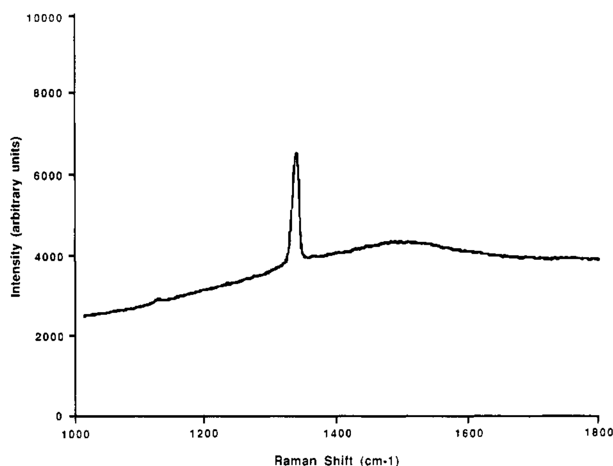

Figure 2. Raman spectrum of the free-standing film showing the characteristic peak for diamond at 1332 cm^{-1}. The shoulder at ~1550 cm^{-1} is virtually absent, indicating compositional purity.

diamond. This graphitic carbon lowers the overall purity and quality of the diamond film. Similar effects may occur in the growth of CVD diamond on other substrates.

To avoid the formation of an excessively graphitic deposit in the initial stages of the deposition, an experimental run was performed with an altered sequence of events. The reactor was pumped down to 10^{-4} Torr as before, but instead of flowing both H_2 and CH_4 simultaneously to raise the pressure to 25 Torr, only H_2 was used. Next the filament was heated to glowing in pure H_2 and then the CH_4 flow was initiated, well after the filament and substrate temperatures were stabilized. This resulted in films that appeared lighter in color on the glass side.

In conclusion, we have demonstrated that it is possible to grow diamond on a nonadhering, amorphous substrate, in this case glass, and this approach provides an entree into the growth of better free-standing films of diamond with macrostructures designed for particular applications. In addition, the morphological and compositional differences in the film adjacent to the glass substrate as compared to that on the outer surface have been noted, and a possible reason for these has been postulated, which may have vital consequences for diamond growth on other substrates.

Acknowledgment. H.C.F. thanks the National Science Foundation for support of this work through the Presidential Young Investigator award (CBT-No. 8657614). We express our thanks to Central Research and Development at Du Pont for the use of the Raman spectrometer.

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Reviews

Chemical Amplification Mechanisms for Microlithography

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Continued advances in microelectronic device fabrication are trying the limits of conventional lithographic techniques. In particular, conventional photoresist materials are not appropriate for use with the new technologies that will be necessary for sub-0.5-μm lithography. One approach to the design of new resist chemistries involves the concept of chemical amplification, where one photochemical event can lead to a cascade of subsequent reactions that allow patterning of the parent material. Generally, chemically amplified resists utilize photochemically generated acid to catalyze cross-linking or deprotection reactions. This paper reviews the chemistries that have been evaluated for chemical amplification resist processes; acid generator, cross-linking, deprotection, and depolymerization chemistry.

Introduction

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 substrate of a semiconducting material such as silicon. The performance of the device is, to a large degree, governed by the size of the individual circuit elements. As a general rule, the smaller the elements, the faster the device and the more operations it can perform. The device structure is produced by a series of steps used to pattern each layer precisely.[1,2] The patterns are formed by lithographic processes that consist of two steps: (1) delineation of the patterns in a thin radiation-sensitive polymer film (resist); (2) transfer of that pattern into the substrate using an appropriate etching technique. A schematic representation of the lithographic process is shown in Figure 1.

Significant advances are continually being made in microelectronic device fabrication and, especially in lithography, the technique that is used to generate the high-resolution circuit elements characteristic of today's integrated circuits. Fifteen years ago, the state-of-the-art device contained up to 8000 transistor elements and had 5-6-μm minimum features. Today, devices with several million transistor cells are commercially available and are fabricated with minimum features in the range of 0.8 μm.[3,4]

(1) Sze, S. M. *VLSI Technology*; McGraw-Hill: New York, 1983.
(2) Wolf, S.; Tauber, R. N. *Silicon Processing for the VLSI Era*; Lattice Press: Sunset Beach, CA, 1986.
(3) *Electronic and Photonic Applications of Polymers*; ACS Advances in Chemistry Series, No. 218; Bowden, M. J., Turner, S. R., Eds.; American Chemical Society: Washington, D.C., 1988.

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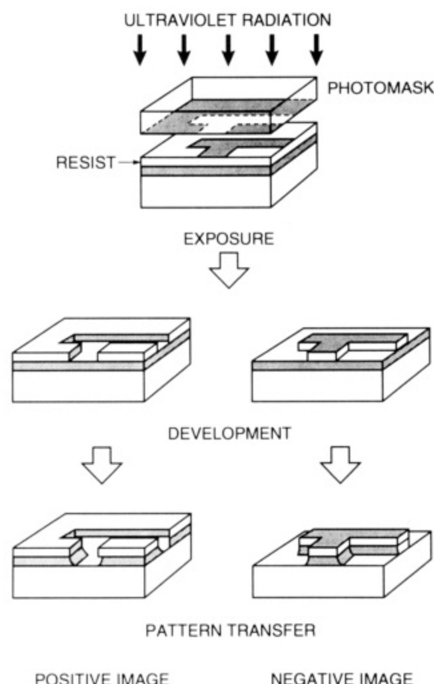


Figure 1. Schematic representation of the lithographic process involving development of a relief image in a polymeric resist. Exposure effects a chemical change in the resist that allows pattern differentiation during development.

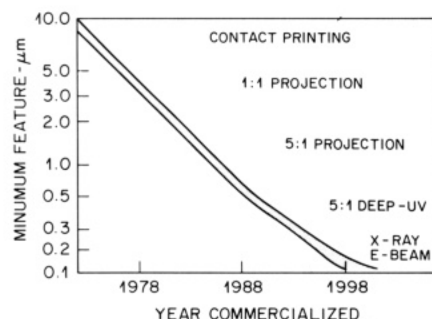


Figure 2. Graphical representation of the minimum feature size vs year of commercialization for MOS devices. Description of the methods of lithographic printing are also given in the figure, and the reader is referred to ref 6 for detailed descriptions of the technologies.

The trend associated with this phenomenon is shown in Figure 2. These accomplishments have been achieved by using "conventional photolithography" (photolithography employing 350–450-nm light) as the technology of choice. Incremental improvements in tool design and performance have allowed the continued use of 350–450-nm light to produce ever smaller features.[5] However, the ultimate resolution of a printing technique is governed, at the extreme, by the wavelength of the light (or radiation) used to form the image, with shorter wavelengths yielding higher resolution. The same physical principles also govern the resolution limits in microscopy.[6] Additionally, the same basic positive photoresist consisting of a photoactive compound that belongs to the diazonaphthoquinone chemical family and a novolac resin (Figure 3) has been in pervasive use since the mid-1970s and will likely be the resist of choice for several more years.[7,8] The cost of introducing

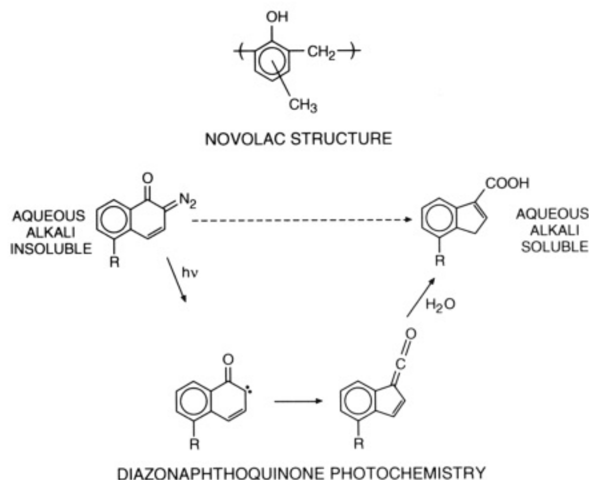


Figure 3. Chemistry associated with a typical conventional positive photoresist. The aqueous insoluble diazonaphthoquinone renders the novolac matrix insoluble in aqueous base. Irradiation generates the indene carboxylic acid, which allows aqueous base development of the exposed regions.

a new technology, which includes the cost associated with the development and implementation of new hardware and resist materials, is a strong driving force 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 (deep-UV, 220–280 nm) photolithography, scanning or projection electron-beam, X-ray, and scanning ion-beam lithography.[3,9]

Unfortunately, conventional photoresists are not appropriate for use with the new lithographic technologies that will be necessary for sub-0.5-μm lithography. The most notable deficiencies of the conventional novolac–quinonediazide resists are the sensitivity and absorption properties of the materials. For most resists, the quantum yield is significantly less than 1.0, and since the new lithographic tools in general have low-brightness sources, highly sensitive resists are required. Additionally in the case of deep-UV lithography, the absorption of conventional photoresists is too high to allow uniform imaging through practical resist film thickness (~1 μm). Thus, no matter which technology becomes dominant after photolithography has reached its resolution limit (0.3–0.5 μm), new resists and processes will be required, necessitating enormous investments in research and process development.[10] The introduction of new resist materials and processes will also require a considerable lead time, probably in excess of five years, to bring them to the performance level currently realized by conventional positive photoresists.

Resist Design Requirements

The focus of this paper concerns the design of polymer/organic materials and chemistry that may prove useful in radiation-sensitive resist films. Such chemistry

(4) Powell, M. W. *Solid State Technol.* **1989**, *32*(3), 66.
(5) McCoy, J. H.; Lee, W.; Varnell, G. L. *Solid State Technol.* **1989**, *32*(3), 87.
(6) Thompson, L. F.; Willson, C. G.; Bowden, M. J. *Introduction to Microlithography*; ACS Symposium Series, No. 219; American Chemical Society: Washington, D.C., 1983.
(7) Reichmanis, E.; Thompson, L. F. *Chem. Rev.* **1989**, *89*, 1273.
(8) Willson, C. G. In *Introduction to Microlithography*; ACS Symposium Series, No. 219; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; American Chemical Society: Washington, D.C., 1983; pp 83–159.
(9) Thompson, L. D. In *Introduction to Microlithography*; ACS Symposium Series, No. 219; Thompson, L. F., Willson, C. G., Bowden, M. J., Eds.; American Chemical Society: Washington, D.C., 1983; pp 2–13.
(10) Reichmanis, E.; Thompson, L. F. In *Polymers in Microlithography: Materials and Processes*; ACS Symposium Series, No. 412; Reichmanis, E., MacDonald, S. A., Iwayanagi, T.; American Chemical Society: Washington, D.C., 1989; pp 1–24.

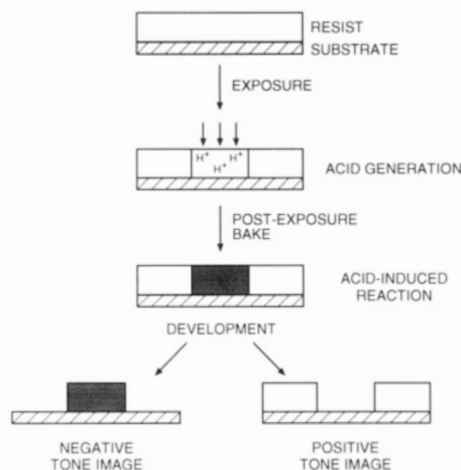


Figure 4. Schematic representation of a generalized chemically amplified resist process.

must be chosen to meet the specific requirements of each lithographic technology. Although these requirements vary according to the radiation source and device process requirements, the following are ubiquitous:[11]

(a) **Sensitivity** is a measure of how efficiently a resist responds to a given amount of radiation and is similar to the "speed" of photographic film. Sensitivity is inversely proportional to absorbed dose, which is measured in units of energy per unit area (for example, millijoules per square centimeter, mJ/cm^2). Thus, smaller dose values represent higher sensitivity.

(b) **Contrast** is a measure of the *rate* of chemical change (solubility change) upon exposure to radiation and is an indication of the resolution capability of a resist. It is determined by measuring the change in resist thickness during development per unit dose.

(c) **Resolution** is the smallest lithographically useful image that can be formed.

(d) **Etching resistance** is the ability of the patterned resist to withstand the liquid or plasma etching conditions used to transfer the resist image into the underlying thin film of metal or semiconductor material.

(e) **Purity** is of paramount importance since semiconductor device performance can be significantly affected by tiny quantities of impurity atoms or ions.

These characteristics can be achieved by careful manipulation of polymer structure, molecular properties, and synthetic methods.[7]

As mentioned above, sensitivity is a key issue that must be addressed in the development of resist materials. One approach to improving sensitivity involves the concept of chemical amplification,[12,13] which employs the photogeneration of species that catalyze many subsequent chemical events such as deblocking of a protective group or cross-linking of a matrix resin (Figure 4). The overall quantum efficiency of such reactions is thus effectively much higher than that for initial catalyst formation. While the active species could be either ionic or radical in nature, this discussion will be limited to acid-catalyzed processes. A chemically amplified resist is thus generally composed of three or more elements: (i) a matrix polymer, (ii) a photoacid generator, and (iii) a moiety capable of effecting differentiation between the exposed and unexposed regions of the film either through a cross-linking reaction or other molecular transformation. These elements may be either discrete molecular entities that are formulated into a multicomponent resist system[12,13] or elements of a single polymer.[14]

The materials issues that must be considered in designing appropriate chemistry are given below. The matrix polymer must (i) exhibit solubility in solvents that allow the coating of uniform, detect-free, thin films, (ii) be sufficiently thermally stable to withstand the temperatures and conditions used with standard device processes, (iii) exhibit no flow during pattern transfer of the resist image into the device substrate, (iv) possess a functionality that will allow pattern differentiation after irradiation, and (v) have absorption characteristics that will permit uniform imaging through the thickness of a resist film. In general, thermally stable (>150 °C), high glass transition temperature (T_g >90 °C) materials with low absorption at the wavelength of interest are desired.

The photoacid generator (PAG) should (i) have sufficient radiation sensitivity to ensure adequate acid generation for good resist sensitivity (for photochemical reactions a quantum yield >0.1 is desirable), (ii) be free of metallic elements such as antimony or arsenic that are perceived to be device contaminants, (iii) be fully compatible with the matrix resin to eliminate the possibility of phase separation, (iv) be stable to temperatures typically seen in device process environments to avoid premature thermal generation of acid, (v) produce species to effect the desired postexposure reaction with high yield, and (vi) for photochemical processes, have absorbance characteristics that are commensurate with uniform absorption of light through the thickness of the resist film.[15]

If other additives are to be employed to effect the desired reaction, similar criteria apply. Specifically, they must be nonvolatile, be stable at typical device process temperatures, possess a reactive functionality that will allow pattern differentiation after irradiation, and have low absorbance.

The discussion regarding the chemistries that have been evaluated for chemically amplified resists is divided into five subject areas: acid generator chemistry, cross-linking chemistry, rearrangement chemistry, deprotection chemistry, and depolymerization chemistry. This discussion will be preceded by a brief overview of Process Considerations.

Process Considerations

The inherent sensitivity associated with most chemically amplified resists emanates from the catalytic action of the acid during the postexposure baking step. Typical turnover rates (catalytic chain length) for each acid molecule in a working resist formulation are in the 800–1200 range.[16] For a given chemistry, the deprotection or cross-linking turnover rates are critically dependent on postexposure bake temperature, time, and the method of bake itself.

(11) Thompson, L. F.; Bowden, M. J. In *Introduction to Microlithography*; ACS Symposium, No. 219; American Chemical Society: Washington, D.C., 1983; pp 162–214.

(12) (a) Crivello, J. V. *Proc. Reg. Tech. Conf. on Photopolymers*; mid-Hudson section, SPE, Nov 8–10, 1982, Ellenville, NY; pp 267–284. (b) Crivello, J. V. In *Polymers in Electronics*; ACS Symposium Series, No. 242; Davidson, T., Ed.; American Chemical Society: Washington, D.C., 1984; pp 3–10.

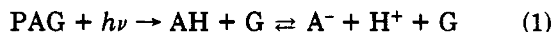
(13) (a) Ito, H.; Willson, C. G. In ref 12a, pp 331–354. (b) Frechet, J. M. J.; Ito, H.; Willson, C. G. *Proc. Microcircuit Engineering 82*; Grenoble, France, 1982; pp 260. (c) Ito, H.; Willson, C. G. In ref 12b, pp 11–23.

(14) Novembre, A. E.; Tai, W. W.; Nalamasu, O.; Kometani, J. M.; Houlihan, F. M.; Neenan, T. X.; Reichmanis, E. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1990**, *31*, 379.

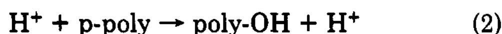
(15) Houlihan, F. M.; Neenan, T. X.; Reichmanis, E.; Kometani, J. M.; Thompson, L. F.; Chin, T.; Nalamasu, O. *J. Photopolym. Sci. Technol.* **1990**, *3*, 259.

(16) McKean, D. R.; Schaedeli, U.; MacDonald, S. A. In *Polymers in Microlithography*; ACS Symposium Series, No. 412; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemistry Society: Washington, D.C., 1989; pp 27–38.

The postexposure-bake (PEB) step has proved to be critical, and in order to understand the processing considerations it is instructive to discuss, qualitatively, the various primary and secondary reactions that occur in these systems during both exposure and PEB.[17] For the sake of simplicity, only a deprotection reaction will be considered. Pertinent reactions are as follows:



$$\mathrm{PAG} + h\nu \rightarrow \mathrm{AH} + \mathrm{G} \rightleftarrows \mathrm{A^-} + \mathrm{H^+} + \mathrm{G} \quad (1)$$



$$\mathrm{H^+} + \text{p-poly} \rightarrow \text{poly-OH} + \mathrm{H^+} \quad (2)$$

$$\mathrm{A^-} + \mathrm{C^+} \rightarrow \mathrm{AC} \quad (3)$$

$$\mathrm{H^+} + \mathrm{D^-} \rightarrow \mathrm{HD} \quad (4)$$

where PAG is the radiation-sensitive acid generator, C^+ is an unknown contaminant that could react with A^-, H^+ is the photogenerated proton that is regenerated after each deprotection reaction (4) and A^- is its counterion, G is a byproduct of the photochemical reaction, D^- is an unknown contaminant that can react with the proton thus depleting the supply of H^+, p-poly is the protected polymer, and poly-OH is the alkali-soluble product polymer. The presence of contaminants such as C^+ and D^- is inferred from observed lithographic results, such as postexposure-bake delay effects.[18] These effects must be considered in the design of chemically amplified resists that operate by any of the mechanisms that will be described in this paper.

The PAG molecule is converted to a strong acid (AH) upon absorption of a photon, and the rate of this reaction is fast, with the extent of reaction being governed by the quantum efficiency of the particular acid generator and exposure energy. The acid effects the desired deprotection reaction (2) with a characteristic rate, which is a function of the acid concentration, $[H^+]$, the temperature, and most importantly the diffusion rate of the acid in the polymer matrix. The diffusion rate in turn depends on the acid structure, the temperature, and the polarity of the polymer matrix. At room temperature, the rate of the deprotection reaction is typically slow and it is generally necessary to heat the film to well above room temperature to increase the rate to acceptable levels. The acid (H^+) is regenerated (reaction 2) and continues to be available for subsequent reaction, hence the *amplification* nature of the system.

From these highly idealized reactions, one can gain an understanding of some potential difficulties and process-related concerns. For this system to work satisfactorily, it would be necessary for the radiation-generated acid concentration, $[H^+]$, to remain uniform throughout the exposed regions. However, in many chemically amplified systems, undesired side reactions prematurely destroy the acid, i.e, reactions with contaminants such as water, ions, or reactive sites on the polymer (reactions 3 and 4). When such reactions occur selectively within the resist film, i.e., at the resist/air interface, resist imaging can be deleteriously affected.[18] While the exact nature of these reactions differs for each type of chemically amplified system and they are not fully understood, the generalized reactions, in conjunction with information concerning the ability of a given acid to diffuse, can be used to design a chemically amplified resist system. An overview of the available chemistries follows.

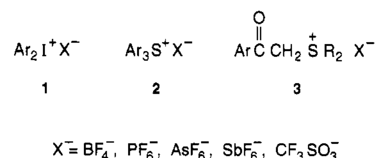
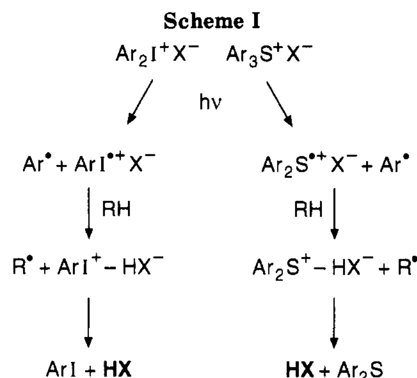


Figure 5. Representative chemical structures of the diaryliodonium salts (1), triarylsulfonium salts (2), and dialkylphenacylsulfonium salts (3).

Scheme I



Acid Generator Chemistry

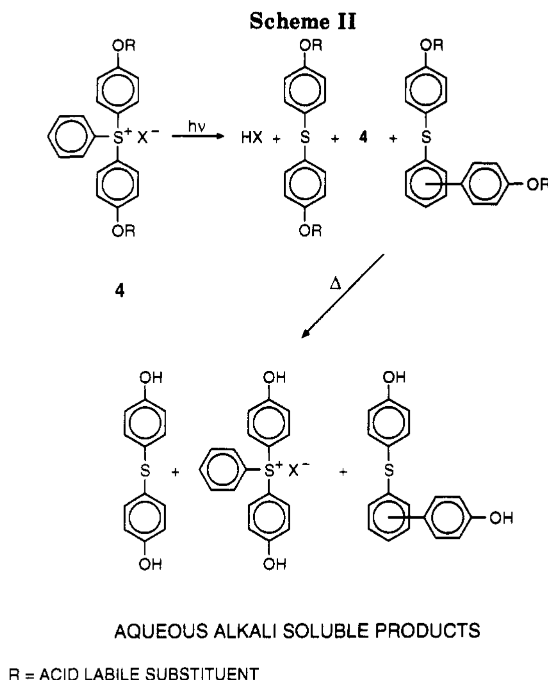
A key and ubiquitous element of chemically amplified resist formulations is the photoacid generator (PAG). A PAG is required for either the cross-linking or deprotection schemes and is also often needed for depolymerization mechanisms. Acid generator chemistry will be discussed separately since any of the available materials might find application in a chemically amplified resist composition. This section is divided into two parts, namely, ionic and nonionic acid generator materials.

Ionic Acid Generators. The dominant ionic photogenerators of acid are a class of materials called onium salts first used by Crivello as photoinitators for cationic polymerization.[19–21] Typical examples are the diaryliodonium salts,[20] **1**, and triarylsulfonium salts, **2** (Figure 5).[22] When these salts are irradiated (at wavelengths in the range 200–300 nm for R = phenyl), they undergo irreversible photolysis with rupture of a carbon–iodine or carbon–sulfur bond. Abstraction of a hydrogen atom from a surrounding "solvent", R–H, results in the formation of a protic acid (Scheme I).[19,22] A special class of onium salts, the dialkylphenacylsulfonium salts,[23] **3**, undergoes reversible dissociation upon irradiation with generation of ylides and protonic acids. One problem associated with the onium salts is that the key step in the photolysis involves the photogeneration of radical and radical cation intermediates, which in many applications may lead to undesirable competitive processes. Additionally, their ionic nature may lead to low solubility in polymer matrices.

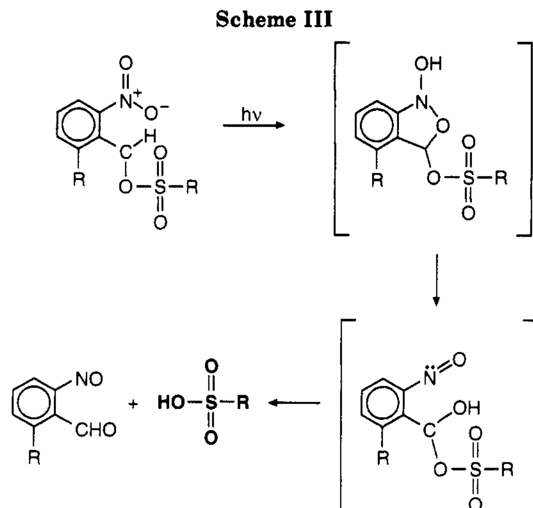
The iodonium and sulfonium salts have several advantages as photochemical acid generators. They can be designed to be thermally stable (>200 °C) and may be structurally modified to alter their spectral absorption characteristics. A wide variety of acids may be photochemically generated from these materials, including such strong inorganic acids as hexafluoroarsenic and hexafluoroantimonic acids. Onium salts are also currently the only known source from which the strongest known organic

(17) Houlihan, F. M.; Reichmanis, E.; Thompson, L. F.; Tarascon, R. G. In ref 16, pp 39–56.
(18) (a) Nalamasu, O.; Reichmanis, E.; Cheng, M.; Pol, V.; Kometani, J. M.; Houlihan, F. M.; Neenan, T. X.; Bohrer, M. P.; Mixon, D. A.; Thompson, L. F. *Proc. SPIE*, in press. (b) MacDonald, S. A.; Snyder, C. D.; Clecak, N. J.; Went, R.; Willson, C. G.; Knors, C. J.; Deyoe, N. B.; Maltabes, J. G.; Morrow, J. R. *Proc. SPIE*, in press.
(19) Crivello, J. V.; Lee, J. L.; Coulon, D. A. *Makromol. Chem., Makromol. Symp.* **1988**, *13/14*, 145.
(20) Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307.
(21) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977.
(22) Dektar, J. L.; Hacker, N. P. *J. Am. Chem. Soc.* **1990**, *112*, 6004.
(23) Crivello, J. V. U.S. Patent 4,245,029, Jan 13, 1981.

Scheme II



Scheme III



acid, triflic acid, may be photogenerated. These materials have also been modified to allow their use as dissolution inhibitors for phenolic matrix polymers. In this novel approach, Schwalm (Scheme II) developed a series of sulfonium salts that themselves contain acid-sensitive solubilizing groups.[24] Upon irradiation, the onium salt generates acid, which removes the protecting groups from the parent onium salt and its irradiation products, rendering them base soluble.

Nonionic Acid Generators. There are many systems described in the literature concerning the photogeneration of acid from nonionic compounds. Many of these involve the generation of sulfonic acids, which are strong organic acids with reasonably low nucleophilicity. Houlihan et al. have described photochemical sulfonic acid generators based upon 2-nitrobenzyl esters.[25-27] These compounds generate acid through the well-known *o*-nitrobenzyl rearrangement, which is a photochemically induced intramolecular rearrangement, shown in Scheme III. Nitrobenzyl esters have certain advantages as photochemical acid generators. The nitro group is a well-known inhibitor for radical processes, and as a result, secondary reactions occurring due to radical generation are minimized. While the unsubstituted 2-nitrobenzyl materials lack adequate thermal stability, 2,6-dinitrobenzyl tosylate is stable up to ~200 °C. The thermal stability of the esters can be dramatically increased by the introduction of an electron-withdrawing, sterically bulky group (Br, CF_3) at the other ortho position of the benzyl moiety. This enhancement in thermal stability allows access to thermally stable photogenerators of acid based upon materials such as pentafluorobenzenesulfonic acid or 2,2,2-trifluoroethanesulfonic acid.[27]

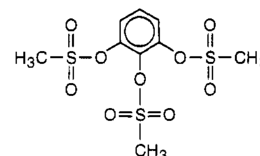
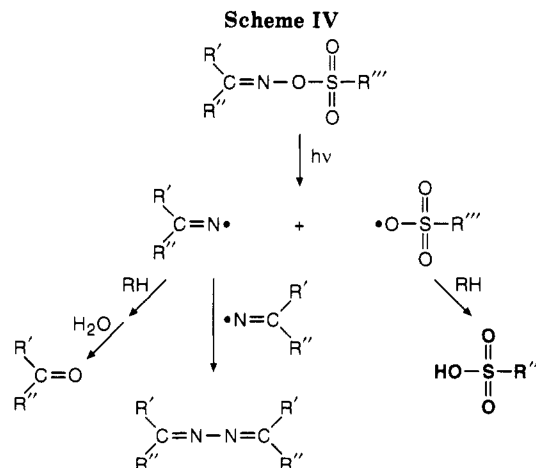


Figure 6. Chemical structure of 1,2,3-tris(methanesulfonyloxy)benzene.

Scheme IV



A positive deep-UV photoresist system has been described by Ueno and co-workers that consists of 1,3,5-tris(methanesulfonyloxy)benzene (Figure 6), bisphenol A protected with *tert*-butoxycarbonyl groups as a dissolution inhibitor, and a novolac matrix polymer.[28] This system is reported to generate methanesulfonic acid with a quantum yield (number of acid moieties generated per photon absorbed) of 19.7. Since the theoretical upper limit for the quantum yield is 3, the mechanism for acid generation was studied in more detail. UV spectroscopic studies showed that the novolac resin itself strongly sensitized tris(methanesulfonyloxy)benzene toward acid generation, presumably via a charge-transfer intermediate.

Imino sulfonate derivatives have recently been proposed as an alternative source of photochemically produced sulfonic acids.[29] These sulfonates are prepared from the reaction of a sulfonyl chloride with an oxime. Since the structure of both the oxime and the sulfonic acid may be varied considerably, the imino sulfonate system is capable of wide variation in terms of both the thermal stability and UV absorption maximum. Both negative and positive photoresists have been formulated with such PAG materials, and recently a chemically amplified system has been

(24) Schwalm, R. *Proc. Polym. Mater. Sci. Eng.* **1989**, *61*, 278.
(25) Houlihan, F. M.; Shugard, A.; Gooden, R.; Reichmanis, E. *Macromolecules* **1988**, *21*, 2001.
(26) Neenan, T. X.; Houlihan, F. M.; Reichmanis, E.; Kometani, J. M.; Bachman, B. J.; Thompson, L. F. *Macromolecules* **1990**, *23*, 145.
(27) Houlihan, F. M.; Neenan, T. X.; Reichmanis, E.; Kometani, J. M.; Thompson, L. F.; Chin, T.; Kanga, R. S. *Chem. Mater.*, in press.
(28) Schlegel, L.; Ueno, T.; Shiraishi, H.; Hayashi, N.; Iwayanagi, T. *Chem. Mater.* **1990**, *2*, 299.
(29) Shirai, M.; Katsuta, N.; Tsunooka, M.; Tanaka, M. *Makromol. Chem.* **1989**, *190*, 2099.

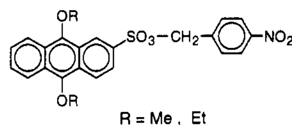
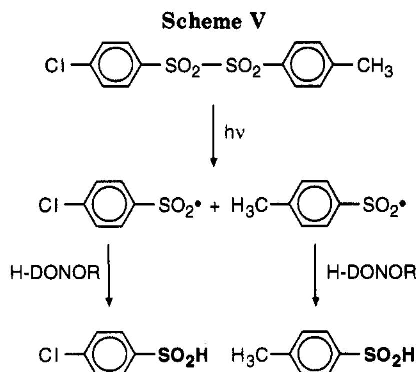


Figure 7. Structural representation of *p*-nitrobenzyl 9,10-ethoxyanthracene-2-sulfonate and *p*-nitrobenzyl 9,10-methoxyanthracene-2-sulfonate.

Scheme V

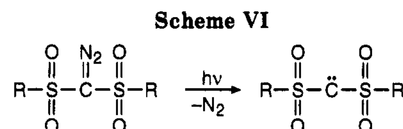


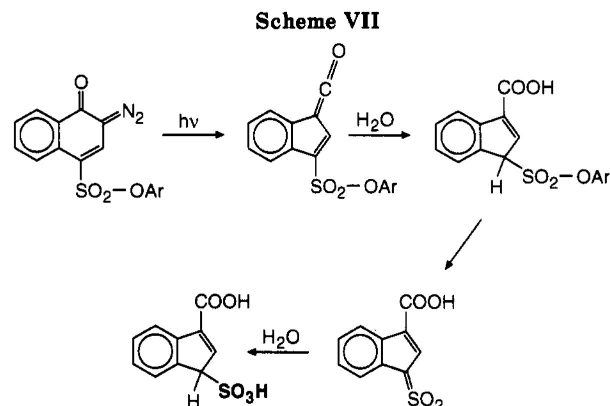
described consisting of an imino sulfonate used in conjunction with poly(*p*-[(*tert*-butoxycarbonyl)oxy]styrene (TBS).[30] The mechanism of acid generation is complex, involving cleavage of the N–O bond followed by abstraction of a hydrogen atom to form a sulfonic acid (Scheme IV). Reaction byproducts include azines, ketones, and ammonia.

An interesting system has been described by Yamaoka and co-workers in which 9,10-diethoxyanthracene-2-sulfonic acid has been photochemically produced from 4-nitrobenzyl 9,10-ethoxyanthracene-2-sulfonate (Figure 7).[31] When used in conjunction with poly(*p*-[(trimethylsilyl)oxy]styrene), high-resolution positive patterns with resist sensitivities of $\sim$15 mJ/cm^2 are obtained. Fluorescence quenching experiments support a mechanism of acid generation consistent with an intramolecular electron-transfer reaction. Moreover, the photodissociation rate of *p*-nitrobenzyl 9,10-methoxyanthracene-2-sulfonate upon irradiation at 436 nm in acetonitrile is independent of concentration, suggesting that electron transfer from the dimethoxyanthracene moiety to the *p*-nitrobenzyl moiety is intramolecular.

Disulfone compounds have also been found to be useful as photogenerators of acid.[32] Their absorbance maxima may be adjusted by varying the substituents on the constituent sulfonate moiety. The disulfones are unique in that two different sulfonic acid molecules are produced by homolytic cleavage of the sulfur–sulfur bond by the mechanism shown in Scheme V. Sulfonyl-substituted diazomethanes are an additional source of photogenerated acid.[33] Upon irradiation, the initially formed carbene is believed to be partially converted to a highly reactive sulfene, which then adds water to give an unusual sulfonic acid (Scheme VI). The generation of sulfonic acids from naphthoquinonediazide-4-sulfonates occurs as shown in Scheme VII. The mechanism involves generation of a ketene intermediate followed by a Wolff rearrangement to afford the indene carboxylic acid. In polar media, and possibly involving proton catalysis, phenol can be eliminated to form an unstable sulfene, which then adds water to generate the sulfonic acid.

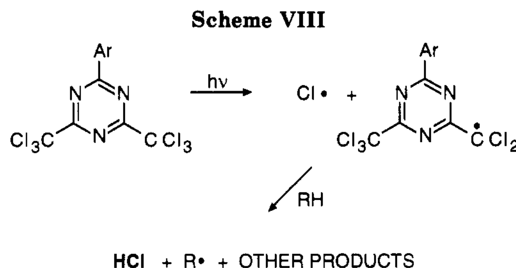
Scheme VI





Scheme VII

Scheme VIII



Materials such as tris(trichloromethyl)-*s*-triazine and many arylbis(trichloromethyl)-*s*-triazines combine high efficiency as photogenerators of hydrochloric acid with facile synthesis.[34] They may be obtained in one step by cotrimerization of an aromatic nitrile with 2 equiv of trichloroacetonitrile in the presence of hydrogen chloride and Friedel–Crafts catalysts. The mechanism of hydrogen chloride production involves homolytic cleavage of a carbon chlorine bond followed by abstraction of a hydrogen atom by the chlorine atom. The absorption maximum of the triazine may be easily adjusted by varying the structure of the precursor aromatic nitrile (Scheme VIII). Very recent work has described photoacid generators based upon *o,o'*-dibrominated phenols, which are reported to be highly soluble both in common casting solvents and in aqueous alkaline developers.[34,35]

Cross-Linking Chemistry

Chemical amplification through acid-catalyzed cross-linking for negative working resist applications has been achieved through various mechanisms. These include cationic polymerization, condensation reactions, and electrophilic aromatic substitution. The acid species has

(30) Masamitsu, S.; Tsunooka, M. *J. Photopolym. Sci. Technol.* **1990**, *3*, 301.
(31) Yamaoka, T.; Omote, T.; Adachi, H.; Kikuchi, N.; Watanabe, Y.; Shirosaki, T. *J. Photopolym. Sci. Technol.* **1990**, *3*, 275.
(32) Aoai, T.; Aotani, Y.; Umehara, A.; Kokubo, T. *J. Photopolym. Sci. Technol.* **1990**, *3*, 389.
(33) Pawlowski, G.; Dammel, R.; Lindley, C. R.; Merrem, H.-J.; Röschert, H.; Lingnau, J. *Proc. SPIE Adv. Resist Technol. Process VII* **1990**, *1262*, 16.
(34) Buhr, G.; Dammel, R.; Lindley, C. R. *Proc. Polym. Mater. Sci. Eng.* **1989**, *61*, 269.
(35) Dossel, K.-F. EP-A0312751, 1989.

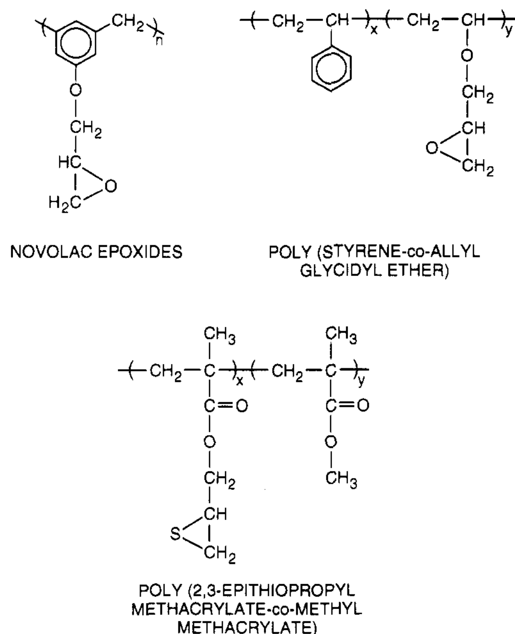


Figure 8. Structural representation of selected epoxy materials used in chemically amplified resist formulations.

been generated from either ionic materials, such as onium salts, or nonionic precursors. While the simultaneous formation of radicals and radical cation intermediates from the photolysis or radiolysis of onium salts may be disadvantageous for deprotection and depolymerization chemistries, their simultaneous formation with a strong acid may actually enhance the cross-linking efficiency in select cases, thus improving the overall sensitivity of a negative resist.

Cationic Polymerization Mechanisms. The first chemically amplified resist systems to be developed were those based on the cationic polymerization of epoxy materials (Figure 8).[12] Better adhesion, low film shrinkage, good swelling resistance to developers, excellent thermal stability of the cured film, and good sensitivity are some of the reasons for the widespread interest in the use of epoxy materials for resist applications. Several kinds of epoxy resins, both aliphatic and aromatic, are commercially available, and they can thus be formulated to work as negative resists. However, aliphatic materials are not generally suitable for resist applications due to inadequate thermal stability for device processing. One example of a resist material based on the above chemistry is a novolac–epoxy resin[36] (Figure 8) formulated with an onium salt acid generator. Ito and Willson[13] have demonstrated 1-μm resolution with a negative resist system comprised of a commercially available epoxy resin (Celanese Epi-Rez SU-8) based upon bisphenol A and acid generators such as the *p*-(*n*-hexyloxy)benzenediazonium halometalates or onium salts. For shorter wavelength exposure, more transparent materials are desirable. This criterion led to the design of styrene–allyl glycidyl ether (SAGE) copolymers of deep-UV lithographic applications.[37] The polymers exhibit the required thermal stability and low absorptivity in the deep-UV region. Resolution to 0.6 μm at a dose of 4 mJ/cm^2 was demonstrated for SAGE formulated with triphenylsulfonium hexafluoroantimonate as the photoacid generator. Features smaller than 0.55 μm displayed solvent-induced swelling effects. Dubois[38] and

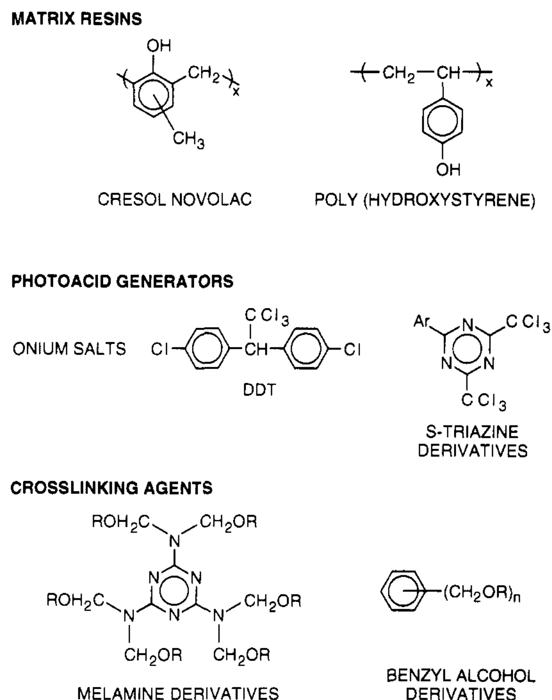


Figure 9. Representative structures of photoacid generators, cross-linking agents, and matrix resins used in acid-catalyzed condensation resist mechanisms.

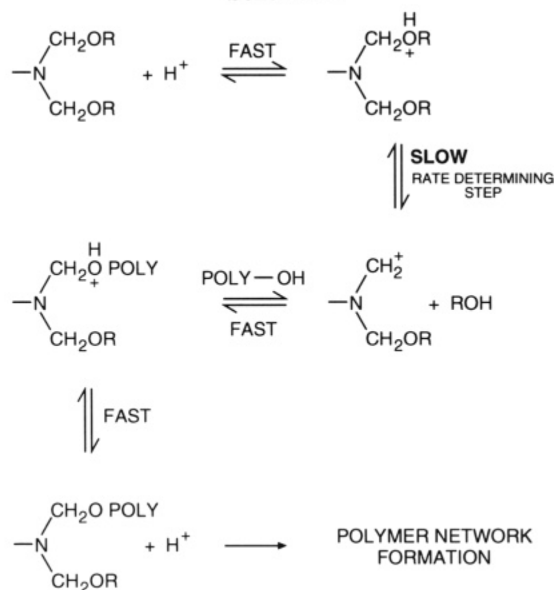
Crivello[12] have reported that copolymers of 2,3-epithiopropyl methacrylate and methyl methacrylate may be employed in negative chemically amplified resist formulations.

Acid-catalyzed cationic polymerization is an attractive method that may be used in the design of resist materials as it not only provides excellent sensitivity owing to the chemical amplification mechanism but also is insensitive to oxygen and trace amounts of water in the resist films. While these properties aid in the design of a negative resist that is not subject to environmental conditions and that possesses good process latitude, the mechanism generally may not be ideal for submicron lithography as features smaller than 1 μm are often subject to distortion due to solvent swelling of the irradiated regions.

Condensation Mechanisms. Condensation mechanisms are probably the most prevalent in the design of chemically amplified negative resists and are the basis for the commercially available, negative acting, chemically amplified resists. Such resist systems generally consist of three essential components: (i) a polymer resin with reactive site(s) (also called a binder) for cross-linking reactions (e.g., hydroxy functional polymer); (ii) a radiation-sensitive acid generator; (iii) an acid-activated cross-linking agent.[39–42] Figure 9 depicts some of the alternative structures for the above components. The photogenerated acid catalyzes the reaction between the resin and cross-linking agent to afford a highly cross-linked polymer network that is significantly less soluble than the unreacted polymer resin. A postexposure bake step prior to development is required to complete the condensation reaction as well as to amplify the cross-linking yield to enhance sensitivity and improve image contrast. This bake step is essential to attain a reasonable lithographic sensitivity because the activation energy of the condensation reaction

(36) Schlessinger, S. I. *Polym. Eng. Sci.* **1974**, *14*, 513.
(37) Stewart, K. J., Hatzakis, M.; Shaw, J. M.; Seeger, D. E.; Neumann, E. *J. Vac. Sci. Technol.* **1989**, *B7*, 1734.
(38) Dubois, J. C.; Eranian, A.; Datmanti, E. *Proc. Electrochem. Soc.* **1978**, *78-5*, 303.
(39) Lingnau, J.; Dammel, R.; Theis, J. *Solid State Technol.* **1989**, *32*(9), 105–112.
(40) Lignau, J.; Dammel, R.; Theis, J. *Solid State Technol.* **1989**, *32*(10), 107–112.
(41) Feely, W. E. *Eur. Patent Appl.* 232,972, 1980.
(42) Buhr, G. *U.S. Patent* 4,189,323, 1980.

Scheme IX



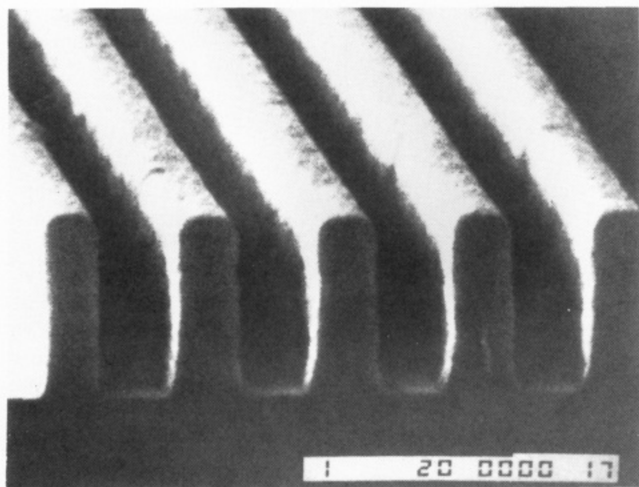
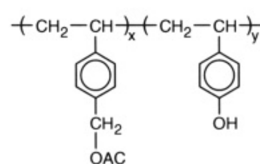


Figure 10. SEM micrograph depicting nominal 0.3-μm line/space images obtained in the negative, deep-UV resist, SNR-248, available from the Shipley Co. (courtesy Shipley Co. Inc.).

for doses corresponding to reasonable lithograpic sensitivity can be as high as 21–57 kJ/mol.[43] The rate-determining step for cross-linking in a system based upon poly(hydroxystyrene), a substituted melamine, and a photoacid generator is the formation of a carbocation from the protonated ether moiety (Scheme IX). Not surprisingly, the cross-linking efficiency (hence sensitivity and contrast) and resolution of these resists are a very strong function of postexposure bake parameters. Sub-half-micron features could be resolved with deep-UV[44] and electron-beam[45] radiation with wide process latitude and high sensitivity using this chemistry. An example of the resolution capability is shown in Figure 10. Very sensitive X-ray and electron-beam resist formulations based on similar chemistry using melamine and benzyl alcohol derivatives as cross-linking agents, formulated with onium salt photoacid generators in novolac or poly(hydroxy-



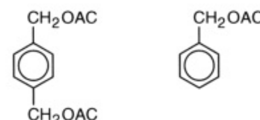
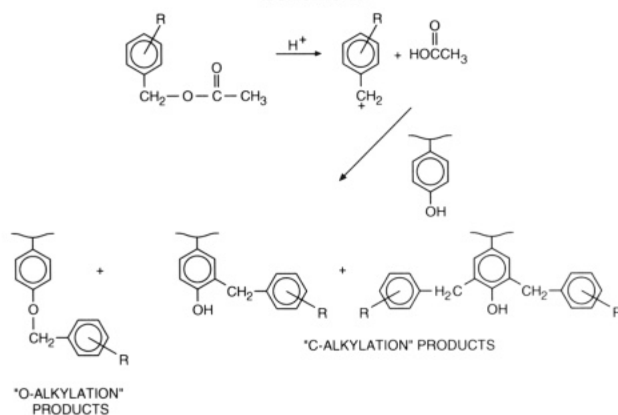


Figure 11. Schematic representation of latent electrophiles that may be used in the development of cross-linking chemically amplified resists.

Scheme X



styrene) binders, have shown 0.2-μm resolution.[39,40]

Photoinduced cross-linking has also been achieved in styrene polymers that are susceptible to electrophilic aromatic substitution by addition of a carbocation precursor and a photoacid generator.[46,47] The photogenerated acid reacts with the latent electrophile during a postexposure bake step to generate a reactive carbocation that reacts with an aromatic moiety in the matrix to result in a cross-linked network. The latent electrophile may be either an additive or a monomer that is copolymerized into the polymer binder (Figure 11). In the former approach, dibenzyl acetate was added as a latent electrophile along with triphenylsulfonium hexafluoroantimonate to novolac or poly(vinylphenol) binders. Alternately, [(acetyloxy)-methyl]styrene serves the same function when incorporated into poly(hydroxystyrene) as a comonomer. Mechanistic studies employing 4-isopropylphenol and a substituted benzyl acetate as model compounds revealed that the rate-determining step was the formation of a benzylic carbocation species (Scheme X) that reacts to give both C- and O-alkylation products. The final reaction mixture apparently always contained some O-alkylation products, and it is believed that acid-catalyzed rearrangement of the "O" to "C" alkylation material occurs readily.

An interesting system consisting of a novolac matrix resin, an onium salt photoacid generator, and silanol

(43) Berry, A. K.; Graziano, K. A.; Bogan, L. E., Jr.; Thackeray, J. W. In *Polymers in Microlithography*; ACS Symposium Series, No. 412; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemical Society: Washington, D.C., 1989; pp 87–99.

(44) Thackeray, J. W.; Orsula, G. W.; Pavelchek, E. K.; Canistro, D. *Proc. SPIE Adv. Resist Technol. Process. VI* **1989**, *1086*, 34.

(45) Liu, H.-Y.; deGrandpre, M. P.; Feely, W. E. *J. Vac. Sci. Technol.* **1988**, *B6*, 379.

(46) Reck, B.; Allen, R. D.; Twieg, R. J.; Willson, C. G.; Matsuszczak, S.; Stover, H. D. H.; Li, N. H.; Frechet, J. M. J. *Polym. Eng. Sci.* **1989**, *29*, 960–4.

(47) Frechet, J. M. J.; Matsuszczak, S.; Stover, H. D. H.; Willson, C. G.; Reck, B. In *Polymers in Microlithography*; ACS Symposium Series, No. 412; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemical Society: Washington, D.C., 1989; pp 74–85.

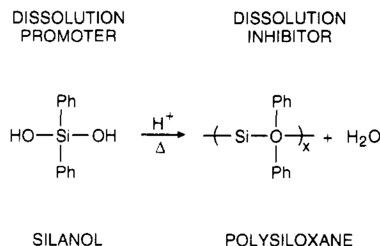
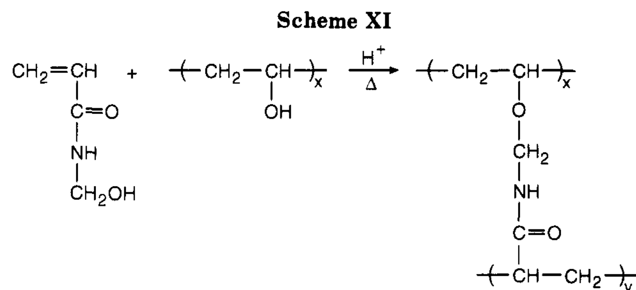


Figure 12. Schematic representation of the chemically amplified resists based on silanol condensation chemistry.

Scheme XI



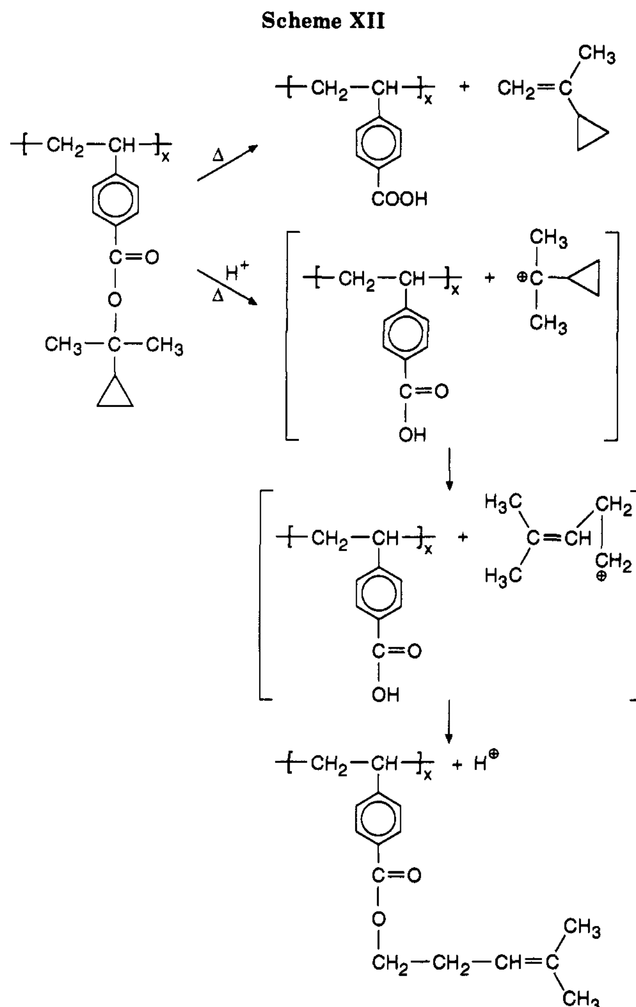
compounds that act as dissolution promoters for novolac resins in aqueous base was described recently.[48] Compound such as diphenylsilanediol (DPS) are readily soluble in aqueous base and may in fact increase novolac solubility in aqueous media by as much as a factor of 5. Upon exposure to light followed by postexposure bake, acid-catalyzed condensation of the silanol additive results in formation of a polysiloxane (Figure 12). While silanols are dissolution promoters, polysiloxanes are hydrophobic, aqueous-base-insoluble resins that may act as dissolution inhibitors. Sufficient differential solubility is achieved between the exposed and unexposed areas of a resist film resulting in negative tone images. A resolution capability of 0.3 μm was demonstrated upon electron-beam exposure with a dose of 0.8 $\mu C/cm^2$ at 30 kV. The shelf life of these formulations is a concern because of the extreme reactivity of the silanols with trace amounts of acid. In a similar approach, McKean et al. have described the use of silsesquioxanes as components in negative, chemically amplified resists.[49]

Simultaneous Radical- and Acid-Catalyzed Cross-Linking Mechanisms. Advantage can be taken of the simultaneous photogeneration of acid and radical intermediates from onium salts in the design of resist chemistries that can cross-link via both pathways. Crivello described[12] such a system that consists of 5–20% *N*-methylolacrylamide in poly(vinyl alcohol) along with a triphenylsulfonium salt. Free-radical-initiated polymerization of *N*-methylolacrylamide and acid-induced condensation of alcohol and methylol groups from the two polymers occur simultaneously to result in a highly cross-linked interpenetrating network (Scheme XI). Aqueous development results in negative tone images.

Acid-Catalyzed Rearrangement Mechanisms

The use of rearrangement mechanisms for the development of chemically amplified resists has been limited. One example involves acid-induced rearrangement of *cis*-4-polyisoprene to afford a polycyclic isomer.[12] Depending on the choice of developer, a resist based on these materials can act in either a positive or negative mode.

Scheme XII



More recently, Ito and co-workers have described interesting negative resist chemistry based upon the rearrangement of cyclopropyl carbinol esters.[50] While poly(2-cyclopropyl-2-propyl 4-vinylbenzoate) undergoes thermally induced deprotection to afford poly(4-vinylbenzoic acid) as the primary product, the acid-catalyzed reaction favors rearrangement over deprotection. The mechanism is believed to involve heterolysis of the C–O bond to generate the dimethylcyclopropyl carbenium ion, which rearranges and recombines with the carboxylic acid to form a primary ester (Scheme XII). This rearrangement allows negative imaging in either organic solvent or aqueous base developers depending upon the postexposure bake conditions.

Deprotection Chemistry

The pioneering work relating to the development of chemically amplified resists based on deprotection mechanisms was carried out by Ito et al.[13] These initial studies dealt with the catalytic deprotection of poly[((*tert*-butoxycarbonyl)oxy)styrene] (TBS) in which the thermally stable, acid-labile *tert*-butoxycarbonyl group is used to mask the hydroxyl functionality of poly(vinylphenol).[51–53]

(48) (a) Toriumi, M.; Shiraishi, H.; Ueno, T.; Hayashi, N.; Nonogaki, S. *J. Electrochem. Soc.* **1987**, *134*, 936. (b) Shiraishi, H.; Fukuma, E.; Hayahsi, N.; Ueno, T.; Tadano, K.; Iwayanagi, T. *J. Photopolym. Sci. Technol.* **1990**, *3*, 385.
(49) McKean, D. R.; Clecak, N. J.; Pederson, L. A. *Proc. SPIE* **1990**, *1262*, 110.
(50) Ito, H.; Ueda, M.; England, W. P. *Macromolecules* **1990**, *23*, 2589.
(51) Frechet, J. M. J.; Eichler, E.; Ito, H.; Willson, C. G. *Polymer* **1980**, *24*, 995.
(52) Ito, H.; Willson, C. G.; Frechet, J. M. J.; Farrall, M. J.; Eichler, E. *Macromolecules* **1983**, *16*, 510.

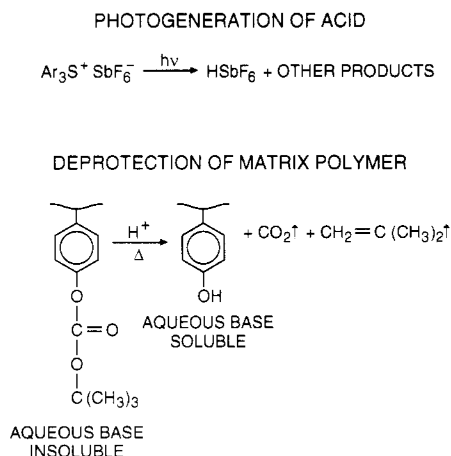


Figure 13. Schematic representation of TBS-based resist systems.

As shown in Figure 13, irradiation of TBS films containing small amounts of an onium salt, such as diphenyliodonium hexafluoroarsenate with UV light, liberates an acid species that upon subsequent baking catalyzes cleavage of the protecting group to generate poly(*p*-hydroxystyrene). While this reaction will take place very slowly at room temperature, it is much faster at 100 °C, requiring only a few seconds of baking. In the absence of an acidic species, the protected polymer undergoes no degradation during prolonged heating at 100 °C, and temperatures in excess of 180 °C are required to initiate the deprotection reaction. Loss of the *tert*-butoxycarbonyl group results in a large polarity change in the exposed areas of the film. Whereas the substituted phenol polymer is a nonpolar material soluble in nonpolar lipophilic solvents, poly(vinylphenol) is soluble in polar organic solvents and aqueous base. This change in polarity allows formation of either positive or negative images, depending upon the developer. Nonpolar solvents such as a mixture of dichloromethane and hexane remove the unirradiated regions, generating a negative image, while an aqueous base developer such as tetramethylammonium hydroxide selectively removes the irradiated regions. In addition to a change in polarity that affects the polymer dissolution characteristics, deprotection also leads to a change in reactivity of the exposed vs unexposed matrix to selected reagents. Specifically, the hydroxy functionalities found in the exposed and baked regions of the film are available for reaction with a variety of silylating agents allowing oxygen plasma development of the resist.[54] The protected styrene-based resists are sensitive to deep-UV and electron-beam irradiation and may be sensitized to longer wavelengths through the addition of appropriate mid- and near-UV dyes. TBS-onium salt resists have also been successfully used in the manufacture of integrated circuit devices owing to their high sensitivity and contrast.[55] The high contrast behavior emanates from the exceptionally nonlinear dissolution response as a function of radiation dose. For the TBS-onium salt resist described above in addition to other analogues (vide infra), the desired dissolution behavior is accomplished by the conversion of the hydrophobic *tert*-butoxycarbonyl group to a hydrophilic hydroxyl group. This conversion, coupled with the fact that solubility in

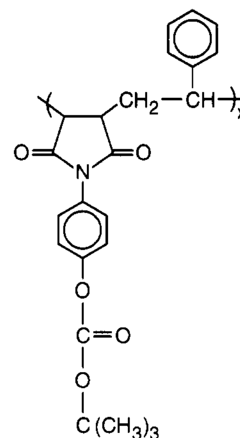


Figure 14. Chemical structure of a substituted *N*-(*p*-hydroxyphenyl)maleimide copolymer.

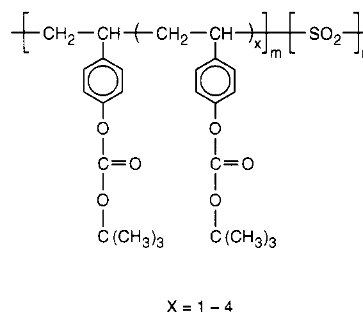


Figure 15. Structural representation of TBSS.

aqueous base is achieved only when >95% of the protecting groups have been removed, results in a very high contrast resist.

Alternate protective groups and parent polymers have been utilized in the design of chemically amplified resists. Generally, thermally stable, acid-labile substituents are desirable as protective groups for aqueous-base-soluble parent polymers. Some typical examples that have been employed include *tert*-butyl ethers[56,57] and esters,[13,53] tetrahydropyranyl ethers,[58–60] and α,α-dimethylbenzyl esters.[59,61,62] In situations where adequate moisture is expected to be present in the film, hydrolyzable groups such as trimethylsilyl have also been utilized.[63] As mentioned above, the parent polymer is typically an aqueous-base-soluble resin. Examples include poly(hydroxystyrene),[13] poly(vinylbenzoic acid),[64] and poly(methacrylic acid).[61] One advantage of the carboxylic acid matrix resins over the phenolic analog-s is that it is not necessary to remove all the protective groups to affect aqueous base solubility. For example, when poly(α,α-dimethylbenzyl methacrylate-*co*-styrene) is used in conjunction with an

(53) Ito, H.; Willson, C. G. *Polym. Eng. Sci.* **1983**, *23*, 1012.
(54) MacDonald, S. A.; Ito, H.; Hiraoka, H.; Willson, C. G. *Proc. Reg. Tech. Conf. on Photopolymers*; mid-Hudson Section SPE, Oct 28–30, 1985; Ellenville, NY; pp 177–196.
(55) Maltabes, J. G.; Holmes, S. J.; Morrow, J. R.; Bart, R. L.; Hakey, M.; Reynolds, G.; Brunsvold W. R.; Willson, C. G.; Clecak, N.; MacDonald, S. A.; Ito, H. *Proc. SPIE Adv. Resist Technol. Process. VII* **1990**, *1262*, 2.
(56) Conlon, D. A.; Crivello, J. V.; Lee, J. L.; O'Brien, M. J. *Macromolecules* **1989**, *22*, 509.
(57) Crivello, J. V. *J. Electrochem. Soc.* **1989**, *136*, 1453.
(58) Hayashi, N.; Hesp. S. M. A.; Ueno, T.; Toriumi, M.; Iwayanagi, T.; Nonogaki, S. *Proc. Polym. Mater. Sci. Eng.* **1989**, *61*, 417.
(59) Frechet, J. M. J.; Kallman, N.; Kryczka, B.; Eichler, E.; Houlihan, F. M.; Willson, C. G. *Polym. Bull.* **1988**, *20*, 427.
(60) Frechet, J. M. J.; Eichler, W.; Gauthier, S.; Kryczka, B.; Willson, C. G. In *The Effects of Radiation on High-Technology Polymers*; ACS Symposium *Series*, No. 381; Reichmanis, E., O'Donnell, J. H., Eds.; American Chemical Society: Washington, D. C., 1989; pp 155–171.
(61) Ito, H., Ueda, M.; Ebina, M. In *Polymers in Microlithography*, ACS Symposium Series, No. 412; Reichmanis, E., MacDonald, S. A., Iwayanagi, T., Eds.; American Chemical Society: Washington, D.C., 1989; pp 57.
(62) Ito, H.; Ueda, M. *Macromolecules* **1988**, *21*, 1475.
(63) Yamaoka, T.; Nishiki, M.; Koseki, K.; Koshiba, M. *Proc. Regional Technical Conference on Photopolymers*; Mid-Hudson Section SPE; Ellenville, NY, Oct 30–Nov. 2, 1988; pp 27.
(64) Ito, H.; Willson, C. G.; Frechet, J. M. J. *Proc. SPIE* **1987**, *771*, 24.

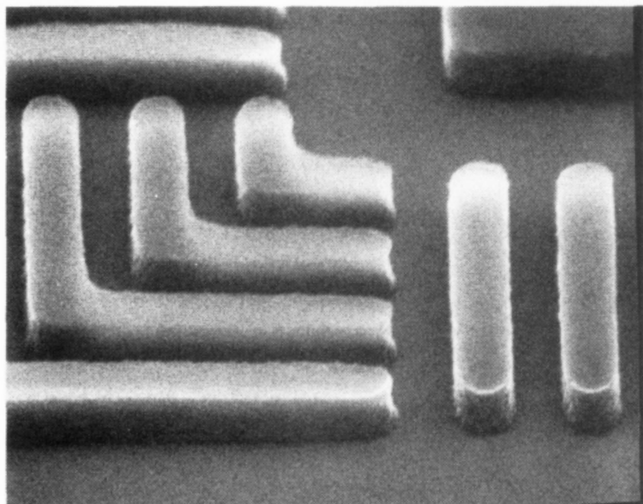


Figure 16. SEM micrograph depicting nominal 0.5-μm images obtained in TBSS formulated with a nitrobenzyl ester PAG upon 248-nm irradiation.

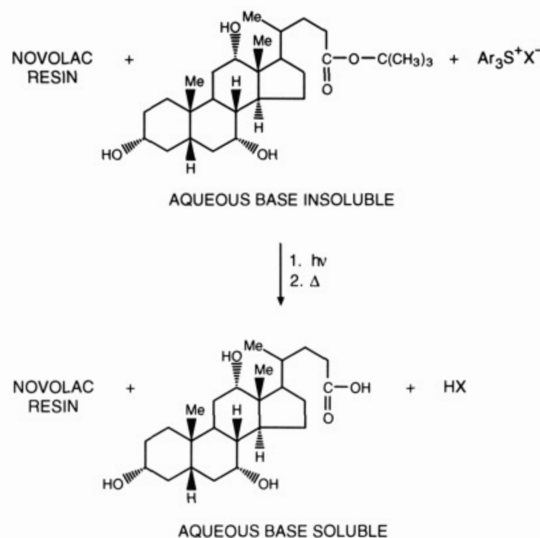


Figure 17. Structural representation of a *tert*-butylcholate-based chemically amplified resist.

onium salt PAG, it is necessary to remove only 25–50% of the protective groups.[61] This fact may present advantages with respect to resist processing and overall sensitivity.

The need for resist materials that do not undergo image deformation due to flow during high-temperature processing has stimulated efforts to design high glass transition temperature (T_g) polymers. This interest has also been extended to the development of high-T_g chemically amplified materials. Examples include the poly(vinylbenzoates)[64] and N-blocked maleimide/styrene resins.[65] Alternatively, a *tert*-butoxycarbonyl group was used to block the hydroxyl functionality of *N*-(*p*-hydroxyphenyl)maleimide (Figure 14) polymers and copolymers.[66] The high T_g of these materials generated images that were resistant to flow when heated at 200 °C for up to 1 h.

A matrix polymer used in a resist formulation currently undergoing development for use in manufacturing is poly(4-[(*tert*-butoxycarbonyl)oxy]styrene sulfone) (Figure 15, TBSS).[67] As in the case of TBS, the *tert*-butoxycarbonyl moiety is used as the acid-labile protective group. The inclusion of sulfur dioxide into the backbone of the polymer affords a high T_g that gives greater flexibility for processing. Additionally, introduction of sulfur dioxide into similar polymers enhances their susceptibility to main-chain scission,[68] which may enhance sensitivity. While no difference in sensitivity between TBS and TBSS was observed when these polymers were used in conjunction with onium salt photoacid generator materials, the resist exposure dose was reduced by as much as a factor of 2.5 when a nitrobenzyl ester acid photogenerator was employed.[17] When exposed to X-ray irradiation, TBSS is an effective single-component chemically amplified resist.[14] Presumably, radiation-induced C–S bond scission leads to generation of either sulfinic or sulfonic acid end groups that subsequently induce the deprotection reaction. Figure 16 depicts 0.5-μm images that were obtained in TBSS formulated with a nitrobenzyl ester acid generator upon 50 mJ/cm^2 exposure to 248-nm irradiation.

The concept of acid-catalyzed deprotection may also be applied to resist formulations utilizing a small molecule acting as a dissolution inhibitor for an aqueous-alkali-soluble resin. When physically incorporated into an otherwise soluble resin, an appropriately designed, hydrophobic species can effectively limit the solubility of the matrix in aqueous alkali. After exposure and postexposure bake, this inhibitor is then converted to a hydrophilic substance, allowing selective dissolution of the exposed regions. Materials that may effectively be used in such processes include carbonates or ethers of phenols,[28,58,69,70] esters of carboxylic acids,[71,72] acetals,[73] or orthocarboxylic acid esters.[73] In one example, the *tert*-butyl ester of cholic acid (Figure 17) is used as a dissolution inhibitor for a phenol–formaldehyde matrix resin.[71] When formulated with an onium salt, irradiation generates a strong acid that upon mild heating liberates cholic acid. The irradiated regions may then be removed by dissolution in aqueous base. One motivating factor leading to the use of the cholate ester is that it is a large-molecule organic ester that undergoes a significant change in aqueous base solubility (the solubility of sodium cholate in water is ~500 g/L, whereas the esters are insoluble).[74] This in turn can lead to a more effective dissolution inhibitor.

Depolymerization Chemistry

Chemically amplified resists that act through a depolymerization mechanism can be broadly divided into two classes: those that act through a thermodynamically induced depolymerization mechanism and those requiring catalytic cleavage of a polymer backbone. The former process depends upon the use of low-ceiling-temperature polymers that have been stabilized by suitable end-capping. Introduction of a photocleavable moiety either at the end-cap or along the polymer backbone may then allow depolymerization to take place after irradiation and mild

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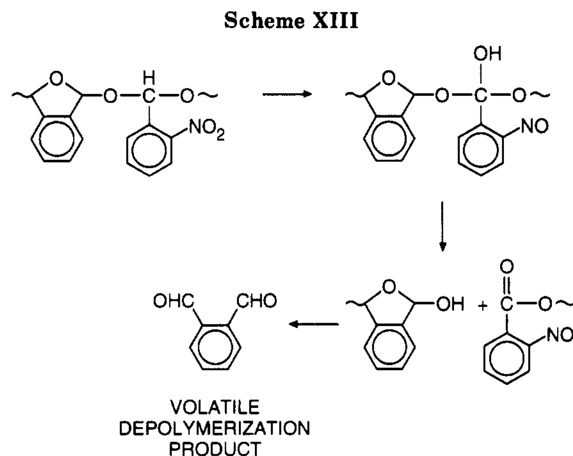
Scheme XIII



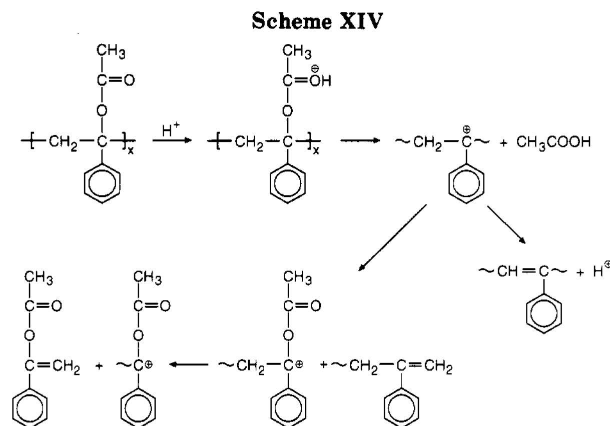
heating. A variant of this approach utilizes an end-cap, or polymer chain, that may be cleaved by photogenerated acid.

The first chemically amplified resists that operated by a thermodynamically induced depolymerization were based on polyacetals (or polyaldehydes).[13,53,75] These polymers have very low ceiling temperatures, but can be stabilized by end-capping.[76] In particular, poly(phthalaldehyde) (PPA) has a ceiling temperature of −40 °C but can be stabilized to 180 °C by end-capping with acetic anhydride. Upon electron-beam or deep-UV irradiation, followed by heating to 100 °C, partially developed images can be obtained. The extent of development can be enhanced if a small amount (3%) of *o*-nitrobenzaldehyde is added to the reaction mixture.[13,53] Effectively, the *o*-nitrobenzaldehyde that is incorporated into the polymer chain can act as a site for photochemical chain cleavage, which then permits the ceiling-temperature equilibrium to reassert itself (Scheme XIII). Introduction of an onium salt such as triphenylsulfonium hexafluoroantimonate (2–10%) into this polyacetal further enhances this reaction and allows resolution of 1-μm images at a dose of 2–5 mJ/cm^2 of deep-UV or 1–2 μC/cm^2 of 20 keV electron-beam radiation.

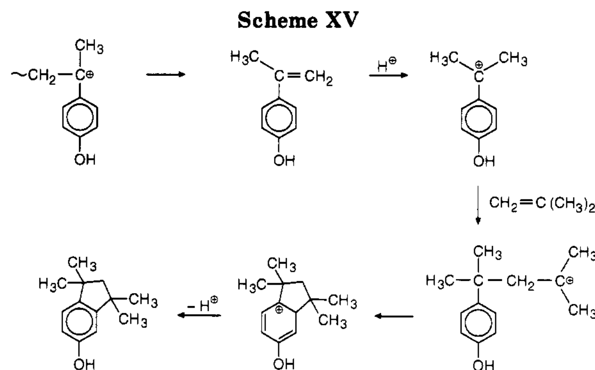
Aliphatic polyaldehyde copolymers such as poly(ethanal-*co*-propanal), poly(ethanal-*co*-butanal), and poly(ethanal-*co*-heptanal)[77] have been reported to be almost completely self-developing, without requiring the incorporation of onium salt or *o*-nitrobenzyl groups upon electron-beam or X-ray exposure. While the sensitivities of these resists are dependent upon the volatility of the aldehyde formed upon irradiation, they are generally less sensitive (300–400 mJ/cm^2) than the PPA-based materials.

Although PPA materials are sensitive self-developing resists, they have two major drawbacks: (i) they liberate a volatile aldehyde during the exposure step that could be injurious to the optics of the exposure tool; (ii) they exhibit poor plasma etching resistance. Recently, it was found that contamination of the optical tool could be reduced by using poly(4-chlorophthalaldehyde) as the matrix resin in conjunction with an onium salt acid generator.[78,79] This resist system does not spontaneously depolymerize upon exposure to radiation but requires a postexposure bake step (thermal development). The problem of plasma etching resistance has been addressed in two approaches. The first is to use silylated PPA derivatives such as poly(4-(trimethylsilyl)phthalaldehyde)[79,80] which can form an SiO_2 barrier layer; the second is to incorporate PPA into a novolac, which is itself more resistant to plasma etching. In the latter case, the aldehyde resin behaves as a dissolution inhibitor.[81]

Scheme XIV



Scheme XV



Other polymers that exhibit chemical amplification through depolymerization reactions are certain styrene derivatives such as poly(4-[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene)[82,83] (TBMS) and poly(α-acetoxystyrene).[83] In addition to depolymerization, these two materials undergo acidolytic side-group cleavage. For poly(α-acetoxystyrene) removal of the acetoxy group generates a carbocation which leads to depolymerization (Scheme XIV). Poly[(*tert*-butoxycarbonyl)oxy]-α-methylstyrene) operates by way of a deprotection mechanism.[17] However, literature reports as to the tendency of this polymer to undergo depolymerization in solution in the presence of acid[52] led to an investigation of its tendency to undergo acid-catalyzed depolymerization in a resist film.[82] Extensive depolymerization was observed after heating irradiated TBMS-onium salt or nitrobenzyl ester matrices. The observed products were 4-hydroxy-α-methylstyrene and 5-hydroxy-1,1,3,3-tetramethylindan. The latter results from the reaction of the α-methylstyrene monomer with isobutylene liberated during deprotection of the pendant side group (Scheme XV). The mechanism for depolymerization was proposed to involve chain scission to form a tertiary benzylic carbocation, further stabilized by the presence of a 4-hydroxy substituent,[82] which could then initiate depolymerization of the polymer. Subsequent work

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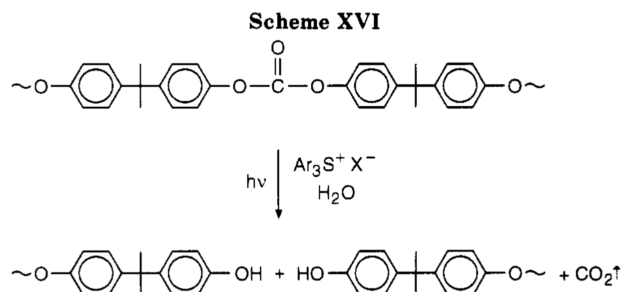
Scheme XVI



showed that depolymerization probably proceeds via reactions of acid with end groups to generate this carbocation rather than chain scission.[83]

A resist system similar to PPA is one based upon polycarbonates derived from *o*-nitrobenzyl glycidyl ether and propylene oxide.[84,85] Here, photochemical cleavage of the pendant *o*-nitrobenzyl group liberates a hydroxyl functionality which during postexposure bake in the presence of photogenerated acid initiates depolymerization to afford cyclic carbonate products.

The second type of chemically amplified depolymerization resist mechanism depends upon the incorporation of C–O bonds into the polymer backbone which can be cleaved by either hydrolysis or acidolysis. This concept was first advanced by Crivello, who proposed that polymers such as polycarbonates and polyesters could undergo photoinduced acid-catalyzed hydrolysis reaction in polymeric films.[12] Although polymers could be designed to undergo catalytic chain cleavage in the presence of acid, such an approach depends upon the inclusion of stoichiometric amounts of water in the polymer films (Scheme XVI). Little further work was reported on this concept until recently, when a new system for dissolution inhibition was described based upon the hydrolysis of polysilyl ethers in a novolac resin.[32]

Much of the work related to the design of chemically amplified resists that depolymerize upon catalytic cleavage of the polymer backbone has been done by Frechet et al.[86-90] In these systems, the polymer film depolymerizes through thermally induced, acid-catalyzed cleavage of tertiary, secondary allylic, or secondary benzylic C–O bonds to form a stable carbocation with at least one α hydrogen. This carbocation can then eliminate to form an alkene with concomitant regeneration of the acid catalyst. The first examples of such resists were based upon polycarbonates that incorporated tertiary carbonate units along the polymer backbone.[86] Typically these materials have a thermal stability of ~200 °C, at which point they undergo decomposition to diols, carbon dioxide, and dienes.[86,87] Such materials also depolymerize upon mild heating in the presence of photogenerated acid.[87] Other similar carbonate resist systems have been described in which secondary

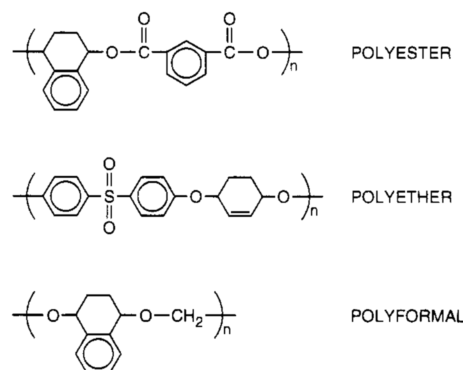
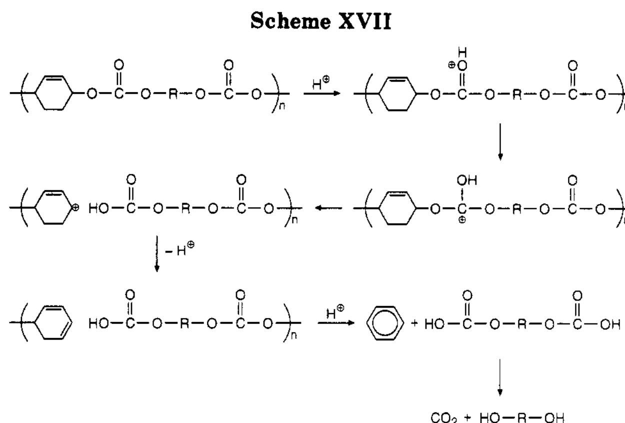


Figure 18. Structural representation of a polyester, polyether, and polyformal employed in a chemically amplified resist.

Scheme XVII



benzylic and secondary allylic units are incorporated along the polymer chain.[87] Of particular interest are the materials based upon 2-cyclohexane-1,4-diol and a dihydroxy compound. Acidolysis causes an aromatization reaction to occur, liberating benzene as well as a free dihydroxyl compound and carbon dioxide (Scheme XVII). Tertiary polycarbonates and secondary allylic polycarbonates give high-quality positive images upon 254-nm exposure. However, these resists are not completely self-developing because of the low volatility of the liberated dihydroxyl compound, and wet development is required. Resist systems based upon secondary benzylic carbon systems give only negative images due to the formation of divinylbenzene, a cross-linking agent.[88]

Polyesters (Figure 18) with tertiary, secondary allylic, and secondary benzylic units and polyethers (Figure 18) containing the latter two groups were also prepared and evaluated as resist materials when used with onium salt PAG materials.[89] Selected resist systems formulated from these polymers and triphenylsulfonium hexafluoroantimonate undergo acidolytic cleavage to afford a neutral olefin or aromatic compound plus a diacid or diol. Polyesters and polyethers may be self-developing if a vacuum is applied during the postexposure bake step. If no vacuum is applied, as in the polycarbonate-based resists, complete removal of the exposed regions is achieved only by using wet development.

Polyformals (Figure 18) containing secondary allylic and secondary benzylic C–O units capable of acidolytic cleavage have also been reported as effective polymers for chemically amplified resist applications.[90] Polyformals undergo acidolysis to afford an aromatic compound, formaldehyde, and water. Because all these compounds are volatile, the resist systems made from these polymers and triphenylsulfonium hexafluoroantimonate are completely self-developing and have been reported to give lithographic sensitivities as high as 15 mJ/cm^2. Features obtained with

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these resist systems, however, tend to be rounded due to the low T_g of the polymer and possible plasticization by the released aromatic compounds before volatilization. Recently, other workers have reported a similar type of resist system based upon polyethers containing alkoxypyrimidine units.[91] Resists made from these materials and triphenylsulfonium triflate exhibited sensitivites of 10 mJ/cm^2 upon irradiation at 250 nm. The products arising from acidolytic cleavage are pyrimidone and compounds containing both alkene and alcohol functionalities.

Conclusion

The aim of this review has been to examine one approach to the design of new resist chemistries for microlithographic applications. Chemical amplification processes utilize a single photochemical event that leads to a cascade of subsequent reactions effecting pattern differentiation within the parent material. The vast majority of materials that have been designed to date utilize a photochemically generated acid to catalyze subsequent cross-linking, deprotection, or depolymerization reactions. Significant efforts have been expended in the design of acid generator chemistries compatible with device processing environments. The most notable examples include the onium salts and nitrobenzyl esters. Additionally, the matrix resin must exhibit suitable characteristics with the most common materials being derived from hydroxyphenols.

Since the conception of chemical amplification mechanisms for microlithographic applications approximately one decade ago, increasing attention has been given to such processes in that they provide advantages in terms of sensitivity and contrast with minimal increase in process complexity. Additionally, a given chemistry may find application to more than one lithographic technology. The original work in chemically amplified resists has spawned many research efforts to define chemistries appropriate for matrix materials and photogenerators of catalysts, primarily strong acids. There continue to be many challenges in the areas of both fundamental and applied materials chemistry as well as process engineering to both understand and develop new chemically amplified resists for use with the future lithographic technologies.

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Articles

Oxovanadium(IV) Hydrogen Phosphate Hydrates: A Time-Resolved Neutron Powder Diffraction Study

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Oxovanadium(IV) pyrophosphate, $(VO)_2P_2O_7$, is the catalytically active phase in the V-P-O system. It can be obtained by pyrolysis of any of the different hydrates of oxovanadium(IV) monohydrogen phosphate, $VO(HPO_4)\cdot yH_2O$ (y = 0.5, 1, 2 (α), 2 (β), 3, 4). The present neutron thermodiffractometric study shows unambiguously that, irrespective of the starting hydrate, the hemihydrate, $VO(HPO_4)\cdot 0.5H_2O$, always crystallizes before $(VO)_2P_2O_7$. The $VO(HPO_4)\cdot 0.5H_2O$ to $(VO)_2P_2O_7$ transformation is not a simple and straightforward process but involves an amorphous intermediate. The conversion of the different hydrates into $VO(HPO_4)\cdot 0.5H_2O$ requires more or less severe structural rearrangements, which, in turn, must affect the morphologic characteristics of the final catalyst.

Introduction

Oxovanadium(IV) hydrogen phosphate hydrates show a large structural diversity[1-5] that results in a very rich experimental magnetic behavior.[5-8] Moreover, they all are pyrolytic precursors of the oxovanadium(IV) pyro-

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