Chemistry and Lithography

Vol. 2: Chemistry in Lithography

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Contents

Chapter 1
Overview of Chemistry in Lithography

> "I do not feel obliged to believe that the same God who has endowed us with sense, reason, and intellect has intended us to forgo their use."
> Galileo Galilei, Letter to the Grand Duchess Christina

In this volume we explore the chemical basis of pattern formation in advanced lithography, which in all its essential aspects is about chemical transformations that are designed to print a relief image of an object on a flat surface or a surface with topography. The object may be a mask containing patterns of integrated circuit devices; the flat surface may be a silicon wafer coated with photo- or radiation-sensitive resist, which upon exposure and development, or imprinting (as in the case of imprint resists) or directed self-assembly [(DSA) as in the case of block copolymer resists], is transformed into the relief image of the mask. Underlying some of these transformations are distinct chemical reactions that are mediated by electrons. By drawing on fundamental, theoretical, and experimental studies of molecular processes in advanced lithography, we deconstruct lithography into its essential chemical principles and situate its various aspects in specific fields of chemistry. We examine and show how electrons mediate the photo- and radiation chemistry of exposure processes of resists (be they organic, organometallic, polymeric, or inorganic), as well as exposure tool sources (be they mercury arc lamp, laser, electron beam, ion beam, or plasma); colloid chemistry of resist formulation and dissolution (be it for positive-tone or negative-tone development), wafer and mask cleaning processes; electrochemistry of mask absorber corrosion, electrostatic discharge, and electromigration; surface chemistry of wafer and mask priming, along with thin film interfacial effects; materials chemistry of resists, exposure tool optics, and masks; environmental chemistry of the exposure environment (be it water, air, or vacuum) as well as of resist poisoning; process chemistry and modeling of wafer and mask-making lithographic unit operations, including substrate priming, coating, exposure,

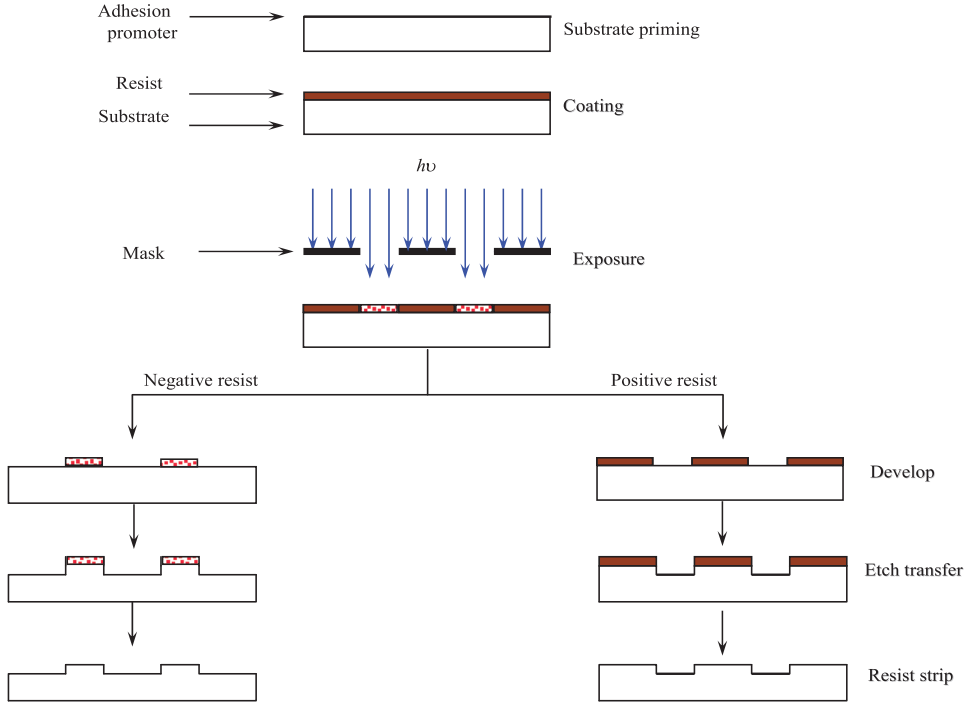


Figure 1.2 The semiconductor lithographic process, showing the unit operations involved.

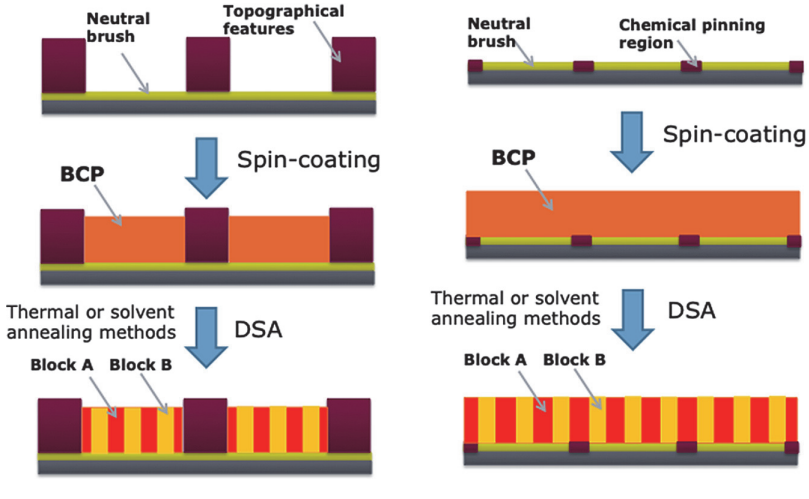


Figure 1.3 Block copolymer self-assembly lithographic processes: (left) graphoepitaxy and (right) chemoepitaxy.

Chapter 2
The Semiconductor Lithographic Process Chemistry

"That's how it is," says Pooh.
A.A. Milne, *Now We Are Six*

2.1 Introduction

Within a semiconductor fabrication facility, popularly called a "fab," the lithography module occupies a very central position, literally in terms of the device fabrication process flow as well as in terms of the importance of the role it plays. Lithography is often considered the most critical step in integrated circuit (IC) fabrication, for it defines the critical dimension—the most difficult dimension to control during fabrication (e.g., polysilicon gate length)—of the device. This explains why the critical dimension (CD) in lithography is often used to define the device technology node or generation.[1] It is estimated that lithography accounts for nearly one-third of the total wafer fabrication cost.[2]

The object of semiconductor lithography is to transfer patterns of ICs drawn on the mask or reticle to the semiconductor wafer substrate. The transfer is carried out by projecting the image of the reticle with the aid of appropriate optical elements of an exposure tool onto a radiation-sensitive resist material coated on the semiconductor wafer, typically made of silicon, and stepping the imaging field across the entire wafer to complete a layer. The shape of the IC pattern transferred to the wafer substrate is entirely dependent

[1]M. Quirk and J. Serda, *Semiconductor Manufacturing Technology*, Prentice-Hall, New Jersey, pp. 336–337 (2001).
[2]S. Campbell, *The Science and Engineering of Microelectronic Fabrication*, Oxford University Press, New York, p. 152 (1996).

2.3 Resist Coating and Thin Film Instabilities

After priming, the wafer is coated with a liquid solution of BARC (in the case of spin-on BARCs), baked, and cooled, before it is coated with a liquid solution of resist. Wafers with inorganic CVD BARCs are coated with resists immediately after priming. There are several methods of coating resists on wafers: spin coating, spray coating, and dip coating. The most widely used methods for coating resist in the semiconductor industry are spin-coating methods.

2.3.1 Resist spin-coating process

In the spin-coating process, a precise amount of liquid resist is dispensed onto a wafer (either statically, i.e., with the wafer at rest, or dynamically, i.e., with the wafer rotating). The wafer is then spun at high speeds until the film thickness reaches a desired value, oftentimes corresponding to a stationary point on the swing curve of the given resist (Fig. 2.4). The process thus uses the dynamics of centrifugal forces to disperse a fluid of polymeric resist material over the entire wafer surface. The flow and rheological properties of the resist do influence the coating process and need to be considered to achieve optimal results.[16] The final thickness and properties of the spin-coated film depend on the nature of the resist solution (viscosity, evaporation rate, percent solids, surface tension) and spin-coating parameters such as final rotation speed, acceleration, and fume exhaust.

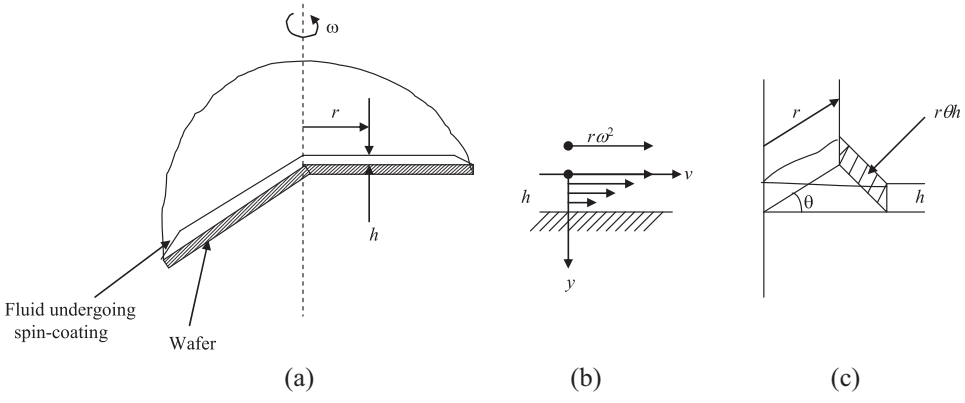


Figure 2.4 Schematics of the spin-coating process, showing (a) liquid flow on a rotating wafer, (b) the velocity profile of the flowing liquid, and (c) a cross-section of a wedge-shaped portion of the flowing liquid.

[16]D. E. Bornside, C. W. Macosko, and L. E. Scriven, "Modeling of spin coating," *J. Imag. Tech.* **13**, pp. 122–130 (1987).

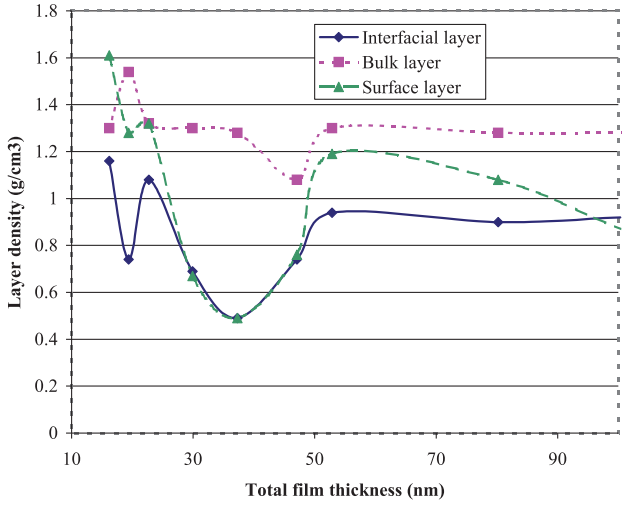


Figure 2.9 Film layer density as a function of total film thickness as determined by x-ray reflectivity. The resist used was Shipley XP-98248 resist. (Reprinted from Okoroanyanwu.[63])

monomeric units of the polymer in this region of the film. These also suggest the onset of thin film instabilities in this thickness range.[64]

Figure 2.10 shows a plot of film layer roughness as a function of total film thickness of XP-98248 resist as determined by fitting the XRR data. While the surface layer is relatively smooth [roughness measured by XRR was ~0.4–0.5 nm, compared to the ~0.2- to 0.3-nm RMS value obtained with the atomic force microscope (AFM)] through the total film thickness range of 16–100 nm, that of the interface between the bulk and surface layer shows significant fluctuations between ~0.4 and 2.7 nm within this thickness range. The film–substrate interface layer, on the other hand, is smooth (roughness ~0.5 nm) in the 47- to 100-nm total film thickness range, below which it shows significant roughness of up to 4.0 nm at a thickness of 30 nm. This result indicates the influence of film–substrate interfacial effects and consequently thin film instabilities.[65]

2.3.6 Ultrathin film defectivity

UTR film defects fall into two main categories based on the mechanism of their origin: Marangoni-effect-driven defects and non-Marangoni effect-driven defects. Both defect types are discussed below.

[63]ibid.
[64]ibid.
[65]ibid.

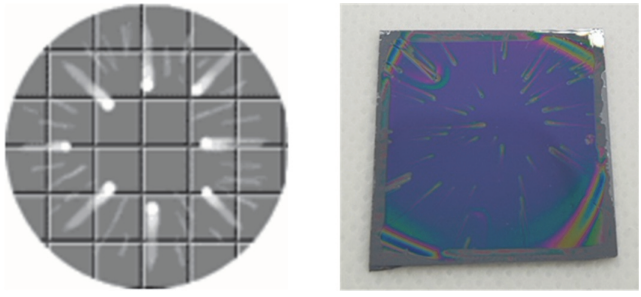


Figure 2.13 Images of comets obtained on a film spin-coated onto a silicon wafer: (left)[93] and (right).[94]

The effects can manifest as roughness, microcracking of the coating upon further drying, etc.

2.3.6.1.1.5 Wafer edge defects

The centrifugal force that underpins the spin-coating process is not uniform throughout the entire wafer; rather, it scales linearly with the radius, with the wafer edge experiencing the highest magnitude of the force. Complicating this process is the fact that once the radially outward flowing solution reaches the edge of the wafer, surface tension effects can make it difficult for the solution to detach from the wafer. A "bead" of liquid can stay attached around the entire perimeter of the wafer, resulting in thicker coatings in this rim zone than at inner locations on the wafer (Fig. 2.14). This results in coating nonuniformity. For substrates that are not round (for example, square or rectangular substrates), the air flow over their corners during spin coating are

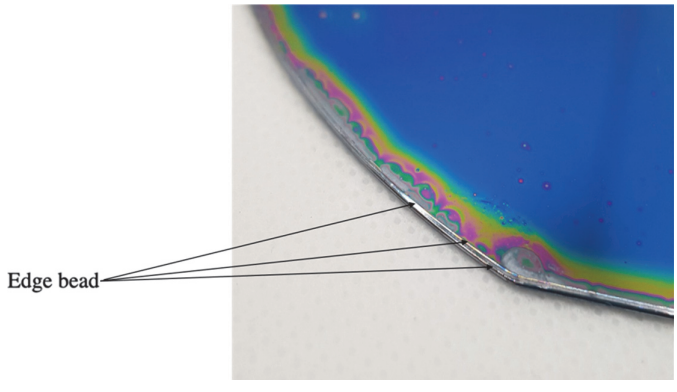
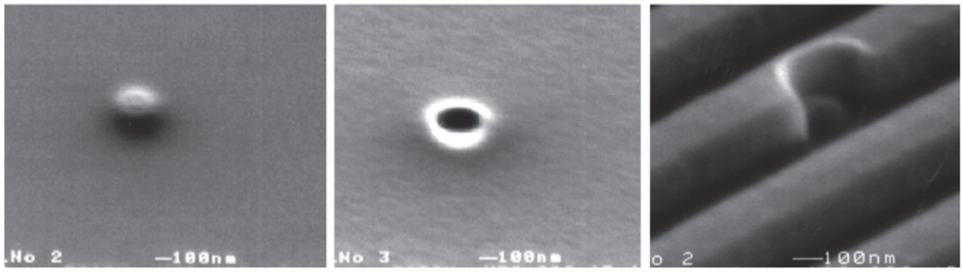


Figure 2.14 Optical image of edge bead defects on a silicon wafer.[95]

[93]https://www.brewerscience.com/processing-theories/spin-coat/
[94]Image from Daeeon Jung, University of Massachusetts Amherst.
[95]ibid.



(a) (b) (c)

Figure 2.18 Evolution of a bubble defect (a) formed at the resist coating, (b) through development, and (c) patterning with the ASML PAS5500/300 KrF stepper. Unexposed resist loss for the UTR film was ~6–10 nm. The poly-Si patterns are 180-nm lines and spaces. Film thickness was ~100 nm. (Reprinted from Okoroanyanwu.[112])

2.3.6.3 Patterning implications of UTR film instabilities

Given the enhanced surface mobility, which is a consequence of the decreased surface density—hence, the increased free volume of UTR film surfaces relative to the bulk and that of the film/substrate interfacial region—the lithographic properties of UTR films are bound to be dominated by interfacial effects. The surface region of such films is usually saturated with water or other solvents that can act as plasticizers. Thus, the T_g value of the surface chains can be further lowered with respect to the bulk chains.[113] The differences between the surface and bulk properties of UTR films can have a significant influence on their dissolution, etching, and diffusional properties.[114]

Figure 2.19 shows SEM images of line-and-space patterns printed with ~60-nm-thick XP-98248 resist on bare silicon and exposed at 157 nm, highlighting the dominant influence of polymer cooperative and surface dynamics near the surface region and interfacial effects related to polymer packing constraints near the substrate region. Poor profiles such as these are also obtained when the same film is processed on anti-reflection coatings (ARCs), implying that the poor lithographic performance of this UTR film cannot be solely due to the reflective swing effects from the silicon substrate. Significant undercutting suggests enhanced dissolution in the film–substrate interfacial region relative to the bulk layer. This is consistent with the XRR results obtained on a similar film of the same resist (see Fig. 2.9), which show the film–substrate interface layer to have a lower density than the bulk layer. This may also be related to polymer chain packing constraints and weak

[112]ibid.

[113]F. Garbassi, M. Morra, and E. Ochiello, *Polymer Surfaces: From Physics to Technology*, 2nd edition, John Wiley & Sons, New York (1998).

[114]U. Okoroanyanwu, "Thin film instabilities and implications for ultra-thin resist processes," *J. Vac. Sci. Technol. B* **18**(6), 3381–3387 (2000); U. Okoroanyanwu, "Limits of ultra-thin resist processes," *Future Fab International* **10**, 157–163 (2001).

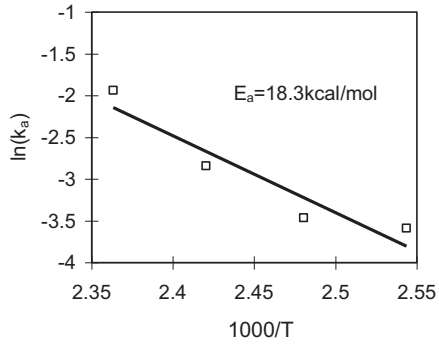


Figure 2.28 Arrhenius plot for resist formulated with poly(CBN-*co*-MAH) and exposed under 193-nm radiation. (Reprinted from Okoroanyanwu Byers, Cao, et al.[153])

sulfonium hexafluoroantimonate (TPSHFA) PAG. The activation energy for the deprotection of the pendant-*t*-butyl group of resists formulated with poly(CBN-*co*-NBCA) made by Pd(II)-catalyzed addition and free radical polymerization techniques was determined to be 6.7 and 9.4 kcal/mol, respectively, over the temperature range of 120 to 150 °C. Figure 2.28 is an Arrhenius-type plot of the deprotection kinetics of resist formulated with poly(CBN-*co*-MAH). The activation energy for the deprotection of the pendant-*t*-butyl group of resist polymer was determined to be 18.3 kcal/mol over the temperature range of 120 to 150 °C. This Arrhenius relationship is not considered valid outside of the region experimentally covered.

The thermal decomposition of DNQs in novolac resist film follows pseudo-first-order reaction kinetics (see Fig. 2.29). The 2,1,4-DNQ photoactive compound (PAC) is more thermally stable than the 2,1,5-DNQs, the activation energy difference between the two isomers being 8 kcal/mole.[154]

2.6.2 Monitoring PAG in thin photoresist films by means of fluorescence spectroscopy

Fluorescence spectroscopic techniques are being used increasingly in a wide range of research fields including biochemical, medical, and chemical research, primarily because of their inherent sensitivity and the favorable time scale of the phenomenon of fluorescence.[155] Some fluorophores have dramatically different emission characteristics in their protonated and unprotonated forms. Using this phenomenon, the photoacid concentrations generated within chemically amplified photoresist systems can be

[153]ibid.
[154]W. M. Moreau, "Thermal stability of naphthodiazoquinone sensitizers," *Proc. SPIE* **3049**, 618–627 (1997).
[155]J. R. Lackowicz, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York, Chapters 1 & 2 (1986).

Exposure-induced chain scissioning that leads to reduction of resist polymer molecular weight is another approach to effecting polarity switching, and hence improving contrast between the exposed and unexposed regions of the film during solvent development. From Flory–Huggins theory discussed in Chapter 3, it can be appreciated that the enthalpic term must be essentially the same in both the starting polymer and the scissioned polymer, indicating that dissolution occurs in this system largely on the basis of the change in molecular weight. The greater the amount of scission-induced molecular weight reduction the greater the solubility of the exposed resist in developers such as methyl ethylketone.

For resists based on exposure-induced functional group transformation such as in CARs, depending on their polarity and the polarity of the developer solvent, different types of interactions mediate the dissolution of the part that is dissolved in the developer. Positive-tone aqueous development of, for example, polar and charged CARs, have ionic interactions driven by highly polar polymer–polymer, hydration, and hydrogen bonding interactions, which decrease and break down the polymer–polymer interactions, making it easier for the water molecules of the developer to displace these interactions and solvate the charged polymeric units, ultimately dissolving them in the developer. In contrast, in negative-tone development in a nonpolar solvent of the above polar and charged CARs, the strong ionic polymer–polymer interactions, driven by polar hydrogen bonds of the exposed part of the film, make it much more difficult for solvent molecules to displace these interactions. Therefore, while the unexposed regions are readily developed away, the exposed polar region excludes solvent penetration, leading to high-contrast unswollen patterns.

2.7.5 Development rate characterization

There are several reasons why it is important to characterize the dissolution or development rate of any given resist. The main reasons tend to be for process control purposes, given that image discrimination in a resist is based on differences in dissolution rates between the image and non-image areas. The two main techniques that are used to characterize the dissolution properties of a resist are laser interferometry and quartz crystal microbalance. Each of these techniques is reviewed below.

2.7.5.1 Laser interferometry

The first use of laser interferometry in monitoring the dissolution rate of a resist during development was by Konnerth and Dill.[182] The basis of their idea is shown in Fig. 2.37. A laser beam is directed toward the film that is

[182]K. L. Konnerth and F. H. Dill, "In-situ measurement of dielectric thickness during etching or developing processes," *IEEE Trans. Electron. Devices* **22**(7), 452–546 (1975); K. L. Konnerth and F. H. Dill, "IOTA, a new computer controlled thin film thickness measurement tool," *Solid-State Electron.* **15**, 371 (1972).

They found that polymer dissolution occurs in two stages. In the first stage, solvent penetrates the glassy polymer, forming a gel layer that separates the polymer matrix from the pure solvent. In the second stage, the polymer coils disentangle from the gel, eventually diffusing into the liquid. Three distinct phases in the steady state dissolution process are[196]

Glassy polymer | Swollen gel | Solvent or solution

Ueberreiter found that, in the polymer systems he studied, the diffusion of the solvent across the gel layer is the rate-determining step (i.e., it is the slowest of all involved steps),[197] and in those cases solvent uptake and the inward movement of the glass–gel interface depend on the square root of time, as is characteristic of Fickian diffusion. In other systems, the processes in the glass–gel interface are rate determining, and solvent uptake and interface movement are linear functions of time. Alfrey, Gurnee, and Lloyd[198] termed this *case II diffusion* or polymer relaxation-controlled mass transfer.[199] Figure 2.40 shows a schematic of time–concentration profiles for the two dissolution modes.

In the following section, we discuss in some depth the dissolution mechanism of phenolic polymer resists such as novolac and PHOST resins, as well as those of acrylate and alicyclic resist polymer platforms. The development of phenolic polymer resins involves similar dissolution stages. Unlike their counterparts that are solvent developable—such as bis-azide/cis-polyisoprene negative resists, which require some degree of swelling for their dissolution—these phenolic polymer resists do not require such adverse swelling for dissolution.[200]

2.7.6.1 Dissolution mechanism of phenolic resists

The mechanism of phenolic polymer resist dissolution has been a hotly contested and debated concept. Many models have been proposed for how this process plays out. Although each of these models has been successful in explaining different aspects (but not the complete mechanism of novolac

[196]A. Reiser, *Photoreactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York, p. 211 (1989).
[197]K. Ueberreiter, in *Diffusion in Polymers*, J. Crank and S. Park, Eds., Academic Press, New York (1968).
[198]T. Alfrey, Jr., E. F. Gurnee, and W. O. Lloyd, "Diffusion in glassy polymers," *J. Polym. Sci., Part C* **12**, 249 (1960).
[199]G. C. Sarti, "Solvent osmotic stresses and the prediction of Case II transport kinetics," *Polymer* **20**, 827 (1979); N. L. Thomas and A. H. Windle, "A theory of case II diffusion," *Polymer* **23**, 529 (1982).
[200]J. P. Huang, T. K. Kwei, and A. Reiser, "Molecular mechanism of positive novolac resists," *Proc. SPIE* **1086**, 74 (1989); H. Shih, T. Yeu, and A. Reiser, "Percolation view of novolak dissolution: 3. dissolution inhibition," *Proc. SPIE* **2195**, 514 (1994); B. W. Smith, "Resist Processing," in *Microlithography: Science and Technology*, J. R. Sheats and B. W. Smith, Eds., Marcel Dekker, Inc., p. 546 (1998).

$$\log\left(\frac{R}{R_1}\right) = -2\log(1 - p_c) + 2\log(p - p_c). \tag{2.44}$$

It is remarkable that these seven structurally different resins all yielded a slope of 2 on log R vs. log $(p - p_c)$ plots for a value of $p_c = 0.2$; all of them mapping perfectly onto the same master curve.[251] A major problem with the percolation model is that it predicts a resist contrast that is far lower than what is observed experimentally.

2.7.6.1.3.5 Critical ionization model

The critical ionization model proposed by Tsiartas et al.[252] states that a resist polymer below its entanglement molecular weight dissolves in a developer whenever a critical fraction of its blocked groups become deblocked. In the specific case of phenolic resins, dissolution proceeds via acid–base reaction between the aqueous developer base and the phenolic group of the resins, leading to deprotonation of the latter and formation of phenolate ions. Dissolution as a result occurs in the phenolic resins only when a critical fraction of the phenol groups in the polymer are ionized (deprotonated). Below this critical ionization fraction, no dissolution of the resin occurs in the developer. This implies that lower-molecular-weight polymers will require fewer deblocking (deprotonation or ionization) events to become soluble compared to their higher-molecular-weight counterparts.

2.7.6.1.3.6 Stone wall model of novolac dissolution

Proposed by Hanabata, Uetani, and Furuta[253] in 1990, the stone wall model states that during development, the low-molecular-weight novolacs and sensitizer (referred to as the mortar of the wall) in the exposed part of DNQ/novolac resist dissolve quickly; this has the effect of increasing the surface areas of the high-molecular-weight novolac (referred to as the "stones" of the wall) that is in contact with the developer, eventually leading to a breakup of the "stone wall," and resulting in dissolution (see Fig. 2.50).

2.7.6.1.3.7 Effects of resin and inhibitor structure on dissolution rate

There is ample evidence that the structural properties of phenolic resins such as novolac and PHOST, as well as the inhibitors associated with them, do

[251]ibid.

[252]P. C. Tsiartas, L. W. Flanagin, C. L. Henderson, W. D. Hinsberg, I. C. Sanchez, R. T. Bonnecaze, and C. G. Willson, "The mechanism of phenolic polymer dissolution: A new perspective," *Macromolecules* **30**(16), 4656–4664 (1996).

[253]M. Hanabata, Y. Uetani, and A. Furuta, "Novolak design for high resolution positive photoresists. II. Stone wall model for positive photoresist development," *Proc. SPIE* **920**, 349–482 (1990).

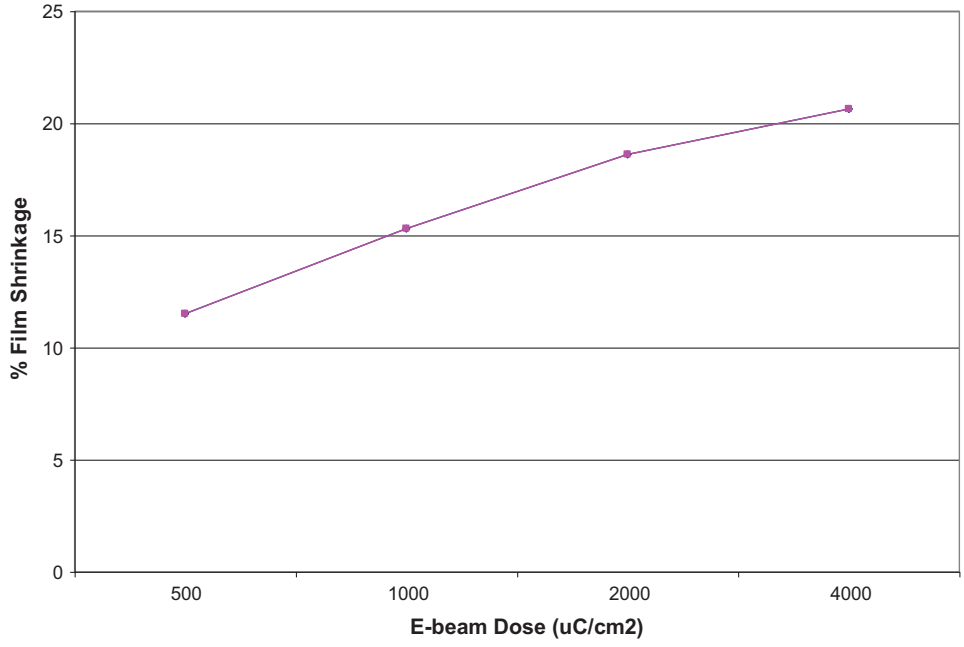


Figure 2.59 Film shrinkage of PAR-700/A4 resist as a function of electron beam dose. The nominal resist thickness was 400 nm [reprinted from U. Okoroanyanwu, *Chemistry and Lithography*, SPIE Press, Bellingham, Washington p. 544 (2010)].

2.9 Resist Etching Chemistry

Following the resist pattern stabilization steps, an etching process is used to transfer the resist pattern into the underlying semiconductor substrate. There are two main forms of etching processes: wet and dry etching. Before the dry etching techniques were developed, all etching processes in semiconductor device fabrication were carried out with wet etching.

2.9.1 Wet etching

In wet etching, the substrate is etched with an etchant solution in a process that involves dipping the patterned resist wafer in the etchant solution and subsequently cleaning and rinsing it with pure de-ionized water. The wet etch rate is mainly dependent on the composition of the etchant solution and the temperature. Given that these two factors and the etching time are easily controllable, the reproducibility of the wet etch result is quite good.[314]

The choice of etchants depends on the nature of the substrate to be etched. Table 2.4 is a list of solutions used in the wet etching of common substrates. Silicon dioxide is etched with a mixture of aqueous solution of

[314]S. Nonogaki, T. Ueno, and T. Ito, *Microlithography Fundamentals in Semiconductor Devices & Fabrication Technology*, Marcel Dekker, Inc., New York, Chapter 5 (1998).

Chapter 3
Chemistry of the Lithographic Exposure Tool and Optical Element Materials

"And the atoms that compose this radiance do not travel as isolated individuals but linked and massed together."
Lucretius, *De Rerum Naturae* [*On the Nature of Things*]

3.1 Introduction

The optical elements of lithographic exposure tools comprise lenses, mirrors, reticles, and pellicles. The materials used in the fabrication of these optical elements are chosen because of their unique physical and chemical properties relative to their exposure wavelength of use.

3.2 Chemistry of Lens Materials

The main optical materials used in UV and visible light lithographic exposure tools fall into two categories: reflective optical materials (mirrors) and refractive optical materials (lenses). Reflective optical materials are advantageous because they can be used with broadband illumination. Also, it is very difficult to design and build high-numerical-aperture (NA) all-reflective optics because of physical interference: some mirrors will block the light path of others. For this reason, lithographic exposure tools utilizing all reflective optics such as production-worthy EUV exposure tools have low NA (0.33), with 0.55-NA systems currently under development. These tools achieve very high resolution because of their short exposure wavelength (13.5 nm). Deep-UV (DUV) lithographic tools have mostly lens-based optics and a few

shape of some stepper alignment signals.[37] Earlier generations of top anti-reflection coatings were designed to be coated from organic solvents that do not attack the resist layer and must be removed before development since they are not aqueous-base soluble. In principle, chlorofluorocarbons (CFCs) may be used for both purposes since they do not attack the resist.[38]

Inorganic anti-reflection coatings are typically deposited by sputtering, and, unlike organic anti-reflection coatings, may in some cases be left in the finished device. Typical inorganic anti-reflection coatings include silicon oxynitride, amorphous silicon, tantalum silicide, titanium nitride, etc.

3.3 Chemistry of Mirror Materials

3.3.1 EUV multilayer mirrors

There are no reasonably EUV-transmissive refractive materials that can be used in EUV optics. Instead, most naturally occurring materials reflect only a very small fraction of the incident EUV photons and tend to absorb most of them from their surface within a fraction of a micron. Therefore, only precisely figured reflective optics, comprising multilayer film reflectors of alternating thin (a few nanometers) layers of molybdenum and silicon can be used as mirrors in the EUV tool. To protect the multilayer coating of the mirror, a capping layer is often deposited on its surface.

3.4 Chemistry of Lithographic Masks and Reticle Materials

There are two main types of optical lithographic masks: binary intensity masks (BIMs) and phase-shifting masks (PSMs). A BIM consists of a clear, transparent quartz substrate with uniform thickness, in which is embedded dark, opaque, non-transmitting patterns made of chromium, a chromium-containing compound layer, or a molybdenum-containing layer of approximately 80-nm in thickness.[39] Chromium and chromium-containing compounds are the most common opaque materials used for fabricating optical lithographic photomasks. Typically, the films of chromium and chromium-containing compounds are sputtered onto the glass substrates to thicknesses between 50 nm and 110 nm.[40] The optical constants of chromium at different lithographic wavelengths are given in Table 3.6. A consequence of the high absorption of chromium at the indicated lithographic wavelengths is

[37]T. Tanaka, N. Hasegawa, H. Shiraishi, and S. Okazaki, "A new photolithography technique with antireflective coating on resist ARCOR," *J. Electrochemical Society* **137**(12), 3900 (1990).
[38]Despite this quality, CFCs cannot be used as solvents for top anti-reflection coatings because they are now banned for their role in the depletion of the ozone layer.
[39]ibid., p. 11.
[40]H. J. Levinson, *Principles of Lithography*, 2nd edition, SPIE Press, Bellingham, Washington, p. 247 (2005).

Chapter 4
Chemistry of Lithographic Patterning Materials

"Why is the grass so cool, fresh and green?
The sky so deep, and blue?
Get to your Chemistry,
You dullard, you!"
Walter de la Mare, "The Dunce"

4.1 Introduction

Present day lithographic patterning materials and chemicals, including inks, resists, anti-reflection coatings, casting solvents, developers, strippers, etc., evolved largely from technologies developed in the printing industry. Integrated circuits (ICs) and circuit boards were unheard of in 1798 when Senefelder invented lithography and in 1826 when Niepcé invented photolithography. Since those early days, lithographic chemicals have evolved from being extracted from natural sources to being derived almost exclusively from synthetic sources today. They have also grown in importance along with the electronics industry, since even the simplest electronic systems today are patterned with resists, using ever more sophisticated arrays of lithographic chemicals. In this chapter we present an overview of lithographic chemicals used in patterning IC devices and printing newspapers, textbooks, posters and the like, while making historical references to similar materials used in lithography in earlier times.

4.2 Resists

As the enabling factor/component for each lithographic printing technique, resists have often determined the successful implementation of each lithography. At times, new resists and related processes developed in anticipation of yet-to-be developed lithographic tools and methods. Other times, the invention of

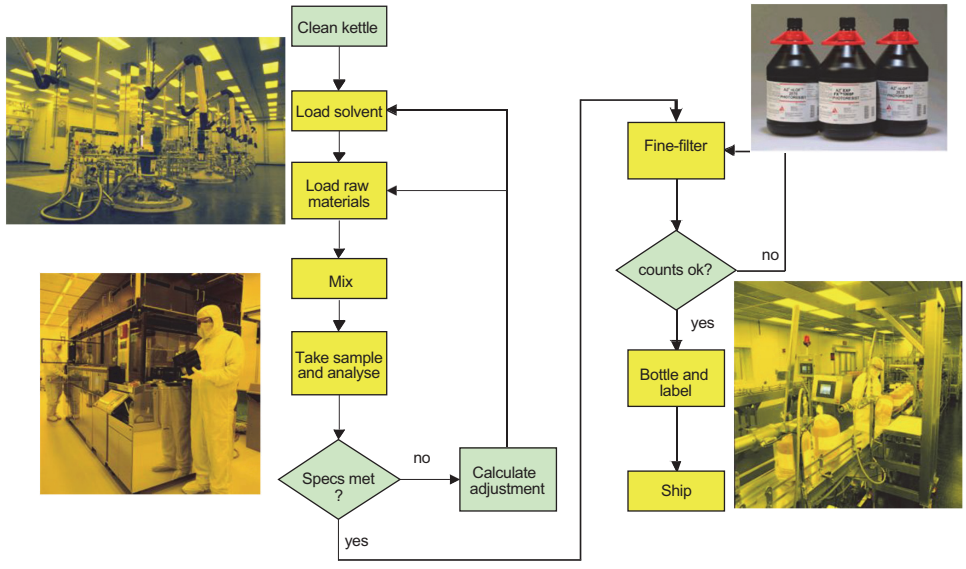


Figure 4.13 Typical process flow for the large-scale manufacturing of advanced commercial resists (figure courtesy of R. Dammel).

appropriately to meet the specification. This iteration loop is executed as many times as necessary until the manufacturer's specification is met.

4.3 Resist Developers and Rinses

Resist developers fall into two main categories, depending on whether they are used for developing negative resists or positive resists. Negative resist developers are typically organic solvents in which the resist resins are soluble. Because the exposed area of the negative resist film is crosslinked and remains on the substrate, the unexposed part, still retaining the solubility characteristics of the parent resist resin, is dissolved away with the developing solvent. The actual negative resist development operation involves the selective dissolution of the unexposed areas. Chemically, the crosslinking caused by the exposure process does not significantly alter the resist polymer enough to prevent a strong interaction with solvents capable of dissolving the unexposed and uncrosslinked polymer. Consequently, swelling of the exposed areas will occur and can affect resist adhesion[10] if it is severe enough; it will continue until equilibrium is reached.[11] Ways to minimize the swelling problem of negative resists include applying adequate exposure to afford sufficient crosslinking, which in turn acts

[10]E. B. Davidson, in *Tech. Papers, Reg. Tech. Conf. Soc. Plast. Eng.*, Mid-Hudson Sec., p. 141, October (1970).
[11]W. S. DeForest, *Photoresist: Materials and Processes*, McGraw-Hill Book Company, New York, p. 242 (1975).

Chapter 5
Photochemistry and Radiation Chemistry in Lithography

"Mehr licht!" [More light!]
Attributed dying words of Johann Wolfgang von Goethe (1749–1832)

5.1 Introduction

Radiations spanning the visible, ultraviolet (UV), vacuum-UV (VUV), and extreme-UV (EUV) bands of the electromagnetic spectrum as well as charged particles such as electrons and ions are routinely used in semiconductor lithography. Photons with wavelengths from the visible (436 nm) through mid-UV (365 nm), deep-UV [(DUV) 248 nm and 193 nm], VUV (157 nm), and EUV (13.5 nm) regions of the spectrum are now routinely used in lithographic patterning of devices of different kinds. These photons mediate a wide range of photochemistry as they mediate the lithographic patterning process. Lithography using photons,[1] otherwise called photolithography or optical lithography, has been and continues to be the preeminent lithographic technique used in fabrication of integrated circuit devices in the semiconductor industry since the late 1950s. Figure 5.1 shows the six basic elements of an optical lithographic exposure tool through which these photons travel: (1) an exposure source, (2) an illumination optics system, (3) a photomask or reticle and its pellicle, (4) a projection optics system, (5) a wafer stage, and (6) a photoresist-coated wafer. The source provides the exposure radiation which, with the aid of illumination optics, illuminates the photomask and transfers the image of the

[1]The term *optical lithography* as used in this book encompasses all lithographic patterning techniques in which photons are used in such a manner that the imaging action obeys the laws of geometric optics—the simple laws of reflection and refraction, to mention but a few. With this usage, the terms photolithography and optical lithography are interchangeable, denoting the fact that photons are the primary agents that initiate the chemical transformations of the resists, resulting in the contrast between the exposed and the unexposed regions, and ultimately leading to the effective transfer of the mask image to the semiconducting substrate.

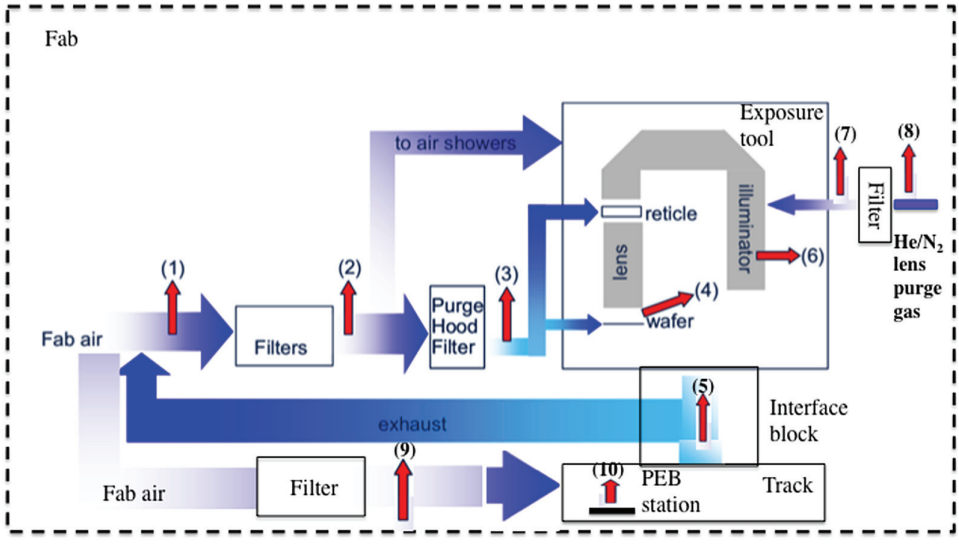


Figure 5.2 Schematic representation of the air and lens purge gas flow through a typical lithographic exposure tool/track cluster, here illustrated with the ASML /1100 ArF lithographic exposure tool/Screen track cluster, and indicating locations used in airborne molecular contamination monitoring. Air and purge gas flows are indicated in blue color. Typical airborne molecular contamination monitoring locations are indicated with red arrows and are associated with numbers.

inspection, blank and patterned mask inspection, mask cleaning, and plasma stripping of resists from wafers and masks.

Distinct photochemical reactions and photophysical processes as well as radiochemical reactions and radiochemical processes are involved in the generation of radiation from lithographic exposure sources, and in the interaction of exposure radiation with lithographic optical elements, constituents of the exposure medium, and resist materials. These photochemical and radiochemical reactions and photophysical and radiochemical processes resulting from the interactions between the exposure radiation and radiation-sensitive resists and their constituents underlie the basis of the contrast between the exposed and the unexposed regions of the resist film. We examine some of these reactions and interactions in the succeeding sections.

5.2 General Considerations on Photochemistry, Photophysics, and Radiation Chemistry in Lithography

The interaction of the exposure radiation with the constituents of the exposure medium can generate reactive species that can degrade optical elements and the unexposed areas of the resist film. The interaction of the exposure radiation with the optical elements can equally degrade the latter. The introductory parts of some of the major sections of this chapter are therefore devoted to the

where $\overline{V}_m$ is mean frequency of absorption in wavenumbers, εdv is experimental molar absorptivity integrated over the width of the absorption band, and ε_{max} is the maximum absorptivity within the absorption band.

The quantum yield is defined as the ratio of the number of excited molecules in each excited state (that decay by that process) to the total number of excited molecules in each state. The fluorescence and phosphorescence quantum yields are expressed as

$$\phi_F = \frac{Rate\ of\ fluorescence\ emission}{Rate\ of\ excitation} = \frac{k_F[S_1]}{I_A} \tag{5.33}$$

and

$$\phi_P = \frac{Rate\ of\ phosphorescence\ emission}{Rate\ of\ excitation} = \frac{k_P[T_1]}{I_A}, \tag{5.34}$$

respectively, where I_A is the rate of radiation absorption.

5.2.1.5 Types of electronic transitions in lithographic systems

Transitions in lithographic systems arise from the absorption of energy (in the form of electromagnetic radiation, electrical discharge, or chemical reactions) by a lithographic material, causing the movement of an electron from one molecular or atomic orbital of the material to another. The nature of the transition is described by the two orbitals involved. Typical transitions in lithography include (1) metal-centered *d–d* transitions between orbitals localized on transition metal atoms such as Sn used in laser-produced plasma for EUV lithography; (2) transitions between molecular orbitals in organic compounds and organometallic compounds in resists as well as in noble gas halides such as KrF and ArF exciplex laser sources; (3) transitions between the valence and conduction bands of impurity atoms that lead to color center formation in lithographic lenses made of quartz.

The lowest-energy transitions observed in lithographic systems are those between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The two most common types of transitions in organic molecules used in lithography (such as photoresists) include $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions; $\sigma \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions are usually of such high energy that they occur in the VUV region. Lithographic organic materials such as photoresists typically containing heteroatoms such as O and N have $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions that are energetically close.

5.3 Radiation Chemistry versus Photochemistry in Lithography

Conventional photochemistry deals with valence or outer-shell electronic excitation associated with radiation lying in the approximate wavelength

the availability of an allylic hydrogen, substituent polymers react with it to produce either dioxetanes or hydroperoxides, whereas polydienes yield endoperoxides.[119] In polymers, light-absorbing impurities (external and/or internal structure irregularities) have been reported to act as potential photosensitizers for the generation of singlet oxygen.[120]

5.8 Photochemistry of Mask and Exposure Tool Lens Contamination and Cleaning

The exposure chamber of an optical lithographic tool is a veritable reaction vessel conducive to oxidative and etching reactions mediated by photoinduced species from the interaction of the exposure radiation with molecular contaminants in the exposure chamber on one hand, and between exposure radiation and mask materials on the other. These oxidation reactions ultimately lead to growth of inorganic salts such as ammonium sulfate and ammonium molybdate as well as carbon deposits on masks and exposure tool lenses. They can also lead to corrosion of the mask (discussed in Chapter 11), mediated via photoelectrochemical processes.

5.8.1 Inorganic salt formation on DUV exposure tool lenses and reticles

Experimental evidence suggests the formation of inorganic crystals that cause haze defects on 193-nm and 248-nm exposure reticles[121] and lenses. These

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Chem. Ed. **14**, 463 (1976); J. F. Rabek and B. Ranby, "Studies on the photo-oxidative mechanism of polymers. VII. The role of singlet oxygen in the dye-photosensitized oxidation of cis-1,4- and 1,2-polybutadienes and butadiene-styrene copolymers," *J. Appl. Polym. Sci.* **23**, 2481 (1979); A. Zwieg and W. A. Henderson, "Singlet oxygen and polymer photooidations. I. Sensitizers, quenchers, and reactants," *J. Polym. Sci. Chem. Ed.* **13**, 717 (1975).

[119]M. L. Kaplan and P. G. Kelleher, "Photo-oxidation of polymers without light: Oxidation of polybutaiene and an ABS polyblend with singlet oxygen," *J. Polym. Sci. Chem. Ed.* **8**, 3163 (1970); H. C. Ng and J. E. Guillet, "Singlet oxygen initiation of polymer photooxidation: photolysis of *cis*-1,4-poly(isoprene hydroperoxide)," *Macromolecules* **11**(5), 929 (1978); C. Tanielian and J. Chaineaux, "Single oxygen reactions with model compounds of *cis* and *trans* polyisoprene containing two units," *J. Photochem.* **9**, 19 (1978); C. Tanielian and J. Chaineaux, "Singlet oxygen reactions with model compounds of *cis*- and *trans*-polyisoprene containing one unit. Kinetic aspects," *J. Polym. Sci. Chem. Ed.* **17**, 715 (1979); C. Tanielian and J. Chaineaux, "Sensitised photo-oxidation of polyisoprene: effect of the presence of hydroxy and hydroperoxyl groups," *Europ. Polym. J.* **16**, 619 (1980).

[120]J. F. Rabek, *Photodegradation of Polymers: Physical Characteristics and Applications*, Springer, New York, p. 87 (1996).

[121]B. Grenon, K. Bhattacharyya, W. Volk, and A. Poock, "Reticle surface contaminants and their relationship to subpellicle particle formation," *Proc. SPIE* **5256** (2003); E. Johnstone, L. Dieu, C. Chovino, J. Reyes, D. Hong, P. Krishnan, D. Coburn, and C. Capella, "193-nm haze contamination: A close relationship between mask and its environment," *Proc. SPIE* **5256** (2003).

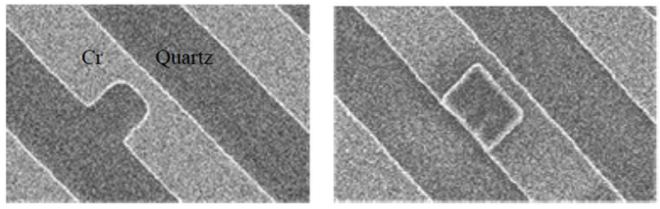


Figure 5.37 Lithographic mask feature with clear defects (left) before electron beam-assisted Pt deposition and (right) after electron beam-assisted Pt deposition from a (methylcyclopentadienyl)platinum complex. (Reprinted from Liang et al.[211])

before and after repair with this technique, illustrating the effectiveness of this approach in repairing such clear mask defects.[211]

$$(CH_3C_5H_4)Pt(CH_3)_3 \xrightarrow{\text{Electron beam}} Pt \qquad [5.42]$$

5.11 Photochemistry and Radiation Chemistry of Resist Systems

5.11.1 Photochemistry of resist exposure

Figure 5.38 presents the main photochemical and radiochemical imaging mechanisms that underlie advanced lithography. There are two tones in photochemical and radiochemical resist imaging: negative and positive tone. For positive resists, the exposed part of the resist film is dissolved away during development, reproducing a positive image of the mask; in negative resists, the unexposed part the resist is dissolved away during development, leaving the exposed part, and reproducing a negative image of the mask. The photochemical and radiochemical reactions that engender negative-tone resist imaging mechanisms include photo- and radiation-initiated polymerization, crosslinking, and polarity switching reactions such as condensation, pinacol rearrangement, esterification, and ligand exchange. Negative-tone imaging mechanisms lead to either a significant increase in molecular weight of the exposed resist (as in polymerization and crosslinking imaging mechanisms), or polarity switching (as in condensation, pinacol rearrangement, esterification, and ligand exchange imaging mechanisms) of the exposed part of the resist relative to the unexposed part.

In contrast, the photochemical and radiochemical reactions that engender positive-tone resist imaging mechanisms include photolysis and radiolysis as well as radiation-induced main-chain scission and depolymerization.

[211]T. Liang, A. Stivers, M. Penn, D. Bald, C. Sethi, V. Boegli, M. Budach, K. Erdinger, and P. Spies, "Demonstration of damage-free mask repair using electron beam-induced processes," *Proc. SPIE* **5446**, (2004).

5.11.5.4 Determination of the crosslinking yield G_x

In the absence of scissioning, the radiation chemical yield of crosslinking[309] is readily determined by monitoring the insolubilization of the polymer. Charlesby and Pinner[310] show that the soluble fraction s as a function of the irradiation dose received by the polymer can be described by an equation of the form

$$s + s^{1/2} = \frac{G_s}{2G_x} + \frac{9.65 \times 10^5}{M_n^0 G_x}\frac{1}{D}. \tag{5.72}$$

In the procedure, the polymer sample is irradiated and then extracted with a suitable solvent, in which the soluble fraction (i.e., the fraction of the material that is not crosslinked) can be determined. A plot of $(s + s^{1/2})$ against $1/D$ yields a straight line from which the value of G_x can be determined from either the intercept or the slope.

In a polymer in which both crosslinking and backbone scission are occurring to a significant degree, the G-values of both processes can be derived simultaneously by measuring the number-average and weight-average molecular weights, M_n and M_w, respectively, of the sample under irradiation. The M_n and M_w values can be expressed by two equations of similar form:

$$\frac{1}{M_n} = \frac{1}{M_n^0} + [G_s - G_x]\frac{D}{100N_A}, \tag{5.73}$$

$$\frac{1}{M_w} = \frac{1}{M_w^0} + [G_s - 4G_x]\frac{D}{100N_A}. \tag{5.74}$$

A plot of the reciprocal molecular weight of the sample as a function of radiation dose yields straight lines, from which slope the values of $[G_s - G_x]$ and $[G_s - 4G_x]$ can be obtained to yield the G-values.

5.11.6 Photochemistry of photoactive compounds

There are three classes of photoactive compounds used in lithography: photoacids, photobases, and photosensitizers. We briefly describe here their photochemistry.[311] In Chapters 6 and 7, we discuss their lithographic

[309]The method presented here is adapted from the treatment of the subject given in A. Reiser, *Photoreactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York, pp. 309–311 (1989).

[310]A. Charlesby and S. H. Pinner, "Analysis of the solubility of irradiated polyethlene and other polymers," *Proc. R. Soc. London, Ser. A* **249**, 367 (1959).

[311]Excellent reviews of the photochemistry of these compounds have been published; the analysis here is drawn largely from M. Shirai and M. Tsunooka, "Photoacid and photobase generators: chemistry and applications to polymeric materials," *Prog. Prolym. Sci.* **21**, 1–46 (1986); C. J. Martin, G. Rapenne, T. Nakashima, and T. Kawai, "Recent progress in development of photoacid generators," *J. Photochem. Photobiol. C: Photochem. Reviews* **34**, 41–51 (2018).

Chapter 6
Chemistry of Photochemical and Radiochemical Imaging Mechanisms of Negative-Tone Resists

"... How charming it would be if it were possible to cause these natural images to imprint themselves durably and remain fixed upon the paper! And why should it not be possible? I asked myself."

William Henry Fox Talbot, *The Pencil of Nature*

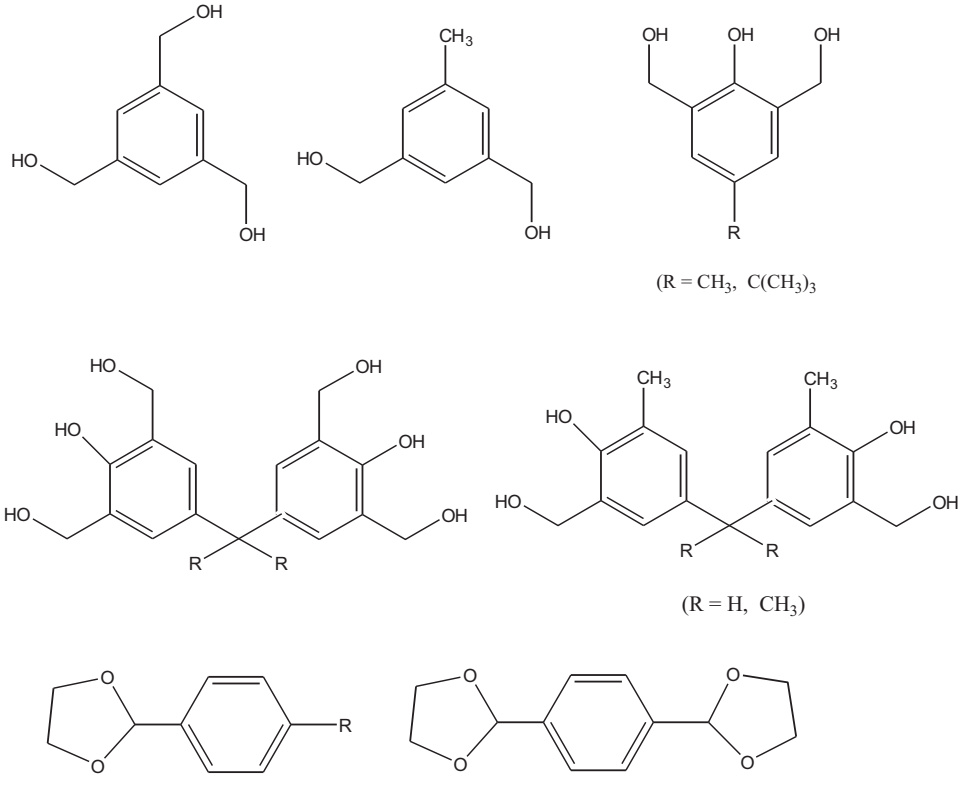
6.1 Introduction

As discussed in Chapter 4, resists in use before the 1960s were all invariably negative resists. These included resist materials such as bitumen of Judea, dichromated gelatin, and other dichromated colloids. The mechanism by which they functioned was not well understood at the time of their discovery. It was only in the 1920s that it was recognized that gelatin and other natural colloids were macromolecules[1] and that rubber vulcanization is a crosslinking process. Only then did the idea begin to take hold that the hardening and insolubilization that occur on exposure of dichromated gelatin are brought about by radiation-induced crosslinking.[2]

Characteristically, negative resists of the modern era (since 1950) have high chemical resistance and good image reproduction qualities. They were widely used in the manufacture of circuit boards and microelectronic devices for these reasons before the advent of positive resists. Because of their high chemical

[1]H. Morawetz, "Difficulties in the emergence of the polymer concept – an essay," *Angewandte Chem. Int. Ed. Engl.* **26**, 93 (1987).
[2]A. Reiser, *Photoreactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York, p. 22 (1989).

by selective removal of the *t*-BOC group in refluxing glacial acetic acid, to afford a copolymer bearing both the latent electrophile and the crosslinking site on the same polymer chain.[138] The formation of carbocation from the protonated ether moiety is the rate-determining step for crosslinking in these resists. Both the *C*-alkylation and *O*-alkylation are responsible for crosslinking and result in the destruction of the base-solubilizing phenolic OH groups in the exposed areas of the film, and hence negative-tone imaging. These condensation negative resists have found widespread application in DUV 248-nm, electron-beam, and x-ray lithographies, where they have provided excellent lithographic performance.[139]



(**XXV**) Examples of latent electrophiles (crosslinkers)

6.3.2.2 Negative resists based on radiation-induced polarity changes

Radiation-induced changes in the polarity of inorganic compounds or molecules or polymer-bound functional groups can significantly alter the

[138]ibid., p. 156.
[139]ibid., pp. 152–156.

dissolution properties of the polymer.[140] This idea has been used widely in the design of a very important class of negative resists, spanning both photolithography and charged-particle lithography. The most prominent examples of non-chemically amplified resists and chemically amplified resists are illustrated below. We follow the approaches reported by D. A. Doane and A. Heller[141] for the non-chemically amplified resists, and the approaches reported by both Reiser[142] and Ito[143] for the chemically amplified resists.

6.3.2.2.1 Non-chemically amplified negative resists based on radiation-induced polarity changes

6.3.2.2.1.1 Metal-chalcogenide resists

Metal-chalcogenide inorganic resists are based on a photodoping phenomenon occurring in chalcogenide glass films, a phenomenon first reported in 1966 by M. T. Kostyshin and coworkers,[144] who showed that chalcogenide films deposited on metal substrates produce visible images upon UV irradiation. It was Shimizu et al.[145] who were the first group to extensively study various metal-chalcogenide systems as imaging materials; they introduced the term "photodoping" in 1971 to refer to the migration of a

[140]The classical example of radiation-induced polarity change is the photodecomposition of diazoquinone into an ionizable compound, the indene carboxylic acid. This reaction is the basis of one of the important positive photoresists discussed in Chapter 7. Attaching diazoquinone units to a polymer backbone, for example, via acrylic side groups, makes the unexposed polymer soluble in organic solvents and the exposed polymer soluble in dilute aqueous basic solutions.

[141]D. A. Doane and A. Heller, Eds., *Proc. Symposium on Inorganic Resist Systems* **82**-9, The Electrochemical Society, Pennington, New Jersey (1982).

[142]A. Reiser, *Photoactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York, pp. 44–46 (1989).

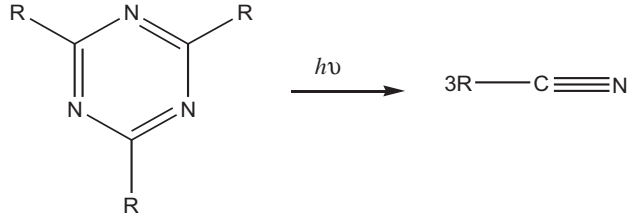
[143]H. Ito, *Chemical Amplification Resists for Microlithography*, *Adv. Polym. Sci.* **172**, Springer-Verlag, Berlin, pp. 149–174 (2005).

[144]The original papers by Kostyshin and co-workers can be found as M. T. Kostyshin, E. V. Mikhailovskaya, and P. F. Romanenko, "Photographic sensitivity effect in thin semiconducting films on metal substrates," *Soviet Phys.-Solid-State* **8**, 451 (1966) [see, for example, D. A. Doane and A. Heller, "An introductory perspective on inorganic resist systems," in *Proc. Symposium on Inorganic Resist Systems* **82**-9, D. A. Doane and A. Heller, Eds., The Electrochemical Society, Pennington, New Jersey (1982)].

[145]I. Shimizu, H. Sakuma, H. Kokado, and E. Inoue, "The photo-doping of metals into solids for new-type imaging systems," *Bull. Chem. Soc. Jap*. **44**, 1173 (1971); H. Kokado, I. Shimizu, and E. Inoue, "Discussion on the mechanism of photodoping," *J. Non-cryst. Sol*. **20**, 131 (1976); I. Shimizu, H. Sakuma, H. Kokado, and E. Inoue, "Metal-chalcogenides systems as imaging materials," *Photogr. Sci. Eng*. **16**, 291 (1972); I. Shimizu, H. Sakuma, H. Kokado, and E. Inoue, "The optical and electrical properties of metal photodoped chalcogenide glasses," *Bull. Chem. Soc. Jap*. **46**, 1291 (1973); T. Shirakawa, I. Shimizu, H. Kokado, and E. Inoue, "Relief image in Ag-chalcogenide glass sensors," *Photogr. Sci. Eng*. **19**, 139 (1975).

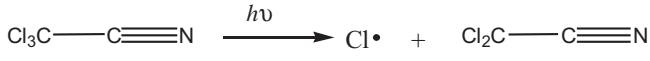
6.6.1.1.2.4 Triazines

Triazines (**XXXVII**) are a class of symmetrical initiators that fragment; upon excitation, they dissociate into three substituted nitriles (**XXXVIII**) (Scheme 6.42).[270] Specifically, the primary photoproducts are not radicals, but they dissociate into radicals in a secondary thermal step (Scheme 6.43).[271]



(**XXXVII**)

Scheme 6.42 Photodecomposition of triazine



(**XXXVIII**)

Scheme 6.43 Photodecomposition of nitriles

6.6.2 Radicals generated by hydrogen abstraction

Abstraction of hydrogen by excited-state molecules makes possible the generation of radicals from molecules with low excitation energies, which effectively extends photoionization (that can initiate photopolymerization of reactive monomers) into the visible part of the spectrum. Examples of H-abstraction reactions include those by the excited triplet states of ketones like anthraquinone (**XXXVIX**). Photoirradiation of anthraquinone, for instance, in the hydrogen donor solvent tetrahydrofuran (THF) leads to the following processes (Scheme 6.44).[272]

In the presence of a reactive monomer, the radicals formed by the hydrogen abstraction initiate chain polymerization. However, in the absence of any other reactive species, the radicals can combine to form dimers. The species that absorbs the radiation (anthraquinone) and gets promoted to an

[270]H. Sakuraji, M. Yoshida, H. Kinoshita, K. Utena, K. Tokumaru, and M. Yoshiro, "Structure-reactivity relationships in triplet sensitized photolysis of aromatic ketone O-acyloximes," *Tetrahedron Lett*. **20**, p. 1529 (1978).
[271]A. Reiser, *Photoactive Polymers: The Science and Technology of Resists*, John Wiley & Sons, New York, p. 113 (1989).
[272]ibid., pp. 113–114.

$$HfCl_4 \xrightarrow{h\nu(13.5)nm} Hf + 2Cl_2 \quad [6.53]$$

Photolysis of hafnium(IV) chloride

Tetraethyl tin is photodecomposed to metallic tin and ethane gas:

$$Sn(CH_3)_4 \xrightarrow{h\nu(13.5)nm} Sn + 2C_2H_6 \quad [6.54]$$

Photolysis of tetraethyl tin

The final step is the dry development of the EUV-patterned film. The substrate is transferred outside the vacuum ambient of the EUV tool before development is performed. Development involves heating the substrate to volatilize the unexposed region, leaving behind the exposed metallic mask. Following lithographic patterning, pattern transfer to the underlying substate is the same as in the conventional hard-mask-etch process.

Another variation of Lam's metal organic EUV resist process involves the CVD deposition of photosensitive metal oxide films such as organotin oxide from the reaction of suitable precursors and CO_2 in a RF plasma. Potential precursors could include, for example, halo alkyltin, alkoxyalkyltin, or amidoalkyltin, with specific examples including trimethyltin chloride, dimethyltin dichloride, methyltin trichloride, tris(dimethylamino)methyl tin(IV), and (dimethylamino)trimethyl tin(IV).[345]

Following the deposition of the photosensitive metal oxide film, the film-coated substrate is transferred under vacuum to an EUV exposure tool for patterning. Upon EUV exposure, the organotin oxide dimerizes in the exposed region of the film, inducing a chemical contrast between the exposed and unexposed areas (Reaction 6.55).

$$CH_3Sn(SnO)_3 \xrightarrow{h\nu(13.5)nm} Sn_2[(SnO)_3]_2 \quad [6.55]$$

Photolysis of alkyl tin oxide

Development involves contacting the exposed film with hot ethanol solution, which removes the unexposed area, leaving behind the metal oxide.

6.10 Lithographic Applications of Photopolymerization Negative Resists

Photoinitiated polymerization in negative resists used in lithography has found its main applications in lithographic offset plates in dry resists used in the printing of wire boards, printed circuit boards, solder masks, etc. Other emerging applications of this class of resists are in thick film imaging for MEMS applications as well as in 3D lithography, which is often referred to as

[345]D. Smith and D. M. Hausmann, "EUV photopatterning of vapor-deposited metal oxide-containing hardmasks," U.S. Patent No. 9,996,004 (2018).

Chapter 7
Chemistry of Photochemical and Radiochemical Imaging Mechanisms of Positive-Tone Resists

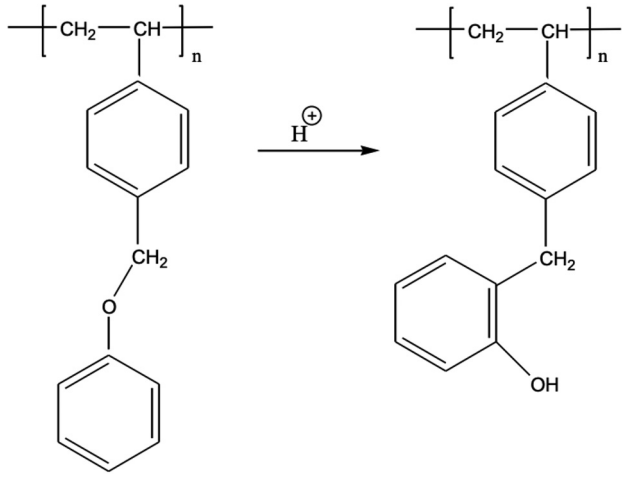
"... and may not bodies receive much of their activity from the particles of light which enter into their composition?"

Isaac Newton, *Opticks*

7.1 Introduction

The essential characteristic of a positive resist is that its exposed part gets dissolved away in a developer solution, while its unexposed part does not. Positive resists differ from their negative counterparts principally in their response to actinic radiation despite the fact that the essential compositions of the two resist types are similar in many ways: each contains sensitizers or appropriate radiation-sensitive compounds, resins, solvents, and additives. As in modern negative resists, the resins for positive resists are polymers, which are large molecules with repetitive sequences of monomers—groups of atoms—connected in a linear or branched fashion, as illustrated in Fig. 4.3. The physical, thermal, mechanical, and molecular weight properties of lithographic polymers are discussed in Chapter 4. Unlike some negative resists, positive resists do not swell in developer. Moreover, the use of aqueous stripping and developing solutions greatly simplifies the equipment selection for positive resists in process equipment tooling by allowing low-cost, readily available plastics to be used as containers. Problems associated with the use of flammable solvents are minimized with positive resists.[1]

[1]W. S. Deforest, *Photoresist Materials and Processes*, McGraw-Hill, New York, p. 47 (1975).



Scheme 7.44 Acid-catalyzed Claisen rearrangement of poly(4-phenoxymethyl styrene)

transformation, the resist polymer changes from the nonpolar to the polar state. Poly(4-phenoxymethyl styrene) is isomerized in a similar manner with an acid as a catalyst to a C-alkylated phenolic structure (Scheme 7.44).[343]

7.2.2.2.1.3 Chemically amplified positive resists based on depolymerization

Poly(phthalaldehyde) resists. Unaware of the first patent granted for a CAR (granted to 3M Corporation), C. G. Willson, J. M. J. Fréchet, and H. Ito set out in the late 1970s to develop chemically amplified DUV resists. Their first attempt,[344] which was the second CAR invented for use in lithographic resist applications, involved the use of poly(phthalaldehyde), which undergoes an equilibrium cyclopolymerization and has a ceiling temperature of about –40 °C. Their idea was to prepare the polymer below its ceiling temperature, then cap it and isolate the intrinsically unstable product. Reasoning that any photochemical event that can generate the anionic chain end above the ceiling temperature should cause spontaneous depolymerization to the monomer, they prepared the polymer by anionic copolymerization of phthalaldehyde and *o*-nitrobenzaldehyde monomers and capped it with acylating agents. They incorporated *o*-nitrobenzaldehyde as a monomer into the polymer to render it photosensitive. Exposing the films of the capped copolymer to DUV radiation resulted in spontaneous relief image formation, but the resulting images could

[343]H. Ito, *Chemical Amplification Resists for Microlithography*, *Adv. Polym. Sci.* **173**, Springer-Verlag, Berlin, p. 148 (2005).

[344]This is the second CAR invented for use in semiconductor lithography. Invented by Willson, Fréchet, and Ito, the resist upon exposure spontaneously and uncontrollably depolymerizes in an exothermic reaction that is sufficiently energetic to evaporate the monomer. These inventors were unaware of the 3M Corporation's patent on a similar concept (G. H. Smith and J. A. Bonham, U.S. Patent No. 3779,778 (1973).

Chapter 8
Chemistry of the Limiting Issues of Photochemical and Radiochemical Resists and Approaches to Their Solutions

"In Nature's infinite book of secrecy a little can I read."
William Shakespeare, *Antony and Cleopatra*

8.1 Introduction

As shrinking integrated circuit (IC) device dimensions, fueled by the need to increase device speed and density, approach dimensions considerably smaller than the practical resolution limit of conventional lithography, several advanced resist processing schemes have been proposed to accommodate the resolution requirements for IC devices at such extremely small technology nodes. These processing schemes were introduced at the 32-nm technology node and were extended to the 22-nm technology node; they have now become firmly established at the sub-22-nm technology nodes of 15 nm, 10 nm, and 7 nm, patterned with immersion ArF and EUV lithography. With the successful implementation of EUV lithography in manufacturing at the 10-nm and 7-nm technology nodes, patterning challenges have shifted from resolution to noise, sensitivity, overlay, and edge placement. Of these challenges, the materials-related issues are sensitivity and noise. Noise in this instance is the natural variation in lithographic pattern placement, shape, and size. It causes line edge roughness, linewidth variation, and stochastic defects. This noise is ultimately due to the random nature of discrete photon events, electron events, molecular positions, and molecular quantities involved in the radiation-based lithographic exposure patterning process. It equally determines the ultimate critical dimension uniformity obtainable with any given radiation-based lithographic exposure process.

8.3.2 Resolution limits due to confinement effects in resists

Resist technologies that will enable EUV lithographic patterning at the sub-22-nm technology nodes must be capable of exceptional CD control, in addition to having low LER. Given the significant attenuation of EUV radiation in organic materials, ultrathin resist (thickness ≤100 nm) imaging appears to be the only viable option for single-exposure patterning at the sub-22-nm technology nodes. The 2008 ITRS specifications call for a resist thickness of 35–65 nm for the 22-nm technology node. However, the stability of ultrathin resist (UTR) films presents very difficult challenges due primarily to confinement effects. In addition, UTR imaging will require materials (resists and underlayers such as hard masks) with superb etch selectivity and etch processes that lead to negligible roughness transfer between layer stacks.

As discussed in Chapter 1, experimental results suggest that material properties of UTR films can differ in significant ways from their bulk counterparts. Of particular interest, because of its influence on the viscoelastic behavior of spin-coated films, is the effect of film thickness on the glass transition temperature T_g (see Fig. 8.18). The T_g decreases with film thickness for the substrate investigated in the study.

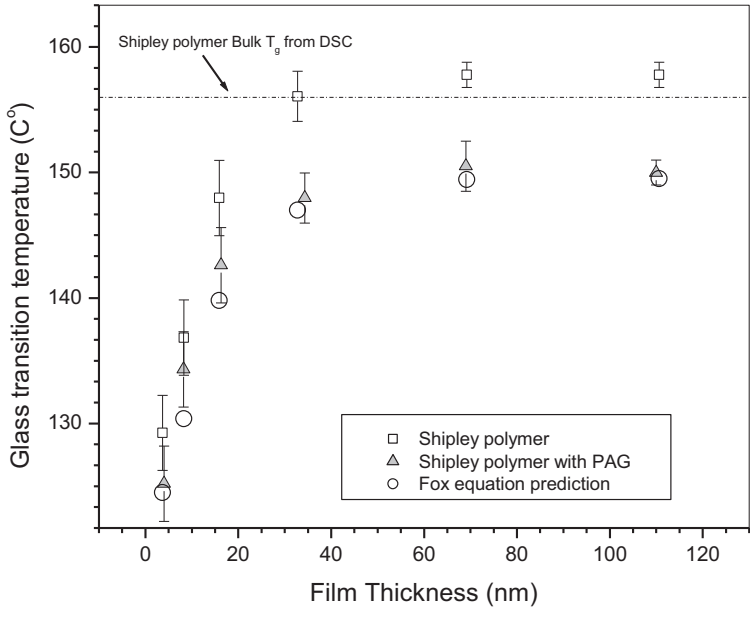


Figure 8.18 Glass transition temperature of a resist polymer and a resist polymer with PAG as a function of film thickness (reprinted from D'Amour, Frank, and Okoroanyanwu[53]).

[53]J. N. D'Amour, C. W. Frank, and U. Okoroanyanwu, "Measuring thermophysical properties of ultrathin photoresist films," *Proc. SPIE* **4690**, 936–942 (2002); J. D'Amour, C. W. Frank, and U. Okoroanyanwu, "Modification to thermophysical behavior in ultrathin polymer films," *Proc. SPIE* **5039**, 996–1007 (2003).

electrons of the metals. Further, the high EUV absorptivity of these metallic hard mask resists enhances their photosensitivity to EUV exposure.

8.5 Resist Materials Outlook for the Advanced Technology Nodes

It is expected that EUV lithography would be used to pattern devices at the advanced technology nodes of 5 nm, 3 nm, and 1.5 nm. To support patterning at these nodes, research efforts should be devoted to developing: (1) high-NA resist concepts beyond CARS that involve high-absorbance materials, including resists and underlayers, and development of new contrast mechanisms for high-NA EUV lithography; and (2) positive-tone metal containing resists or other resist concepts. Resists based on the condensation mechanism of metal oxo-hydroxo networks with organic and peroxo ligands, formulated from clusters with uniform molecular weights, appear to be promising candidates for these applications.

The chemical amplification concept has served the lithographic community well over many technology nodes. It still has a lot to give but is almost operating at its limits. Image blur caused by acid diffusion into unexposed areas of resists can only be limited, but not eliminated, if high sensitivity due to chemical amplification is to be maintained. This is because the mechanisms responsible for high sensitivity in CARs are intimately tied to the processes that lead to image blurring. This makes it extremely difficult, if not impossible, to strike the right resolution–LER–sensitivity trade-off balance with CARs based on the conventional design concepts. To this end, novel resist design concepts such as the multi-trigger resist concept and the photosensitization chemical amplification concept (both discussed above) are gaining traction within the semiconductor industry. So far, both techniques have demonstrated promising performance results with respect to meeting the resolution–LER–sensitivity target for some of the advanced technology nodes. In addition, the development of vapor deposited, dry developed metallic hard mask resists offers significant opportunities for improving sensitivity, LER, and linewidth variation.

Other new resist design concepts incorporating different polymer architectures and PAGs that can achieve high sensitivity are currently under serious exploration. Such alternative resist design concepts could incorporate photocatalysts with well-defined limited lifetimes, whose diffusion length at a nominal processing temperature could be targeted to match the resolution requirements at advanced technology node design rules. This will ensure that, at the barest minimum, the acid can only diffuse to a manageable distance that should fall within the geometry of the given advanced technology node design rules.

Chapter 9
Chemistry of Self-Assembling Lithographic Imaging Mechanisms

"The cause is hidden. The effect is visible to all."
Publius Ovidus Nasso [Ovid]

9.1 Introduction

Lithography based on self-assembly exploits the thermodynamic drive of certain systems such as block copolymers,[1] colloidal particles, and monolayers to spontaneously self-assemble into ordered structures. Three main variants of this phenomenon are exploited in lithography: block copolymer self-assembly, colloidal particle self-assembly, and monolayer self-assembly. Of these three variants of directed self-assembly (DSA) phenomena, directed block copolymer self-assembly is the one that has generated most interest in the semiconductor industry, where it is seen as a potential technology for complementary patterning to traditional radiation-based lithographic techniques in advanced technology nodes.[2] It is a patterning technique capable of pitch reduction and

[1]A detailed treatment of the theory of block copolymer self-assembly lithographic imaging mechanisms has been provided elsewhere; see, for example, U. Okoroanyanwu, *Molecular Theory of Lithography*, SPIE Press, Bellingham, Washington, Chapter 5 (2015). We highlight here essential chemical aspects of this theory, drawn largely from the above reference. We also examine the chemical aspects of a variety of strategies employed in lithographically directed block copolymer self-assembly, monomolecular-layer self-assembly lithography, and colloidal particle self-assembly lithography.

[2]K. Lai, C.-C. Liu, H. Tsai, Y. Xu, C. Chi, A. Raghunathan, P. Dhagat, L. Hu, O. Park, S. Jung, W. Cho, J. Morillo, J. Pitera, K. Schimdt, M. Guillorn, M. Brink, D. Sanders, N. Felix, T. Bailey, and M. Colburn, "Design technology co-optimization assessment for directed self-assembly-based lithography: Design for directed self-assembly or directed self-assembly for design?" *J. Micro/Nanolith. MEMS MOEMS* **16**(1), 013502 (2017); R. Tiron, A. Gharbi,

9.2.2 Block copolymer synthesis via controlled radical polymerization

The strategy underlying controlled radical polymerization is to establish a dynamic equilibrium between a small fraction of growing free radicals and a large majority of dormant species, while eliminating or suppressing undesired termination and chain transfer reactions.[172] Such a dynamic and rapid equilibrium permits an equal opportunity for all growing or dormant chains to propagate via the frequent interconversion between the active and dormant species, leading to nearly uniform chains with narrow molecular-weight distribution. This technique reduces the rate of radical recombination by lowering the effective concentration of radicals.

The polymerization mechanism in controlled radical polymerization comprises: the initiation step, where the initiating radicals are formed via homolytic or heterolytic cleavage of the initiator into radicals, followed by addition of the radical across the double bond of the monomer; the propagation step, in which the monomers successively insert into the bond between the growing chain end and the radical; and the chain termination, where radicals combine with each other to form stable species. The propagation and termination of the generated free radicals proceed as in conventional radical polymerization, although the presence of a small fraction of radicals prevents premature termination.

The two main types of controlled radical polymerization techniques currently in use are: (1) stable free-radical polymerization (SFRP), involving the use of stable free-radicals such as nitroxides as reversible terminating agents to control the polymerization process,[173,174] and (2) atom transfer polymerization (ATRP).

As the living radical polymerization mechanism involves propagation through radicals, considerations involving monomer purity and reactivity in conjunction with relative rates of crossover and propagation reactions for the second monomer are factored into the overall sequential monomer addition synthetic strategy. The intermediate product formed after the polymerization of the first monomer must be able to initiate the polymerization of the second monomer. Often, this may require the purification of the intermediate product to eliminate all traces of the first monomer. Furthermore, if purification of the intermediate product is not done, statistical copolymerization of the second block may occur.

9.2.2.1 Block copolymers synthesis via atom transfer polymerization (ATRP)

In the ATRP technique, radicals are generated through a reversible redox process, catalyzed by transition metal complexes of Cu, Ru, Fe, Ni, Rh, or Pd, such as, for example, CuX/bipyridine, that undergo a one-electron

[172]K. Matjaszewski, "Mechanistic Aspects of Atom Transfer Radical Polymerization," in *Controlled Free Radical Polymerization*, K. Matyjaszewski, Ed., *ACS Symposium Series* **685**, American Chemical Society, Washington, D.C., pp. 258–283 (1998).

[173]G. Moad, E. Rizzardo, and D. H. Solomon, "Selectivity of the reaction of free radicals with styrene," *Macromolecules* **15**, 909 (1982).

[174]M. K. Georges, R. P. N. Veregin, P. M. Kazmaier, and G. K. Hamer, "Narrow molecular weight resins by a free-radical polymerization process," *Macromolecules* **26**, 2987 (1993).

9.2.6.4.5 Soft lithography

In the soft lithography method, resist is imprinted with a PDMS stamp to create grating patterns, following which a BCP film is spin-coated onto the space between the gratings to template the location of copolymer domains, which in turn self-assemble and align parallel to the gratings in an orientation perpendicular to the substrate.[301]

9.2.7 Scaling block copolymer domain periodicity

As described above, the BCP composition determines the block domain periodicity or pitch L_0, and by extension, the CDs that are patternable with the BCP; other factors that determine the block domain periodicity include the domain orientation and the overall pattern formation process. The directly controllable primary physical parameters are monomer type, compositional ratio, molecular weight, and polydispersity, as well as the purity of the BCP and the Flory–Huggins interaction parameter χ. The periodicity is related to the polymer chain length L_0, which in turn is related to the total degree of polymerization for each block. This implies that the length of each block, as controlled by the number of monomers in the block, is the determinant factor for the periodicity of the domain. Figure 9.14 illustrates how a BCP assembles to form the defined CD within the two guide parameters. Two polymer chains with similar ends interact to define the CD, shown as either blue or red domains. Because the two blocks have different polarities, phase separation ensures that the two ends of the BCP must have similar polarities to interact with each other. Thus, the two blue ends of the BCP in Fig. 9.14 must interact with each other.[302]

Polydispersity of the blocks of the BCP, a measure of the distribution of the molecular weight, plays a critical role in determining the uniformity or variability of domain pitch and CD uniformity. BCPs with blocks of unity monodispersity that have uniform chain lengths will yield more-uniform domain pitches and CDs, while BCPs with blocks that are polydispersed with polymer chains that are not of a uniform length will yield less-uniform domain pitches and CDs, and will also be more prone to imperfections during the self-assembly process.

A major factor that affects domain spacing is the ability of each block in the BCP to segregate into its own domain. The interaction parameter χ is a major determinant of this ability to self-segregate away from the other block. The stronger the interaction parameter χ between the blocks the easier it is for the two chains to assemble into their own domains, even when the chains are

[301]L. Li and H. Yokoyama, "Aligning single-layer cylinders of block copolymer nanodomains using soft molding," *Adv. Mater.* **17**, 1432–1436 (2005).
[302]D. J. Guerrero, "A lithographer's guide to patterning CMOS devices with directed self-assembly," *Spotlight Series*, SPIE Press, Bellingham, Washington, p. 4 (2020).

Chapter 10
Chemistry of Imprint Lithographic Imaging Mechanisms

"A small rock holds back a great wave."
Homer, *The Odyssey*

10.1 Introduction

Imprint lithography, invented by Chou and co-workers,[1] is a $1\times$ printing technique based on the principle of mechanical deformation of a thin thermoplastic polymeric film (in the case of thermal imprint lithography) or photocurable resist liquid film, comprising monomers, oligomers, additives, and initiators (in the case of UV imprint lithography), brought about by directly pressing the resist with a template/mold/stamp containing a negative of the pattern of the features to be printed such that the resist flows and fills the open areas of the mold, replicating the desired pattern. As its imaging mechanism is not mediated by photons or charged beam particles such as electrons or ions, which suffer from diffraction or beam scattering, imprint lithography can achieve resolutions beyond the limitations set by diffraction. Its resolution depends mainly on the minimum template feature size that can be fabricated, oftentimes with electron beam lithography. Among its many attractive attributes are high resolution, low cost of ownership, and its ability to pattern large-area structures in both planar and roll-to-roll formats, to mention but a few. One significant advantage of imprint lithography over standard photolithography is its ability to pattern three-dimensional (3D) topographies in a single step, thus reducing the cost of fabricating such a device.[1] Such topographies are critical for connecting different layers on an

[1]S. Y. Chou, P. R. Krauss, and P. J. Renstrom, "Imprint of sub 25 nm vias and trenches in polymers," *Appl. Phys. Lett.* **67**, 3114–3116 (1995).

Chapter 11
Lithographic Electrochemistry

"Much have I traveled in the realms of gold
And many goodly states and kingdoms seen."
John Keats, *On First Looking in Chapman's Homer*

11.1 Introduction

Some lithographic operations and processes are based on electrochemical phenomena. Two notable examples include (1) corrosion of metallic chrome (Cr) and molybdenum silicon (MoSi) absorber structures in optical masks and (2) electrochemical imprint lithography. Both phenomena are based on electrochemical anodic oxidation. We explore in this chapter the electrochemical basis of these two phenomena.

11.1.1 Corrosion in lithography

Like most metals in everyday use, metals used in lithography tend to revert to their thermodynamically stable state, which is usually an oxide; as examples, chromium oxide is the basis of the scale or crud on corroded chrome mask absorbers in optical lithography, and silicon dioxide is the basis of anodically oxidized patterned structures transferred to silicon substrates patterned with an electrochemical imprint mask coated with noble metals such as platinum and gold. Note that any oxidation is, strictly speaking, electrochemical in nature since it is a chemical reaction involving the transfer of electrons.

Although the formation of chromium oxide on optical lithographic masks and silicon dioxide on patterned silicon substrates is based on electrochemical anodic oxidation, the formation of each differs from the other in its essential aspects. The formation of chromium oxide crud on optical lithographic masks is an unintended process-induced consequence of a specific lithographic unit operation, namely, extended irradiation of chrome-on-glass masks in an exposure chamber with 6.4-eV photons and with an appreciable amount of residual moisture that can settle on the surface of the masks, which forms an

Chapter 12
Lithographic Colloidal Chemistry

"Here the boundaries meet and all contradictions exist side by side."
Fyodor Dostoevsky, *The Brothers Karamazov*

12.1 Introduction

We encounter many types of colloidal[1] systems in lithography. These systems involve dispersion of one finely divided or microscopic phase (typically solid particles) in another (typically a liquid).[2] Examples of colloidal dispersions in lithography are shown in Table 12.1. These lithographic resist colloidal solutions must be distinguished from molecular mixtures or true solutions that are encountered in lithography, such as optical lithographic photoresist formulations that are formed from the dissolution of resist polymeric resins and additives in appropriate solvents, or from the dissolution of exposed positive-tone photoresists in 0.24 N tetramethyl ammonium hydroxide aqueous developer, or from the negative-tone development of unexposed photoresists in organic solvents such as n-butyl acetate.

[1]The term *colloid* is derived from the Greek word *kola* for glue. It was originally used to refer to gelatinous polymeric colloids, which Thomas Graham identified in 1860 in his experiments on osmosis and diffusion. Today, a colloid refers to a particle in the size range of 50 Å to 50 μm. The theories that explain the characteristics of colloids, including their stability and related phenomena, are sufficiently treated within the general topics of interfacial and electrostatic phenomena in classical texts on colloid chemistry [see, for example, J. T. Davies and E. K. Rideal, *Interfacial Phenomena*, Academic Press, New York (1961)] as well as in applied texts [such as R. M. Pashley and M. E. Karaman, *Applied Colloid and Surface Chemistry*, John Wiley & Sons, Ltd., Chichester (2004)]. We adapt the formalisms of these theories to the specific cases of the colloids used in technological applications in lithographic inks and resists. We adopt the notation and aspects of the derivations used by Pashley and Karaman in their text.

[2]This dispersion of one finely divided phase in another is quite different from molecular mixtures.

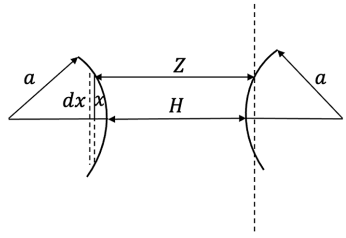


Figure 12.10 Diagram illustrating the Derjaguin approximation for the interaction between two spherical lithographic colloidal particles.

$$V_s \approx 2\pi \int_{Z=H}^{Z=\infty} V_F x dx. \tag{12.57}$$

Rearranging Eq. (12.57), we obtain

$$V_s \approx \pi a \int_{Z=H}^{Z=\infty} V_F dZ. \tag{12.58}$$

Substituting Eq. (12.56) into Eq. (12.58), we obtain the corresponding electrostatic interaction energy between the two spheres:

$$V_s \approx 2\pi a \varepsilon_0 D \psi_0^2 \exp(-\kappa H), \tag{12.59}$$

where H is the distance between the spheres. Equation (12.59) indicates that the interaction energy decays exponentially and is strongly dependent on both the surface electrostatic potential and the electrolyte concentration.

12.2.2 The DLVO theory of colloidal stability

The DLVO theory (named after Derjaguin, Landau, Verwey, and Overbeek) explains the tendency of colloids to agglomerate or remain stable (or dispersed). It uses the balance between two opposing forces—electrostatic repulsion and van der Waals attraction—to explain the stability of colloidal systems. We discussed repulsive electrostatic interaction in the previous section. The electrostatic interaction between two interacting spherical particles is given by Eq. (12.59). Van der Waals attraction, on the other hand, is the result of forces between individual molecules in each colloid. Its effect is additive and involves the total interaction of every molecule in one particle with that in the other particle. The van der Waals attraction between two interacting spherical colloids (Fig. 12.11) is given by

$$V_{123}(D) = -\frac{aA_{121}}{12H}, \tag{12.60}$$

Uzodinma Okoroanyanwu, a research associate professor in the department of polymer science and engineering of University of Massachusetts at Amherst, conducts research aimed at developing materials and devices used in electrochemical energy storage; chemical sensing; printed, flexible, flexible/hybrid and wearable electronics; and electromagnetic interference shielding. He is an SPIE Fellow and an associate editor of the *Journal of Micro/Nanopatterning, Materials, and Metrology*. He is also the founder of Enx Labs, a company that translates his research results into devices and instruments that help to improve the human condition and sustain the environment. He worked previously at Advanced Micro Devices, where he spent 12 years conducting research on advanced lithography and organic polymer memories, and at GLOBALFOUNDRIES, where he spent 4 years conducting research on advanced lithography. He is the author of several books, including *Chemistry and Lithography*, *2nd edition, Vol. 1*: *The Chemical History of Lithography* (SPIE Press, 2020); *Molecular Theory of Lithography* (SPIE Press, 2015); and *Chemistry and Lithography* (SPIE Press & John Wiley & Sons, 2010). A holder of 37 U.S patents, he was educated at The University of Texas at Austin, where he earned the following degrees: Ph.D. physical chemistry (1997), M.S. chemical engineering (1995), M.A. physical chemistry (1994), B.S. chemistry and chemical engineering (1991).