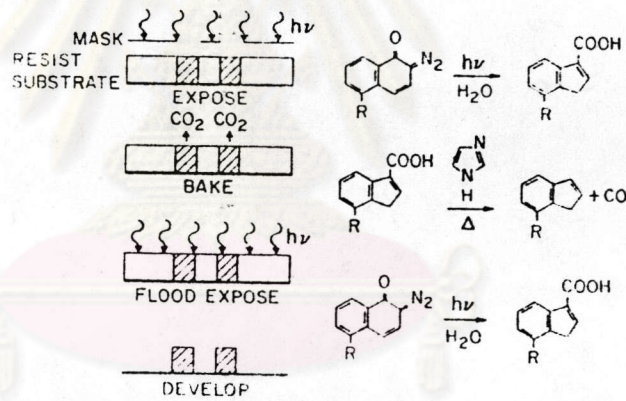


Figure 1.11 Image reversal process and related chemistry based on a conventional positive photoresist and monoazoline.

indenecarboxylic acid destroyed the aqueous base solubility of the exposed resist. Subsequent flood exposure renders the previously masked regions soluble in aqueous base, allowing generation of negative-tone patterns. It is not always necessary to add the base to resist prior to exposure.



Alternating image reversal processes have been developed involving treatment of exposed photoresist with a gaseous amine in a vacuum environment.

As device features move into the submicron regime requiring development of advanced processing techniques and introduction of new lithographic technologies, resist materials with improved etching resistance, resolution, and sensitivity will be required. One approach to improve sensitivity involves the concept of chemical modification. Aryldiazonium, diaryliodonium, and triarylsulfonium metal halides, for example, are dissociated upon irradiation to produce an acid that can, in turn, catalyze a variety of bond-forming or bond-breaking reactions in a surrounding matrix. The quantum efficiency for such reaction is thus effectively much higher than the quantum yield for initial onium salt dissociation.

This principle has been used to design a number of negative resists based on acid catalyzed cationic polymerization of appropriate monomers. However, such materials generally exhibit poor contrast and resolution. A notable exception is a three-component resist developed by Feely et al consisting of a blend of novolac resin, melamine cross-linking agent, and acid generator. Irradiation of this three-component resist generates an acid catalyst that induces formation of a cross-linked network between the novolac matrix resin and amine additive.



### 1.5.3 Multilevel Resist Chemistry

The increasing complexity and miniaturization of the integrated circuit technology are pushing conventional single-layer resist processes to their limit. The demand for improved resolution requires imaging features with increasingly higher aspect ratios and smaller line-width variation over steep-substrate topography. The decrease in feature size can lead to other problems associated with the particular lithographic technique employed. For instance, in photolithography, feature size can be affected by standing wave-effects and reflections from the substrate surface, which limit the resolution attained with optical techniques. A number of schemes have been proposed to address these problems, including the use of polymeric planarizing layers, antireflection coatings, and contrast enhancement materials. These techniques can be conveniently divided into two broad categories. The first one includes those systems employing a separated planarizing layer that may be developed with wet or dry (RIE) techniques. The second category uses thin organic films that have precisely designed light absorption characteristics. Antireflective coatings are designed to be highly absorbing at the exposure wavelength and are applied between the substrate and the resist. Contrast enhancement materials are generally applied to the surface of the resist and through photochemical bleaching during exposure, in order to improve the quality of the aerial light image.

The available planarization processes are summarised in Figure 1.12. Most of these approaches are based on spin coating thickness (1-2  $\mu\text{m}$ ) of films of thermoplastic materials such as



PMMA, polystyrene, polyimide, or novolac resins (usually in conventional photoresist formulations) onto the surface of the wafer. There are two types of planarizing that are important for lithography : (1) local planarization, which is the ability to planarize closely spaced features, and (2) global planarization, which is the extent to which a large area (wafer) with both closely spaced and isolated features are planarized.

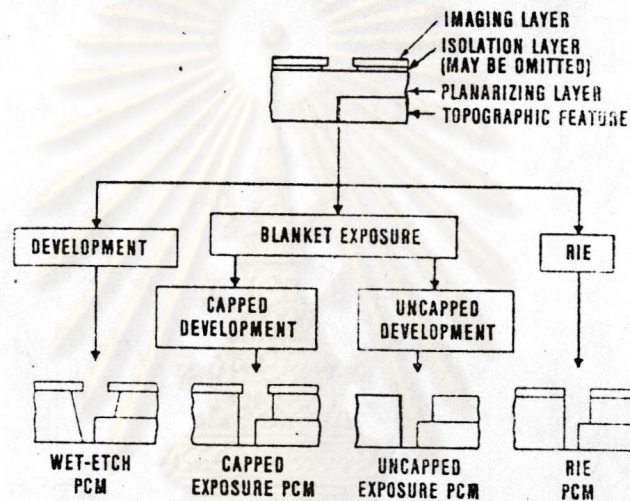


Figure 1.12 Process sequence for several multilevel resist schemes.

Local planarization is easily achieved by spin coating a polymer and baking; however, global planarization is almost never achieved by this process. Global planarization is important to produce a perfectly level surface that will minimize depth-of-focus problems associated with variation in film thickness resulting from topographic features on the wafer surface, induced from previous process. Important characteristics for a planarizing polymer system induce dry-etching resistance, solution viscosity, flow characteristic at





both room and elevated temperature, thermal stability, and ease of final stripping.

A novel multilevel technique, known as contrast enhancement (CEL), addresses the problem associated with a reduction in the contrast of the aerial image that occurs as the resolution limit of an optical imaging system is approached. As line width decreases, the contrast between the projected clear and opaque regions of a mask deteriorates as does the ability of the resist to resolve those features. The CEL technique improves contrast of the aerial image in the resist, thereby leading to a sharper latent image and improves resolution. The process utilizes photobleachable materials that are opaque before exposure but bleach (i.e., become transparent) on exposure to radiation. The materials are coated directly onto the surface of the resist. The dynamics of the bleaching process are such that the transmitted image is of much higher contrast than the incident aerial image, thereby improving the resist ability to discriminate mask features. The optical density of CEL films should be greater than 2 for thickness less than  $0.5 \mu\text{m}$ .

The first CEL systems described by Griffing and West [6] consisted of an organic dye dispersed in an inert polymer film. The material is spin cast onto the surface of the resist and subsequently removed following exposure but prior to resist development. The chemistry of this system is based on the photoisomerization of an aromatic dye to an oxaziridine. Several applications have been presented to demonstrate the advantages of this two-level CEL process over conventional



single-level lithography.

A single-component CEL system based on the photo-bleaching of polysilanes was reported by Hofer et al [7]. This mid-UV material takes advantage of the shift in the absorption maximum of polysilanes to shorter wavelengths upon radiation-induced chain scission.

It is predicted that CEL techniques will extend resolution to feature size as small as  $0.4 / \text{NA}$ , or  $\sim 0.6 \mu\text{m}$  for currently available exposure tools operating at 405 and 436 nm [NA is the numerical aperture of the exposure system]. The currently available materials afford improved resolution, improved yield, and increased process latitude. Further developments to achieve practical wafer-soluble systems plus a better match with the absorption characteristics of the resist would be desirable.

#### 1.5.3.1 Multilevel Resist Processes Employing Reactive Ion Etching Pattern - Transfer Techniques

The contrast enhancement and antireflective coating materials discussed in the previous section both are used in conjunction with the standard wet-developed photoresist process. Multilevel resist processes that utilize a thick planarizing layer differ from the above processes in both purpose and process complexity. The purpose of these techniques is to separate the imaging layer from the process etch mask, and they provide improved imaging characteristics for the



overall lithographic process. There are two generic types of processes used, i.e., liquid-developed and dry developed. The liquid-developed processes will not be covered in this section. The dry-developed processes that use reactive ion etching (RIE) for pattern transfer into the planarizing layer have received considerable attention and use materials with properties that depended on the specific strategy employed. There are two schemes that have been used -trilevel and bilevel- and these are discussed below.

Trilevel processing begins with the planarization of device topography with a thick layer of some organic polymer such as a polyimide or positive photoresist that has been "hard-baked" (baked to induce cross-linking), or otherwise treated, to render it insoluble in most solvents. Next, an intermediate RIE barrier such as silicon dioxide is deposited, and finally the structure is coated with the desired resist material. A pattern is delineated in the top resist (imaging) layer and subsequently transferred into the planarizing layer by dry-etching techniques.

Several variations of this generic process have been reported. The most common intermediate oxygen RIE barrier layer of  $\text{SiO}_2$  may be deposited by sputtering, plasma CVD, or spin coating  $\text{SiO}_2$  organic precursors. The organic precursors are often referred to as spin-on-glasses (SOG). While SOG layers greatly simplify trilevel processing to the elimination of costly vapor phase deposition steps, they are likely to contain a higher number of defects than vapor-deposited films. Proper storage and dispensing techniques can minimize these problems



but they increase the complexity of processing. Alternative intermediate layers include silicon nitride, silicon, germanium, and arsenic sulfide. Antireflection properties can be incorporated either through the use of an inherently highly absorbing polymer as the planarizing layer or by the addition of a dye into the planarizing layer. Alternatively the absorber can be incorporated into the intermediate RIE barrier layer.

While trilevel lithography is a time-consuming process requiring precise control of several processing steps, it improves the resolution capability of conventional resists by separating the imaging function of the resist from the subsequent etch mask function and permits imaging a relatively thin resist film.

Organosilicon polymers are ideal candidates for bilevel lithography. Treatment of organometallic compounds, particularly organosilicon materials, with an oxygen plasma leads to the formation of the corresponding metal oxide. The surface passivation results from the formation of protective coating of  $\text{SiO}_2$  on the polymer surface. There are numerous silicon-containing resist systems for bilevel lithography utilizing RIE pattern transfer. However, there are several problems with silicon-containing polymers that may interfere with their lithographic performance. A decrease in glass transition temperature ( $T_g$ ) often accompanies the incorporation of silicon into a polymer chain and may cause dimensional instability of pattern during processing. In addition, most useful silicon substituents are hydrophobic in nature, which potentially could cause problems for those resist systems that



use aqueous-base developers.

#### 1.5.4 Gas-Phase Functionalization

Gas-phase functionalization is a new technique that is received increased attention as a method for combining the advantages of multilevel processing and solventless development in a single layer. One of the first such systems involved radiation-induced vapor phase grafting of styrene onto a silicon resin that was coated onto a thick planarizing of organic polymer. The grafted styrene pattern that formed on the surface of silicon resin served as a  $\text{CF}_4$  RIE mask for removal of unirradiated silicon resin. Oxygen RIE was then used to transfer the pattern to the substrate. Submicron resolution was demonstrated; however, the dose requirements were high ( $\sim 80 \mu\text{C. cm}^{-2}$ ).

#### 1.5.5 Design and Selection of Resists

The polymer materials that are useful as radiation-sensitive resist film must be carefully designed to meet the specific requirements of each lithographic technology and device process. Although these requirements vary according to the radiation sources and device process requirements, the following are ubiquitous : sensitivity, contrast, etching resistance, shelf life, and purity. These properties can be achieved by careful manipulation of the polymer structure and molecular properties.

Resists function by altering their solubility through



radiation-induced chemicals reaction. These reactions can either increase the solubility (positive mode) or decrease the solubility (negative mode) of the irradiated regions. The terms positive and negative resists reflect this change in solubility.

Sensitivity and contrast of resist are determined by measuring the change in solubility as a function of the radiation dose received by the polymer. Although these two parameters are dependent on many variables such as developer strength, photon or particle energy, and processing conditions, a standard method has been developed that is useful for comparing the sensitivity and contrast of different polymers. A thin film of the resist of known thickness is deposited via spin coating onto a suitable substrate and baked to remove excess solvent (prebaked). The film is exposed to a range of radiation doses and developed in a "standard" developer for the particular resist. The thickness of each exposed area is measured and normalized to the original film thickness. The normalized thickness is plotted as a function of  $\log(\text{dose})$  to provide the "sensitivity curve". From this curve, sensitivity and contrast can readily be determined (Figure 1.13). The contrast



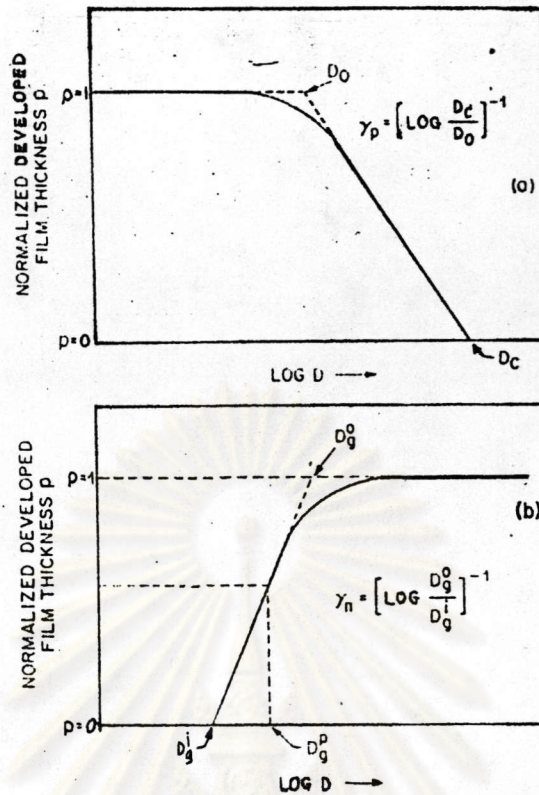


Figure 1.13 Representative contrast curves for  
 (a) positive resists (b) negative resists.

for either a positive or negative resist,  $\gamma_p$  or  $\gamma_n$ , is determined from the slope of the linear portion of the curve shown in Figure 13. The sensitivity for a positive resist is  $D_c$  and for a negative resist it is  $D_g^p$ , where  $D$  is usually 0.5-0.7.

Resolution is another property that is difficult to quantify since many external variables affect the size of the minimum feature that can be resolved. Resolution of a resist is generally the smallest feature that can be perfectly and cleanly resolved over a large area and must be evaluated for dense pattern in a resist thickness that is useful for pattern transfer ( $>0.4 \mu\text{m}$ ).